

Multiple nitrene insertions into metal–sulfur bonds of dithiocarbamate complexes: synthesis of sulfido-amido and zwitterionic tetraamido complexes

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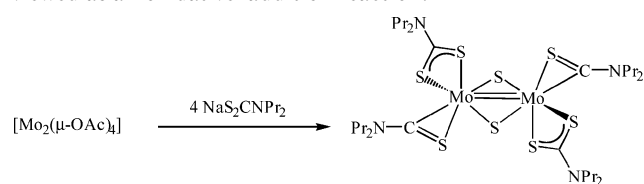
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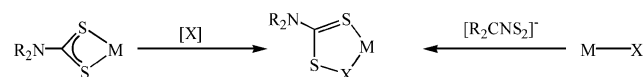
The iodine(III) reagent, $\text{PhI}=\text{NTs}$, acts as a source of the nitrene fragment NTs , which undergoes facile insertion into the metal–sulfur bonds of a range of dithiocarbamate complexes. Addition of two equivalents of $\text{PhI}=\text{NTs}$ to $[\text{M}(\text{S}_2\text{CNR}_2)_2]$ affords sulfido-amido complexes $[\text{M}\{\text{SC}(\text{NR}_2)\text{SNTs}\}_2]$ ($\text{M}=\text{Ni}, \text{Cu}$), which insert two further nitrene fragments to afford zwitterionic tetraamido complexes $[\text{M}\{\text{TsNSC}(\text{NR}_2)\text{SNTs}\}_2]$ ($\text{M}=\text{Co}, \text{Ni}, \text{Cu}$). Crystallographic studies have been carried out on both types of complex allowing possible resonance hybrids of the new ligand types to be assessed.

Introduction

Dithiocarbamates are an important class of ligand, being capable of stabilising transition metals in a wide range of oxidation states, and in by far the vast majority of instances, they act merely as non-sterically demanding ancillary ligands.¹ It is, however, becoming increasingly clear that under certain circumstances the ligand can behave in a non-innocent fashion. Ricard and co-workers reported the first example of this behavior in 1973.² They showed the complex formed from the reaction of $[\text{Mo}_2(\mu\text{-OAc})_4]$ and four equivalents of $\text{NaS}_2\text{CNPri}_2$ was the molybdenum(IV) dimer, $[\text{Mo}(\mu\text{-S})(\text{S}_2\text{CNPri}_2)(\eta^2\text{-SCNPr}_2)_2]$, resulting from the cleavage of a carbon–sulfur bond, generating sulfido and thiocarboxamide ligands; a process that can be viewed as an oxidative–addition reaction.

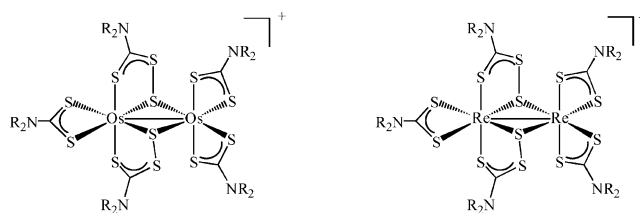


Over the next thirty years an increasing number of examples of the non-innocent behavior of dithiocarbamates have been reported.¹ By far the majority of these involve the cleavage of one (or both) of the sulfur–carbon bonds, although a number of other different types of non-innocent behavior have been found. These include the addition of dithiocarbamates to unsaturated ligands (X), and the insertion of the unsaturated groups into metal–sulfur bond(s) of dithiocarbamates. The latter has important implications in the rubber vulcanization process when $[\text{Zn}(\text{S}_2\text{CNMe}_2)_2]$ is utilized; the insertion of sulfur into a zinc–sulfur bond being proposed as a key step.³

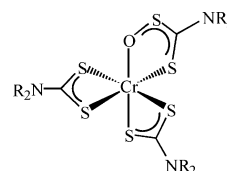


However, while the insertion of sulfur into the metal–sulfur bonds of related xanthate complexes is known,⁴ to date no such insertion has been noted for mononuclear dithiocarbamate complexes. Indeed, trithiocarbamates (the expected products

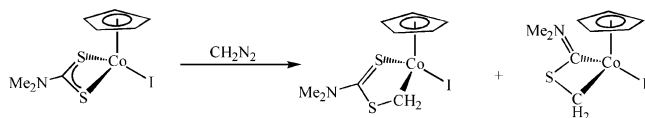
of the insertion of sulfur into dithiocarbamates) remain elusive at mononuclear centres.⁵ This ligand has, however, been prepared and isolated in a bridging capacity. For example, heating $[\text{Os}(\text{S}_2\text{CNR}_2)_3]$ ($\text{R} = \text{Me}, \text{Et}$) with elemental sulfur in DMF yields trithiocarbamate complexes, $[\text{Os}_2(\text{S}_2\text{CNR}_2)_3(\mu\text{-S}_3)(\mu\text{-S}_3\text{CNR}_2)]$ and $[\text{Os}_2(\text{S}_2\text{CNR}_2)_3(\mu\text{-S}_3\text{CNR}_2)_2]^+$, the former being converted into the latter upon reaction with thiuram disulfide.^{5–7} Related dirhenium trithiocarbamate complexes have also been prepared.⁸ Thus, $[\text{Re}_2(\mu\text{-S})(\text{S}_2\text{CNR}_2)_2]$ undergo a reversible one-electron oxidation which in the presence of thiuram disulfide afford rhenium(III) complexes, $[\text{Re}_2(\mu\text{-S}_3\text{CNR}_2)_2(\text{S}_2\text{CNR}_2)_3]^+$. At the diosmium centre, the mode of formation of the trithiocarbamate ligand is not clear and could result from sulfur insertion into the dithiocarbamate. In contrast, at the dirhenium centre it is clearly formed upon dithiocarbamate addition to a bridging sulfido group.



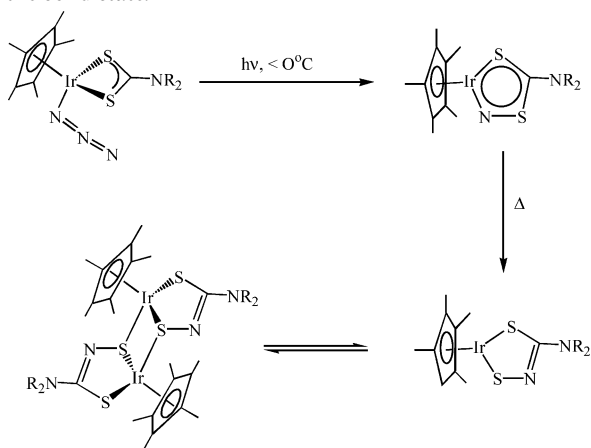
The insertion of the isoelectronic oxo moiety has also not been unequivocally shown, although again, oxygen-expanded dithiocarbamate ligands have been isolated. Thus, $[\text{Cr}(\text{S}_2\text{CNR}_2)_2\{\text{OSCN}(\text{R}_2\text{S})\}]$ are formed along with $[\text{Cr}(\text{S}_2\text{CNR}_2)_3]$ from the reaction of dichromate and dithiocarbamate salts.^{9,10} Presumably these oxygen-expanded ligands result from addition of the dithiocarbamate to the preformed metal-oxide, and as such are better considered as examples of dithiocarbamate addition reactions.



The insertion of a methylene fragment into a cobalt–sulfur bond of $[\text{CpCoI}(\text{S}_2\text{CNMe}_2)]$ has been reported,¹¹ reaction with diazomethane affording two products, namely $[\text{CpCoI}\{\eta^2\text{-CH}_2\text{SC}(\text{NMe}_2)\text{S}\}]$ and $[\text{CpCoI}\{\eta^2\text{-CH}_2\text{SC}(\text{=NMe}_2)\}]$. The first results from insertion of a methylene group into a cobalt–sulfur bond, while the second is a consequence of insertion followed by sulfur loss.



Very recently, Suzuki, Mayer and Di Pasquale have reported the novel insertion of a nitrogen atom into an iridium–sulfur bond.¹² Photolysis of the azide complexes, $[\text{Cp}^*\text{Ir}(\text{N}_3)(\text{S}_2\text{CNR}_2)]$ ($\text{R} = \text{Me}, \text{Et}$), at below 0°C results in the loss of nitrogen and formation of $[\text{Cp}^*\text{Ir}\{\eta^2\text{-NSC}(\text{NR}_2)\text{S}\}]$. At higher temperatures, they isomerize to the disulfur-ligated complexes, $[\text{Cp}^*\text{Ir}\{\eta^2\text{-SNC}(\text{NR}_2)\text{S}\}]$, which while monomeric in solution, are dimeric in the solid state.



Isoelectronic with oxo and sulfido groups is the nitrene (NR) moiety. During the course of our studies on the copper-catalysed aziridination of alkenes, we have made extensive use of the iodine(III) reagent $\text{PhI}=\text{NTs}$ as a nitrene source.¹³ While developing a range of catalysts with the *soft* dithiocarbamate donor set, we noted that when using the copper(III) complex $[\text{Cu}(\text{S}_2\text{CNMe}_2)_2][\text{FeCl}_4]$ as catalyst, at the end of the catalytic run it was transformed into the new zwitterionic tetraamido complex, $[\text{Cu}\{\text{TsNSC}(\text{NMe}_2)\text{SNTs}\}_2]$ (**1a**). Formation of the latter results from nitrene (NTs) insertion into each of the four copper–sulfur bonds.¹⁴ We now describe this transformation in more detail, showing that it occurs in the absence of alkene, is not unique to copper, and occurs in a step-wise manner *via* a sulfido-amido intermediate.

Results and discussion

(i) Synthesis and characterisation of sulfido-amido and zwitterionic tetraamido complexes

While our initial observation concerning the multiple nitrene insertion into copper–sulfur dithiocarbamate bonds was based on an experiment utilizing the copper(III) complex, $[\text{Cu}(\text{S}_2\text{CNMe}_2)_2][\text{FeCl}_4]$ in the presence of styrene, it became quickly apparent that the transformation was not limited to copper(III) and that the styrene played no role. Indeed, while

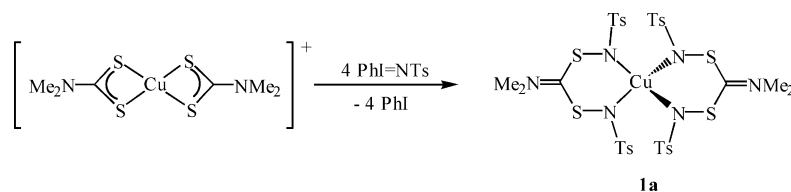
copper(III) complexes do undergo multiple nitrene insertions, they do not occur as cleanly as with the analogous copper(II) bis(dithiocarbamate) complexes, presumably as a result of the need to oxidise the copper centre, and thus our later work has focussed exclusively on the study of copper(II) bis(dithiocarbamate) complexes.

Addition of four equivalents of $\text{PhI}=\text{NTs}$ to dark brown $[\text{Cu}(\text{S}_2\text{CNR}_2)_2]$ ($\text{R} = \text{Me}, \text{Et}, \text{Pr}, \text{Bu}$) in dichloromethane at room temperature results in a colour change to light green with the concurrent dissolution of polymeric $\text{PhI}=\text{NTs}$. After a simple work-up the zwitterionic tetraamido complexes $[\text{Cu}\{\text{TsNSC}(\text{NR}_2)\text{SNTs}\}_2]$ (**1a–d**) were isolated as dry light green solids in yields of between 69–85%. No further products could be isolated suggesting that the transformation is essentially quantitative.

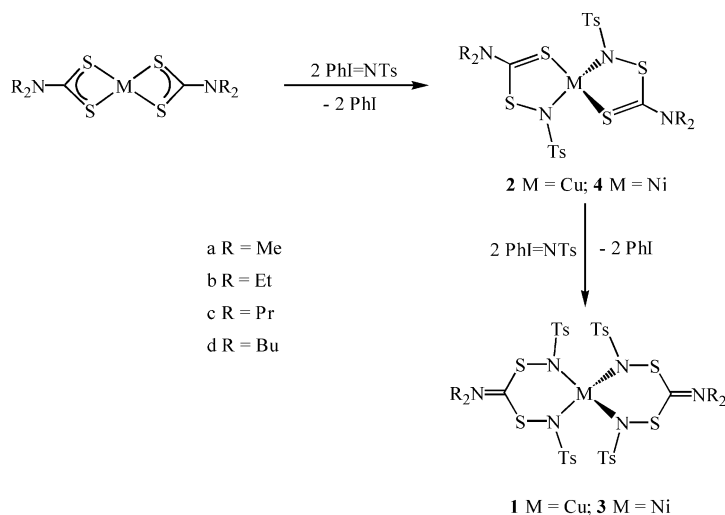
The insertion of the nitrene fragments occurs in a step-wise fashion. Thus, addition of two equivalents of $\text{PhI}=\text{NTs}$ to $[\text{Cu}(\text{S}_2\text{CNR}_2)_2]$ proceeded in a similar fashion, the dark brown solution becoming lighter in a matter of minutes. No further colour change occurred even after prolonged stirring and a similar work-up afforded the sulfido-amido complexes $[\text{Cu}\{\text{SC}(\text{NR}_2)\text{SNTs}\}_2]$ (**2a–d**) in 76–80% yield. Further, in a separate experiment, addition of another two equivalents of $\text{PhI}=\text{NTs}$ to $[\text{Cu}\{\text{SC}(\text{NBu}_2)\text{SNTs}\}_2]$ (**2d**) resulted in the rapid lightening of the initial dark green solution with the concomitant clean formation of $[\text{Cu}\{\text{TsNSC}(\text{NBu}_2)\text{SNTs}\}_2]$ (**1d**).

All nitrene-inserted complexes are soluble in dichloromethane, but insoluble in diethyl ether and petrol, further purification being carried out by recrystallisation from dichloromethane upon slow mixing with methanol. As expected, all are paramagnetic and we found the most useful characterisation tool (after elemental analysis) to be positive ion FAB mass spectrometry. Here all show prominent signals corresponding to their expected molecular ions, while the tetraamido complexes also show prominent signals due to loss of one and two NTs moieties. Further loss of NTs was also observed in some instances for both **1** and **2**. The IR spectra all show prominent peaks in the $400\text{--}900\text{ cm}^{-1}$ region, which are largely absent in the starting materials and this was a useful guide to reaction completion. Another feature of the IR spectra was that the absorption assigned to C=N stretching mode of the dithiocarbamate unit. This is found at higher frequencies than the same absorption in the copper(II) dithiocarbamate complexes, the resonance for **2** coming about half way between that of the starting material and **1**. For example, in the case of the copper butyl complexes, the C=N absorptions were found at $1495, 1515$ and 1540 cm^{-1} , respectively, for $[\text{Cu}(\text{S}_2\text{CNBu}_2)_2]$, $[\text{Cu}\{\text{SC}(\text{NBu}_2)\text{SNTs}\}_2]$ (**2d**) and $[\text{Cu}\{\text{TsNSC}(\text{NBu}_2)\text{SNTs}\}_2]$ (**1d**).

Nitrene insertion is not limited to copper and reactions at the nickel(II) centre also proved successful. Thus, addition of two equivalents of $\text{PhI}=\text{NTs}$ to green nickel(II) dithiocarbamates, $[\text{Ni}(\text{S}_2\text{CNR}_2)_2]$ ($\text{Me}, \text{Et}, \text{Pr}, \text{Bu}$), gave dark brown products identified as $[\text{Ni}\{\text{SC}(\text{NR}_2)\text{SNTs}\}_2]$ (**4a–d**), while with four equivalents of $\text{PhI}=\text{NTs}$ blue products were generated being identified as $[\text{Ni}\{\text{TsNSC}(\text{NR}_2)\text{SNTs}\}_2]$ (**3a–d**). All are soluble in dichloromethane but insoluble in diethyl ether and petrol. Yields ranged from 78–83% for the two insertion products and 69–81% for the fully inserted complexes, and analytically pure samples were generated upon slow mixing of methanol with dichloromethane solutions. Characterisation was similar to that for the copper complexes. All mass spectra showed prominent molecular ions, while most of the tetraamido complexes also



1a



showed prominent peaks due to loss of one and two nitrene moieties.

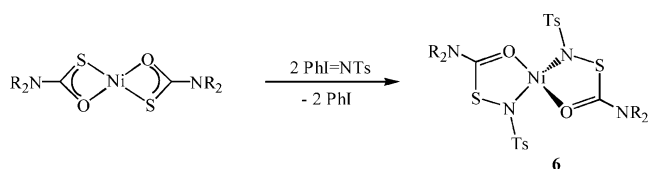
Nitrene insertion reactions into cobalt(III) and iron(III) tris(dithiocarbamates) were unsuccessful, with only starting materials being recovered at the end of the reaction. Nitrene insertions into the *in situ* generated cobalt(II) complexes, $[\text{Co}(\text{S}_2\text{CNR}_2)_2]$ (R = Me, Et, Pr, Bu), were successful. The latter were prepared by reducing $[\text{Co}(\text{S}_2\text{CNR}_2)_3]$ with zinc amalgam. They were not isolated, but filtered under rigorously anhydrous conditions onto appropriate quantities of PhI=NTs and stirred for at least a day. In this way, the tetraamido complexes $[\text{Co}\{\text{TsNSC}(\text{NR}_2)\text{SNTs}\}_2]$ (**5**) were isolated as blue solids in yields of 54–59%. Attempts to obtain two insertion products, however, were unsuccessful, and even when a deficiency of PhI=NTs was used the only new products were the tetraamido complexes. One possible reason for this is that not all the cobalt(III) dithiocarbamate was fully reduced before reaction with PhI=NTs. This supposition was supported by the observation that that mass spectrum of the crude products showed prominent peaks corresponding to $[\text{Co}(\text{S}_2\text{CNR}_2)_3]$ and yields were lower than those obtained with nickel and copper dithiocarbamates, (*ca.* 55% compared to *ca.* 80%). It would seem that reduction of Co(III) to Co(II) is required before the nitrene insertion was achieved.

We did attempt a similar reduction of $[\text{Fe}(\text{S}_2\text{CNR}_2)_3]$ to the iron(II) bis(dithiocarbamate) complexes, $[\text{Fe}(\text{S}_2\text{CNR}_2)_2]$,¹⁵ but upon addition of PhI=NTs no insertion products could be isolated. This is probably as a result of the extremely air and moisture sensitive nature of the iron(II) complexes.

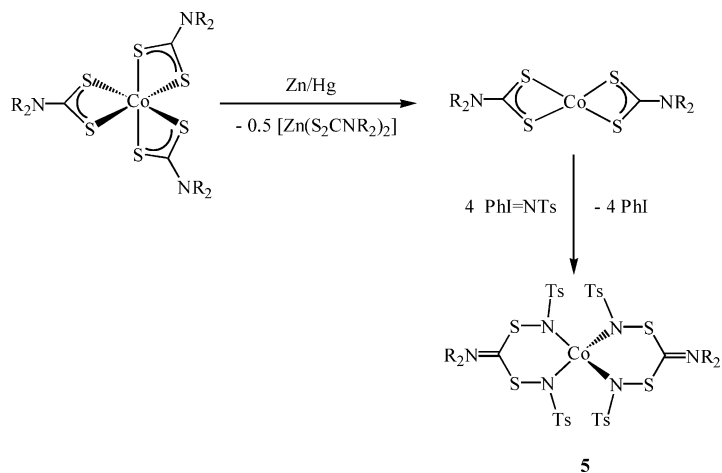
The results of nitrene insertion reactions into palladium and platinum bis(dithiocarbamates) were inconclusive. For palladium, colour changes from the yellow–orange to red–brown

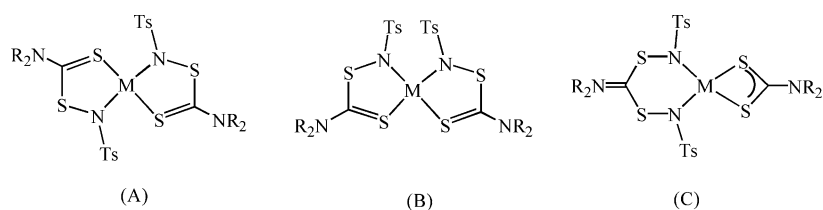
occurred during the reactions with concomitant dissolution of PhI=NTs. Analysis of the products did not support nitrene insertion into palladium–sulfur bonds and none of the products could be isolated pure. Further, attempts at nitrene insertion into lanthanum tris(dithiocarbamates) were also unsuccessful; only the starting materials being recovered.

Addition of two equivalents of PhI=NTs to the yellow–green nickel bis(thiocarbamate) complexes, $[\text{Ni}(\text{OSCN}(\text{R}_2)_2)_2]$ (R = Et, Pr, Bu), resulted in the formation of a ginger–brown solution over a few hours, and resulted in the isolation of ginger–brown powders identified as $[\text{Ni}\{\text{TsNSC}(\text{NR}_2)\text{O}\}_2]$ (**6b–d**) in yields of 53–60%. As expected, further addition of PhI=NTs did not result in insertion into the nickel–oxygen bond(s). Elemental analyses obtained for (**6b–d**) were in good agreement with the calculated values for the two insertion products but mass spectra were disappointing, showing no molecular ion peaks or discernible fragmentations.



Copper(II) xanthates are unstable since the oxidizing nature of the xanthate ligand leads to the reduction of the metal centre to copper(I). Nitrene insertion reactions were attempted with the nickel(II) xanthate complexes, $[\text{Ni}(\text{S}_2\text{COR})_2]$ (R = Me, Et, Pr), however, none of the mass spectra obtained showed peaks of molecular ions or indeed any peaks due to discernible fragmentations. IR spectra clearly showed that a reaction had occurred, as in each case there were several prominent new





bands in the region 900–450 cm^{-1} . However, from the data obtained it was not possible to postulate the precise nature of the transformation. Insertion reactions using $\text{PhI}=\text{O}$ were also attempted with both copper and nickel bis(dithiocarbamates) but in each case no significant reaction was observed.

(ii) Structural studies

Both copper(II) and nickel(II) bis(dithiocarbamate) complexes adopt a square-planar geometry at the metal centre and if such an arrangement was maintained upon nitrene insertion then insertion of two nitrene groups could lead to three possible structural types (A–C). The *trans* isomer (A) would occur if the initial insertion resulted in an activation of the M–S bond *trans* to the one already reacted, while if insertion deactivated the *trans* M–S bond the *cis* isomer (B) would be expected. Steric factors are also expected favour the *trans* isomer (A). Isomer (C) in which the two insertions occur into the same dithiocarbamate ligand is in theory possible but can be discounted on the basis of the IR spectra which only show a single C=N stretch.

In order to elucidate the precise nature of the new sulfido-amido ligand type and also to distinguish between *cis* and *trans* isomers we have determined the crystal structures of $[\text{Cu}\{\text{SC}(\text{NEt}_2)\text{SNTs}\}_2]$ (**2b**) and $[\text{Ni}\{\text{SC}(\text{NEt}_2)\text{SNTs}\}_2]$ (**4b**) the results of which are summarised in Figs. 1 and 2, respectively. Both confirm the insertion of two NTs groups into the bis(dithiocarbamate) complexes, and while the coordination geometry at the metal centre is severely distorted from an ideal square-plane, the approximate *trans* arrangement of the inserted nitrogen atoms is apparent [N(1)–Cu(1)–N(3) 169.85(13)°, N(1)–Ni(1)–N(3) 173.6(2)°]. The distortion away from square-planar is clearly apparent from the relative position of the metal-bound sulfur atoms [S(3)–Cu(1)–S(6) 147.34(5)°, S(3)–Ni(1)–S(6) 160.86(7)°], a comparison of which reveals that the distortion is much greater at copper. Insertion of the nitrene fragment leads to a significant increase in the bite-angle of the

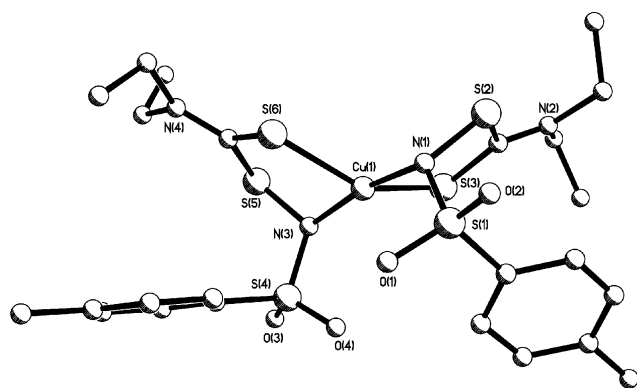


Fig. 1 Molecular structure of $[\text{Cu}\{\text{SC}(\text{NEt}_2)\text{SNTs}\}_2]$ (**2b**) with selected bond lengths (Å) and angles (°); Cu(1)–N(1) 1.949(3), Cu(1)–N(3) 1.954(3), Cu(1)–S(3) 2.2969(11), Cu(1)–S(6) 2.3188(10), N(1)–S(2) 1.680(3), N(3)–S(5) 1.670(3), S(2)–C(8) 1.768(4), S(3)–C(8) 1.691(4), S(5)–C(20) 1.770(4), S(6)–C(20) 1.702(4), C(8)–N(2) 1.313(5), C(20)–N(4) 1.310(5); N(1)–Cu(1)–S(3) 88.97(9), N(3)–Cu(1)–S(6) 88.21(9), N(1)–Cu(1)–N(3) 169.85(13), S(3)–Cu(1)–S(6) 147.34(5), Cu(1)–N(1)–S(2) 116.72(17), N(1)–S(2)–C(8) 101.93(17), Cu(1)–S(3)–C(8) 101.31(14), S(2)–C(8)–S(3) 119.3(2), Cu(1)–N(3)–S(5) 115.60(17), N(3)–S(5)–C(20) 101.57(17), Cu(1)–S(6)–C(20) 100.01(13), S(5)–C(20)–S(6) 119.4(2).

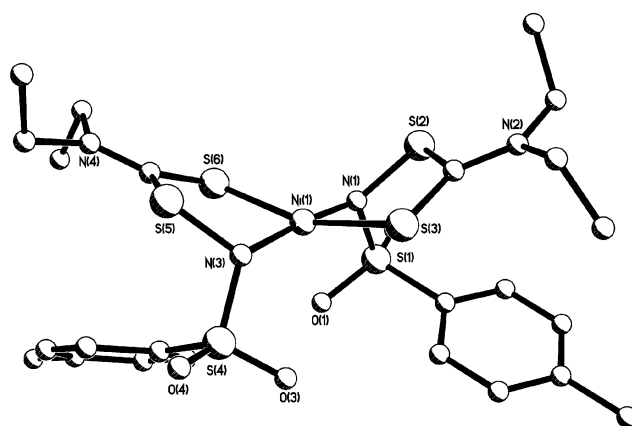
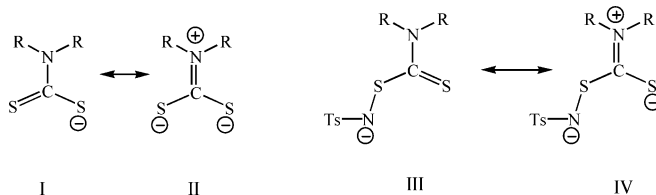


Fig. 2 Molecular structure of $[\text{Ni}\{\text{SC}(\text{NEt}_2)\text{SNTs}\}_2]$ (**4b**) with selected bond lengths (Å) and angles (°); Ni(1)–N(1) 1.897(4), Ni(1)–N(3) 1.904(4), Ni(1)–S(3) 2.2183(15), Ni(1)–S(6) 2.1977(15), N(1)–S(2) 1.683(5), N(3)–S(5) 1.688(5), S(2)–C(8) 1.764(6), S(3)–C(8) 1.703(5), S(5)–C(20) 1.767(6), S(6)–C(20) 1.701(5), C(8)–N(2) 1.318(7), C(20)–N(4) 1.303(7); N(1)–Ni(1)–S(3) 89.33(14), N(3)–Ni(1)–S(6) 89.68(14), N(1)–Ni(1)–N(3) 173.6(2), S(3)–Ni(1)–S(6) 160.86(7), Ni(1)–N(1)–S(2) 115.4(3), N(1)–S(2)–C(8) 100.1(2), Ni(1)–S(3)–C(8) 100.77(19), S(2)–C(8)–S(3) 118.2(3), Ni(1)–N(3)–S(5) 112.3(3), N(3)–S(5)–C(20) 100.5(2), Ni(1)–S(6)–C(20) 102.7(2), S(5)–C(20)–S(6) 117.3(3).

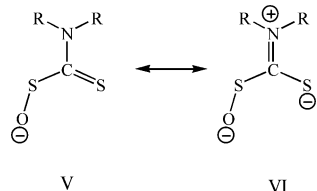
ligand from around 76–77° in the dithiocarbamate complexes¹ to 88–89° in **2b** and **4b**.

It is well known that dithiocarbamates can potentially adopt two different resonance forms (I) and (II), the thioureide form (II) resulting from delocalisation of the nitrogen lone-pair.¹ Likewise resonance hybrids (III) and (IV) can be considered for the new sulfido-amido ligands shown here.



A closer look at the bond lengths within the new ligand type sheds some light on the relative importance of each resonance form. Thus, in each there is one long and one short carbon–sulfur bond. The shorter of the two is that to the metal-bound sulfur atom and varies between 1.670(3)–1.703(5) Å, while the longer varies between 1.770(4)–1.764(6) Å—differences ranging from 0.077–0.061 Å. These differences seem to suggest that thioureide-type resonance form (IV) is a major contributor. However, it should also be noted that the carbon–nitrogen bonds are quite short, ranging from 1.303(7)–1.318(7) Å, as compared with a mean value of 1.324 Å found in dithiocarbamate complexes,¹ which suggests that resonance form (III) is also a major contributor. The sulfur–nitrogen interactions of between 1.670(3)–1.688(5) Å are consistent with a single sulfur–nitrogen bond, while copper–sulfur [Cu(1)–S(3) 2.319(1), Cu(1)–S(6) 2.297(1) Å] and nickel–sulfur [Ni(1)–S(3) 2.218(2), Ni(1)–S(6) 2.198(2)] are comparable with the mean values of found 2.250 and 2.207 Å found in copper and nickel dithiocarbamate complexes, respectively.

Closely related to the new ligands seen in **2b** and **4b** is the oxygen-expanded ligand in the chromium(III) complexes $[\text{Cr}(\text{S}_2\text{CNR}_2)(\text{OS}_2\text{CNR}_2)]$, one example of which ($\text{R} = \text{Et}$) has been crystallographically characterised. The latter is, however, complicated by the disorder of the oxygen-expanded dithiocarbamate ligand over three sites.¹⁰ Nevertheless, on the basis of the observations that the oxygen-expanded complexes were more easily oxidised than the analogous tris(dithiocarbamate) complexes and that the cations generated exhibited greater stability, the resonance state (VI) is believed to be a major contributor.¹⁶ The presence of the electron-withdrawing tosyl group in **2** and **4** may serve to stabilize the development of negative charge at nitrogen and thus the thioureide-type resonance hybrid (IV).



Resonance hybrids (VII) and (VIII) can be considered for the zwitterionic tetraamido complexes resulting from the insertion of NTs groups into all four metal–sulfur bonds. In order to probe this further we have carried out the X-ray crystal structures of two examples, namely $[\text{Cu}\{\text{TsNSC}(\text{NMe}_2)\text{SNTs}\}_2]$ (**1a**) and $[\text{Co}\{\text{TsNSC}(\text{NEt}_2)\text{SNTs}\}_2]$ (**5b**) the results of which are given in Figs. 3 and 4, respectively. Both confirm the insertion of four NTs groups into the bis(dithiocarbamate) complexes. Now the coordination geometry at the metal centre is even further distorted away from an ideal square-plane as shown by the approximate bond angles subtended at the metal centres. Thus, in **1a** the *trans* nitrogen interactions $[\text{N}(1)\text{--Cu--N}(1\text{A}) 157.0(2), \text{N}(2)\text{--Cu--N}(2\text{A}) 154.5(2)^\circ]$ are distorted to an even greater

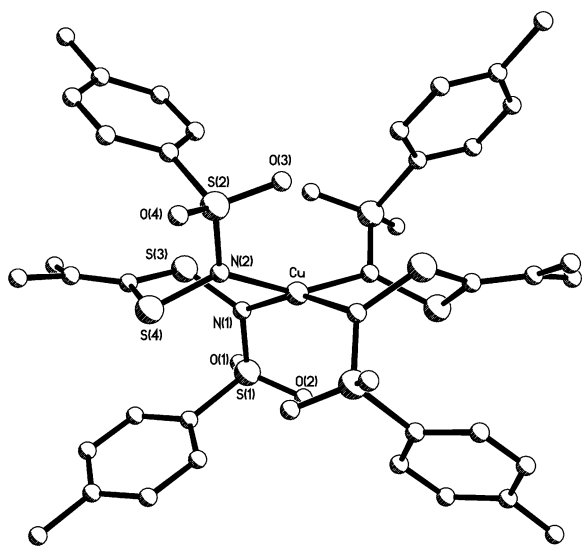
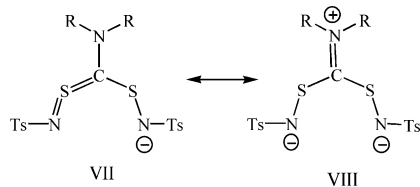


Fig. 3 Molecular structure of $[\text{Cu}\{\text{TsNSC}(\text{NMe}_2)\text{SNTs}\}_2]$ (**1a**) with selected bond lengths (Å) and angles ($^\circ$); Cu–N(1) 2.005(4), Cu–N(2) 2.016(4), S(1)–N(1) 1.642(4), S(2)–N(2) 1.649(4), S(3)–N(1) 1.687(4), S(4)–N(2) 1.694(4), S(3)–C(30) 1.759(5), S(4)–C(30) 1.781(5), N(3)–C(30) 1.330(6); N(1)–Cu–N(2) 87.4(2), N(1)–Cu–N(2A) 97.7(2), N(1)–Cu–N(1A) 157.0(2), N(2)–Cu–N(2A) 154.5(2), Cu–N(1)–S(3) 124.3(2), N(1)–S(3)–C(30) 103.5(2), S(3)–C(30)–S(4) 119.3(3), C(30)–S(4)–N(2) 103.5(2), S(4)–N(2)–Cu 124.1(2).

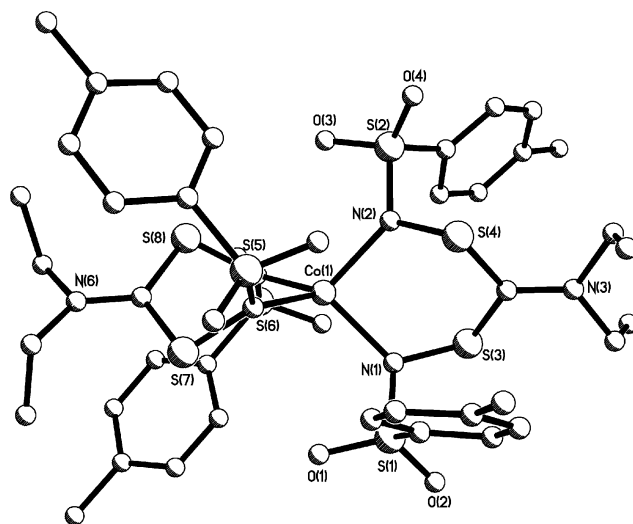
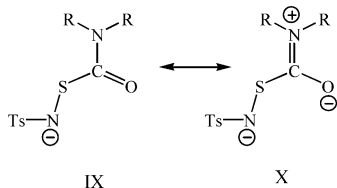


Fig. 4 Molecular structure of $[\text{Co}\{\text{TsNSC}(\text{NEt}_2)\text{SNTs}\}_2]$ (**5b**) with selected bond lengths (Å) and angles ($^\circ$); Co(1)–N(1) 2.003(4), Co(1)–N(2) 1.985(4), Co(1)–N(4) 1.992(4), Co(1)–N(5) 1.979(4), N(1)–S(3) 1.673(4), N(2)–S(4) 1.674(4), N(4)–S(7) 1.681(4), N(5)–S(8) 1.678(4), S(3)–C(15) 1.751(6), S(4)–C(15) 1.730(5), S(7)–C(34) 1.735(5), S(8)–C(34) 1.755(5), C(15)–N(3) 1.311(6), C(34)–N(6) 1.310(6); N(1)–Co(1)–N(2) 92.89(16), N(4)–Co(1)–N(5) 92.89(16), N(1)–Co(1)–N(4) 115.79(16), N(2)–Co(1)–N(5) 117.51(17), N(1)–Co(1)–N(5) 124.64(17), N(2)–Co(1)–N(4) 115.02(17), Co(1)–N(2)–S(4) 118.3(2), Co(1)–N(1)–S(3) 121.1(2), Co(1)–N(4)–S(7) 117.7(2), Co(1)–N(5)–S(8) 120.3(2), N(1)–S(3)–C(15) 105.4(2), N(2)–S(4)–C(15) 104.4(2), N(4)–S(7)–C(34) 104.1(2), N(5)–S(8)–C(34) 103.5(2), S(3)–C(15)–S(4) 120.3(3), S(7)–C(34)–S(8) 120.2(3).

extent than the value of $169.85(13)^\circ$ found in **2b**. The bite-angle of $87.4(2)^\circ$ for the tetraamido ligand in **1a** varies only slightly from those in **2b** suggesting that insertion of the second nitrene group does not ease the ring strain significantly. Bite-angles of $92.89(16)^\circ$ at the cobalt(II) centre in **5b** are slightly larger and here there is a very severe distortion away from square-planar. Indeed, interligand bond angles of between $115.02(17)$ – $124.64(17)^\circ$ suggest that the coordination geometry is best considered to be a distorted tetrahedron. The copper–nitrogen bonds of $2.016(4)$ – $2.005(4)$ Å in **1a** are slightly longer than those of $1.949(3)$ – $1.954(3)$ Å in **2b**; which may be a consequence of the different coordination geometries at the two metal centres. Cobalt–nitrogen bonds in **5b** lie intermediate between the two extremes noted above, varying between $1.979(4)$ – $2.003(4)$ Å.

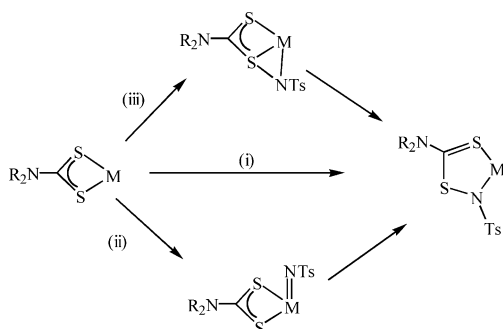
Resonance hybrids (VII) and (VIII) can be considered for the new tetraamido ligands. In each tetraamido ligand one short and one long sulfur–carbon bond is seen, although the difference between the two is not as marked as found in the sulfido-amido complexes. Thus in **1a** the crystallographically unique tetraamido ligand is characterised by carbon–sulfur bonds of $1.759(5)$ and $1.781(5)$ Å [$\Delta 0.022$ Å], which can be compared to the pairs of carbon–sulfur bonds in **5b** [$1.755(5)$ and $1.735(5)$ Å, $\Delta 0.020$ Å; $1.751(6)$ and $1.730(5)$ Å, $\Delta 0.021$ Å]. In each case, the shorter of these is indicative of only a small degree of double bond character. The sulfur–nitrogen bond lengths of $1.694(4)$ – $1.687(4)$ Å in **1a** and $1.681(4)$ – $1.673(4)$ Å in **5b** are very similar to those of $1.688(3)$ – $1.670(5)$ Å found in the sulfido-amido complexes. Perhaps significantly, in the latter neither resonance form demands any sulfur–nitrogen double bond character, and the similarity of these bonds between ligand types might suggest that the thioureide-type resonance form (VIII) dominates here. This would lead to a significant degree of carbon–nitrogen double bond character, and this is certainly seen in the cobalt(II) complex **5b**, where short interactions of $1.311(6)$ and $1.310(6)$ Å are observed. Thus, we favour a dominant contribution to the bonding from the thioureide-type resonance hybrid (VIII), leading to our assertion that these are best considered as zwitterionic tetraamido complexes.

Unfortunately we were unable to crystallographically characterize an example of the nitrene-expand thiocarbamate complexes **6**. Nevertheless, resonance hybrids (IX) and (X) can be envisaged and we favour the latter as the dominant form on the basis of the increased electronegativity of oxygen *versus* sulfur.

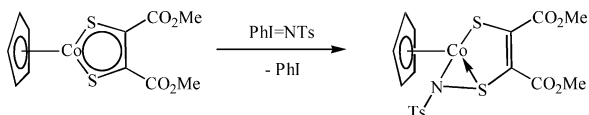


(iii) Mechanism of nitrene insertion?

How the nitrene insertion reaction occurs in these dithiocarbamate complexes is not clear. Three possible routes might, however, be envisaged; (i) direct insertion, (ii) initial formation of a metal–nitrene complex, possibly as a result of a change in hapticity of the dithiocarbamate, followed by insertion, (iii) initial addition at the metal–sulfur bond followed by later insertion. While we have no evidence in favour or against any particular route, we tend to favour the latter in which initial addition to sulfur occurs. Route (ii) seems improbable as low-valent transition metal nitrene complexes are virtually unknown and those that are known are found to be highly reactive. While in light of the recent isolation of a low-valent nickel nitrene complex,¹⁷ one may be inclined to support this route, it seems highly unlikely that related copper–nitrene complexes would be stable. The direct insertion process (i) may occur, but it is difficult to see why this would not be a general process for both divalent and trivalent complexes.



Recent work by Kajitani and co-workers potentially sheds some light on the process.¹⁸ Thus, they used $\text{PhI}=\text{NTs}$ to prepare the imido-bridged cobalt complex $[\text{CpCo}\{\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2\}(\text{NTs})]$. This 3-membered cobaltthiaziridine ring is formed by reacting $[\text{CpCo}\{\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2\}]$ with $\text{PhI}=\text{NTs}$ in a dichloromethane–benzene solution at room temperature, the NTs group being inserted into a cobalt–sulfur bond.



If indeed the insertion reaction does occur *via* an initial addition of the nitrene across the metal–sulfur bond, then a rationalisation for the lack of reactivity of octahedral metal(III) complexes may be; (i) that there is not enough space for the addition process, and (ii) the increasing charge on the metal ion makes the metal–sulfur bond less electron-rich—and thus addition of the electron-deficient tosyl nitrene fragment is disfavoured.

Experimental

General

Dithiocarbamate and monothiocarbamate complexes and $\text{PhI}=\text{NTs}$ were prepared using standard literature methods. All

reactions were carried out in pre-dried solvents under a nitrogen atmosphere, but work-up and all subsequent crystallisations were carried out in air in non-dried solvents.

Synthesis of $[\text{Cu}\{\text{TsNSC}(\text{NR}_2)\text{SNTs}\}_2]$ (1**).** To $[\text{Cu}(\text{S}_2\text{CNR}_2)_2]$ (0.50 mmol) dissolved in dichloromethane (20 cm^3) was added $\text{PhI}=\text{NTs}$ (2.20 mmol). On mixing the solution became green. After stirring overnight, the solution was filtered and volatiles were removed under reduced pressure to give a green solid which was washed with diethyl ether and dried. The resulting green powder was identified as $[\text{Cu}\{\text{TsNSC}(\text{NR}_2)\text{SNTs}\}_2]$ (**1**). Dark green crystals of **1a** suitable for X-ray crystallography were grown upon slow evaporation of a dichloromethane solution in air.

1a (69%). IR (KBr) ν/cm^{-1} 1629w, 1599w, 1551m, 1493w, 1446w, 1404w, 1299w, 1283m, 1163w, 1146s, 1085m, 1021w, 895m, 815m, 656m, 579m, 548m; mass spectrum (FAB) m/z 980 (M^+), 855, 460, 396, 217; Anal. Calc. for $\text{C}_{34}\text{H}_{40}\text{N}_6\text{O}_8\text{S}_8\text{Cu}_1 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$, C, 40.51, H, 4.01, N, 8.22; Found C, 40.89, H, 4.15, N, 7.65.

1b (78%). IR (KBr) ν/cm^{-1} 1638w, 1617w, 1597w, 1532m, 1495w, 1455m, 1443m, 1386w, 1353w, 1301s, 1283s, 1193w, 1148s, 1085m, 891s, 819s, 789m, 742w, 727w, 706w, 655m, 577s, 548m, 467w; mass spectrum (FAB) m/z 1036 (M^+), 549, 488; Anal. Calc. for $\text{C}_{38}\text{H}_{48}\text{N}_6\text{O}_8\text{S}_8\text{Cu}_1 \cdot 2\text{CH}_2\text{Cl}_2$, C, 39.82, H, 4.31, N, 6.97; Found C, 40.22, H, 4.60, N, 6.75.

1c (85%). IR (KBr) ν/cm^{-1} 1735m, 1701s, 1685s, 1676m, 1653m, 1648w, 1637m, 1617s, 1560m, 1306m, 1170m, 1105m, 840w, 685w, 545m; mass spectrum (FAB) m/z 1094 (M^+), 923 ($\text{M}-\text{NTs}$), 754 ($\text{M}-2\text{NTs}$), 516, 397; Anal. Calc. for $\text{C}_{42}\text{H}_{56}\text{N}_6\text{O}_8\text{S}_8\text{Cu}_1$, C, 46.17, H, 5.13, N, 7.70; Found C, 46.66, H, 5.66, N, 7.71.

1d (79%). IR (KBr) ν/cm^{-1} 1600m, 1540m, 1309w, 1301m, 1285w, 1147vs, 1085m, 893m, 814m, 795w, 656m, 577m, 551w, 546m; mass spectrum (FAB) m/z 1150 (M^+), 981, 544, 289; Anal. Calc. for $\text{C}_{64}\text{H}_{64}\text{N}_6\text{O}_8\text{S}_8\text{Cu}_1 \cdot \text{CH}_2\text{Cl}_2$, C, 45.76, H, 5.35, N, 6.82; Found C, 46.12, H, 5.27, N, 6.86.

Synthesis of $[\text{Cu}\{\text{SC}(\text{NR}_2)\text{SNTs}\}_2]$ (2**).** To $[\text{Cu}(\text{S}_2\text{CNR}_2)_2]$ (0.50 mmol) dissolved in dichloromethane (20 cm^3) was added $\text{PhI}=\text{NTs}$ (1.20 mmol). The brown suspension was stirred for *ca.* 8 h during which time the solution became clear. After filtration, volatiles were removed under reduced pressure and the remaining brown solid was washed with diethyl ether and dried. The resulting brown powder that was identified as $[\text{Cu}\{\text{SC}(\text{NR}_2)\text{SNTs}\}_2]$ (**2**). Dark brown crystals of **2b** suitable for X-ray crystallography were grown upon mixing of toluene with a dichloromethane solution.

2a (76%) IR (KBr) ν/cm^{-1} 1585w, 1541w, 1527m, 1397m, 1300w, 1284m, 1162w, 1144s, 1084m, 880w, 810s, 660m, 580m, 548m; mass spectrum (FAB) m/z 642 (M^+), 515, 460, 428, 396; Anal. Calc. for $\text{C}_{20}\text{H}_{26}\text{N}_4\text{O}_4\text{S}_6\text{Cu}_1$, C, 37.41, H, 4.05, N, 8.73; Found C, 36.82, H, 4.15, N, 7.89.

2b (90%). IR (KBr) ν/cm^{-1} 1518s, 1458w, 1440m, 1383w, 1354w, 1301m, 1283m, 1200w, 1147s, 1085m, 1020w, 978w, 882m, 791w, 662m, 582m, 551m, 469w; mass spectrum (FAB) m/z 698 (M^+); Anal. Calc. for $\text{C}_{24}\text{H}_{34}\text{N}_4\text{O}_4\text{S}_6\text{Cu}_1$, C, 41.29, H, 4.87, N, 8.03; Found C, 41.12, H, 4.71, N, 7.95.

2c (80%). IR (KBr) ν/cm^{-1} 1683m, 1654w, 1543w, 1440w, 1301m, 1282w, 1163w, 1146s, 1084m, 1030w, 810m, 660m, 580m, 555m; mass spectrum (FAB) m/z 754 (M^+), 585 ($\text{M}-\text{NTs}$) 415, 397; Anal. Calc. for $\text{C}_{28}\text{H}_{42}\text{N}_4\text{O}_4\text{S}_6\text{Cu}_1 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$, C, 41.50, H, 5.25, N, 6.68; Found C, 39.48, H, 4.70, N, 5.97.

2d (84%) IR (KBr) ν/cm^{-1} 1697m, 1540w, 1515m, 1457w, 1436w, 1301m, 1284w, 1262w, 1226m, 1146s, 1084m, 1039w, 1016w, 889m, 811s, 790w, 658m, 578m, 549m; mass spectrum (FAB) m/z 810 (M^+), 640 ($\text{M}-\text{NTs}$), 471, 437; Anal. Calc. for $\text{C}_{32}\text{H}_{50}\text{N}_4\text{O}_4\text{S}_6\text{Cu}_1 \cdot 1/2\text{CH}_2\text{Cl}_2$, C, 45.77, H, 5.99, N, 6.57; Found C, 45.98, H, 5.80, N, 6.24.

Synthesis of $[\text{Ni}\{\text{TsNSC}(\text{NR}_2)\text{SNTs}\}_2]$ (3**).** To $[\text{Ni}(\text{S}_2\text{CNR}_2)_2]$ (0.30 mmol) dissolved in dichloromethane (20 cm^3) was

added PhI=NTs (1.30 mmol). The colour initially became burgundy-brown and after *ca.* 4 h it turned blue. After stirring overnight, the blue mixture was filtered and volatiles removed under reduced pressure. The solid was washed with diethyl ether and dried to give a slate-blue powder identified as $[\text{Ni}\{\text{TsNSC}(\text{NR}_2)\text{SNTs}\}_2]$ (**3**).

3a (70%). IR (KBr) ν/cm^{-1} 1735m, 1701m, 1675m, 1685s, 11636m, 1590m, 1560m, 1455w, 1440m, 1420m, 1165w, 1085w, 810m, 670m, 585w; mass spectrum (FAB) m/z 637, 516, 467, 428, 313, 225, 190, 172, 155; Anal. Calc. for $\text{C}_{34}\text{H}_{42}\text{N}_6\text{O}_8\text{S}_8\text{Ni}_1\text{CH}_2\text{Cl}_2$, C, 39.64, H, 3.96, N, 7.93; Found C, 39.57, H, 4.35, N, 7.42.

3b (69%). IR (KBr) ν/cm^{-1} 1637m, 1595m, 1540m, 1445m, 1285w, 1263m, 1164s, 1147s, 1085m, 1020w, 880m, 812s, 705m, 664m, 660w, 580m, 549m; mass spectrum (FAB) m/z 1031 (M^+), 999, 967, 943, 862 (M-NTs), 830, 693 (M-2NTs), 644, 603, 578, 576, 529; Anal. Calc. for $\text{C}_{38}\text{H}_{48}\text{N}_6\text{O}_8\text{S}_8\text{Ni}_1\cdot\frac{1}{2}\text{CH}_2\text{Cl}_2$, C, 43.08, H, 4.57, N, 7.83; Found C, 43.23, H, 4.78, N, 7.08.

3c (81%). IR (KBr) ν/cm^{-1} 1685w, 1637m, 1599w, 1543m, 1458w, 1439w, 1384w, 1262s, 1164w, 1144m, 1086s, 1021m, 808vs, 668m, 580w, 545m; mass spectrum (FAB) m/z 1087 (M^+), 769 (M-2NTs).

3d (80%). IR (KBr) ν/cm^{-1} 1653m, 1598m, 1578w, 1542w, 1521m, 1459w, 1438m, 1381w, 1285s, 1262vs, 1230w, 1166w, 1148m, 1087m, 1035m, 810vs, 661s, 582m, 549m; mass spectrum (FAB) m/z 1144 (M^+), 810 (M-2NTs); Anal. Calc. for $\text{C}_{64}\text{H}_{64}\text{N}_6\text{O}_8\text{S}_8\text{Ni}_1\text{CH}_2\text{Cl}_2$, C, 45.95, H, 5.38, N, 6.84; Found C, 44.22 H, 6.07, N, 6.34.

Synthesis of $[\text{Ni}\{\text{SC}(\text{NR}_2)\text{SNTs}\}_2]$ (4**).** To $[\text{Ni}(\text{S}_2\text{CNR}_2)_2]$ (0.50 mmol) dissolved in dichloromethane (20 cm^3) was added PhI=NTs (1.20 mmol). On mixing the colour became a dark burgundy-brown. This was stirred overnight, the colour remaining unchanged. After filtration, the volatiles were removed under reduced pressure to afford a burgundy-brown product. This was washed with diethyl ether and dried, resulting in a very dark brown powder identified as $[\text{Ni}\{\text{SC}(\text{NR}_2)\text{SNTs}\}_2]$ (**4**). Dark blue crystals of **4b** suitable for X-ray crystallography were grown upon slow evaporation of a dichloromethane solution in air.

4a (80%). IR (KBr) ν/cm^{-1} 1700m, 1735m, 1684s, 1676m, 1654m, 1648s, 1637m, 1617m, 1560s, 1540s, 1420m, 1270m, 1155w, 1095m, 1030w, 815m, 600w; mass spectrum (FAB) m/z 637 (M^+), 516 (M-(S_2CNMe_2)), 467 (M-NTs), 427, 313, 266; Anal. Calc. for $\text{C}_{20}\text{H}_{26}\text{N}_4\text{O}_4\text{S}_6\text{Ni}_1$, C, 37.71, H, 4.08, N, 8.80; Found C, 37.01, H, 4.44, N, 7.15.

4b (80%). IR (KBr) ν/cm^{-1} , 1630m, 1597w, 1520s, 1459w, 1440m, 1383w, 1354w, 1314m, 1281m, 1201m, 1149s, 1085m, 1020w, 869w, 814m, 665m, 583m, 550m; mass spectrum (FAB) m/z 693 (M^+), 526, 524 (M-NTs), 488, 418, 319; Anal. Calc. for $\text{C}_{24}\text{H}_{34}\text{N}_4\text{O}_4\text{S}_6\text{Ni}_1$, C, 41.56, H, 4.91, N, 8.08; Found C, 41.88, H, 4.43, N, 7.48.

4c (78%). IR (KBr) ν/cm^{-1} 1739w, 1683m, 1654w, 1601w, 1524s, 1463m, 1437m, 1411w, 1308m, 1259m, 1196w, 1149vs, 1090vs, 1023m, 980w, 895w, 853m, 805s, 748w, 666m, 580m, 550m, 472w; mass spectrum (FAB) m/z 749 (M^+), 580 (M-NTs), 411 (M-2NTs).

4d (83%). IR (KBr) ν/cm^{-1} 1540s, 1458m, 1437m, 1383m, 1299w, 1262s, 1227m, 1182w, 1148s, 1087s, 1046w, 1020w, 807vs, 664s, 580m, 547m; mass spectrum (FAB) m/z 805 (M^+), 636 (M-NTs), 467 (M-2NTs); Anal. Calc. for $\text{C}_{32}\text{H}_{50}\text{N}_4\text{O}_4\text{S}_6\text{Ni}_1\cdot\text{CH}_2\text{Cl}_2$, C 44.52, H 5.85, N 6.30; Found C 43.67, H 6.06, N 5.54.

Synthesis of $[\text{Co}\{\text{TsNSC}(\text{NR}_2)\text{SNTs}\}_2]$ (5**).** To $[\text{Co}(\text{S}_2\text{CNR}_2)_2]$ (0.20 mmol) dissolved in dichloromethane (20 cm^3) was added an excess of zinc amalgam. This was stirred for 3 h during which the initial green colour became much darker. This solution was then filtered onto PhI=NTs (1.00 mmol) and stirred for 24 h, by which time the colour had become dark brown. After filtration, volatiles were removed under reduced pressure to afford a dark brown powder identified as $[\text{Co}\{\text{TsNSC}(\text{NR}_2)\text{SNTs}\}_2]$ (**5**). Blue

crystals of **5b** suitable for X-ray crystallography were grown upon slow evaporation of a dichloromethane solution in air.

5a (54%). IR (KBr) ν/cm^{-1} 1742w, 1677m, 1598m, 1543s, 1442m, 1407m, 1382w, 1356m, 1301w, 1262s, 1164w, 1144w, 1087s, 1054w, 1016w, 957w, 881m, 814s, 737m, 704w, 669s, 579w, 548m, 449w; mass spectrum (FAB) m/z 970 (M^+), 802 (M-NTs), 448, 299 (M-4NTs).

5b (57%). IR (KBr) ν/cm^{-1} 1743w, 1634w, 1599m, 1527s, 1495w, 1445m, 1408m, 1383w, 1356m, 1301w, 1264m, 1211w, 1163m, 1142w, 1087s, 1056w, 1016w, 957w, 881m, 815s, 738w, 704w, 668s, 579w, 552m, 439w; mass spectrum (FAB) m/z 1027 (M^+), 858 (M-NTs), 503, 355 (M-4NTs); Anal. Calc. for $\text{C}_{38}\text{H}_{48}\text{N}_6\text{O}_8\text{S}_8\text{Co}_1$, C, 44.23, H, 4.66, N, 8.15; Found C, 43.76, H, 4.78, N, 7.98.

5c (56%). IR (KBr) ν/cm^{-1} 1736w, 1681w, 1604m, 1534m, 1500w, 1457m, 1407m, 1304m, 1264w, 1222w, 1161s, 1121w, 1096m, 1060w, 1020w, 905m, 846w, 815s, 705w, 673m, 588w, 556w, 535m, 427w; mass spectrum (FAB) m/z 1087 (M^+), 1031, 587 503, 411 (M-4NTs).

5d (59%). IR (KBr) ν/cm^{-1} 1734w, 1684m, 1599m, 1539w, 1515m, 1459w, 1439w, 1406w, 1372w, 1296m, 1262w, 1226m, 1164s, 1147m, 1088s, 1053m, 1017w, 873m, 814s, 738m, 704w, 664s, 552s, 445w; mass spectrum (FAB) m/z 1139 (M^+), 671, 636 (M-3NTs), 467 (M-4NTs).

Synthesis of $[\text{Ni}\{\text{OC}(\text{NR}_2)\text{SNTs}\}_2]$ (6**).** To a dichloromethane (20 cm^3) solution of $[\text{Ni}(\text{OSCNR}_2)_2]$ (0.68 mmol) was added PhI=NTs (1.53 mmol). The solution soon became yellow-green and after stirring overnight was ginger-brown. Volatiles were removed under reduced pressure and resulting solid washed with diethyl ether. This was dried resulting in a ginger-brown powder identified as $[\text{Ni}\{\text{OC}(\text{NR}_2)\text{SNTs}\}_2]$ (**6**).

6b (53%). IR (KBr) ν/cm^{-1} 1679m, 1600m, 1543w, 1495w, 1458w, 1416m, 1382w, 1358m, 1305w, 1261s, 1216m, 1166s, 1142w, 1120w, 1087s, 1037w, 942w, 877w, 812s, 740w, 666s, 578w, 547m, 427w; Anal. Calc. for $\text{C}_{24}\text{H}_{34}\text{N}_4\text{O}_6\text{S}_4\text{Ni}_1\cdot\frac{1}{2}\text{CH}_2\text{Cl}_2$, C, 41.79, H, 4.98, N, 7.96; Found C, 41.35, H, 4.78, N, 6.93.

6c (57%). IR (KBr) ν/cm^{-1} 1603m, 1547w, 1495w, 1461w, 1417m, 1382m, 1342w, 1262s, 1163m, 1089s, 1021m, 973w, 876w, 804s, 706w, 659m, 581w, 548m, 420w; Anal. Calc. for $\text{C}_{28}\text{H}_{42}\text{N}_4\text{O}_6\text{S}_4\text{Ni}_1\cdot\text{CH}_2\text{Cl}_2$, C, 43.39, H, 5.49, N, 6.98; Found C, 43.04, H, 6.06, N, 6.61.

6d (60%) IR (KBr) ν/cm^{-1} 1669w, 1619s, 1542w, 1460w, 1420m, 1379w, 1340w, 1262s, 1164m, 1120w, 1090m, 1020w, 952w, 807s, 703w, 664w, 591w, 543w, 418w; Anal. Calc. for $\text{C}_{32}\text{H}_{50}\text{N}_4\text{O}_6\text{S}_4\text{Ni}_1\cdot\text{CH}_2\text{Cl}_2$, C, 46.15, H, 6.06, N, 6.53; Found C, 46.01, H, 6.00, N, 6.59.

X-Ray data collection and solution

Details of the crystal structure analyses of $[\text{Cu}\{\text{TsNSC}(\text{NMe}_2)\text{SNTs}\}_2]\cdot 2\text{CH}_2\text{Cl}_2$ (**1a**) $\cdot 2\text{CH}_2\text{Cl}_2$ have been communicated previously.¹⁴ A single crystal was mounted on a glass fibre and all geometric and intensity data were taken from this sample using an automated four-circle diffractometer (Nicolet R3mV) equipped with Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$) at $293 \pm 2 \text{ K}$. Lattice parameters were identified by application of the automatic indexing routine of the diffractometer to the positions of a number of reflections taken from a rotation photograph and centred by the diffractometer. The ω - 2θ technique was used to measure reflections and three standard reflections (remeasured every 97 scans) showed no significant loss in intensity during data collection. The data was corrected for Lorentz and polarisation effects and unique data with $I \geq 2\sigma(I)$ were used to solve and refine the structure. This was solved by direct methods and developed by using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealised positions (C-H 0.96 \AA) and assigned a common isotropic thermal parameter ($U = 0.08 \text{ \AA}^2$). Final difference-Fourier map was featureless and contained no peaks greater than 1.00 e \AA^{-3} .

Structure solution used the SHELXTL PLUS program package on an IBM PC.

Crystallographic data for $[\text{Cu}\{\text{TsNSC}(\text{NMe}_2)\text{SNTs}\}_2] \cdot 2\text{CH}_2\text{Cl}_2$ (**1a**)· $2\text{CH}_2\text{Cl}_2$; green block, dimensions $0.36 \times 0.26 \times 0.24$ mm, monoclinic, space group $C2/c$, $a = 12.457(2)$, $b = 22.648(5)$, $c = 19.224(4)$ Å, $\beta = 106.59(3)^\circ$, $V = 5198(2)$ Å³, $Z = 4$, $F(000)$ 2364, $d_{\text{calc}} = 1.470$ g cm⁻³, $\mu = 0.998$ mm⁻¹. 4469 reflections were collected, 4274 unique [$R(\text{int}) = 0.0420$] of which 3086 were observed [$I > 2.0\sigma(I)$]. At convergence, $R_1 = 0.0624$, $wR_2 = 0.1462$ [$I > 2.0\sigma(I)$] and $R_1 = 0.0908$, $wR_2 = 0.1765$ (all data), for 285 parameters.

The structures of **2b**, **4b** and **5b** recorded using a Nonius Kappa CCD diffractometer, with a detector-to-crystal distance of 25 mm. Crystals were mounted in a thin glass capillary with a drop of mother liquor using a fast setting epoxy resin. A total of 90 oscillation frames each of 60 s exposure time with 2° rotation in ϕ were recorded. The crystal was indexed from the first ten frames using the DENZO package¹⁹ and positional data were refined along with diffractometer constants to give the final unit cell parameters. After integration and scaling, the whole data set was corrected for Lorentz and polarisation effects. The structure was solved using the direct methods option of SHELXS-97 and developed via alternating least squares cycles and difference Fourier synthesis (SHELXL-97) with the aid of the program RES2INS.²⁰ All non-hydrogen atoms were modeled anisotropically, while hydrogen atoms were assigned an isotropic thermal parameter 1.2 times (1.5 for CH₃ groups) that of the parent atom and allowed to ride.

Crystallographic data for $[\text{Cu}\{\text{SC}(\text{NEt}_2)\text{SNTs}\}_2] \cdot \text{CH}_2\text{Cl}_2$ (**2b**)· CH_2Cl_2 ; black prism, dimensions $0.50 \times 0.20 \times 0.20$ mm, monoclinic, space group $P2_1/c$, $a = 12.7830(4)$, $b = 14.5350(4)$, $c = 19.6760(4)$ Å, $\beta = 102.5320(10)^\circ$, $V = 3568.72(17)$ Å³, $Z = 4$, $F(000)$ 1620, $d_{\text{calc}} = 1.458$ g cm⁻³, $\mu = 1.148$ mm⁻¹. 43653 reflections were collected, 6115 unique [$R(\text{int}) = 0.0420$] of which 5209 were observed [$I > 2.0\sigma(I)$]. At convergence, $R_1 = 0.0490$, $wR_2 = 0.1303$ [$I > 2.0\sigma(I)$] and $R_1 = 0.0601$, $wR_2 = 0.1386$ (all data), for 379 parameters.

Crystallographic data for $[\text{Ni}\{\text{SC}(\text{NEt}_2)\text{SNTs}\}_2] \cdot \text{CHCl}_3$ (**4b**)· CHCl_3 ; blue block, dimensions $0.32 \times 0.27 \times 0.25$ mm, monoclinic, space group $P2_1/c$, $a = 12.8318(4)$, $b = 14.6975(4)$, $c = 19.5611(5)$ Å, $\beta = 99.5790(10)^\circ$, $V = 3637.70(18)$ Å³, $Z = 4$, $F(000)$ 1680, $d_{\text{calc}} = 1.484$ g cm⁻³, $\mu = 1.134$ mm⁻¹. 22274 reflections were collected, 6216 unique [$R(\text{int}) = 0.0600$] of which 5166 were observed [$I > 2.0\sigma(I)$]. At convergence, $R_1 = 0.0667$, $wR_2 = 0.1820$ [$I > 2.0\sigma(I)$] and $R_1 = 0.0799$, $wR_2 = 0.1936$ (all data), for 389 parameters.

Crystallographic data for $[\text{Co}\{\text{TsNSC}(\text{NEt}_2)\text{SNTs}\}_2] \cdot 0.25\text{H}_2\text{O}$ (**5b**); red prism, dimensions $0.30 \times 0.20 \times 0.20$ mm, monoclinic, space group $P2_1/c$, $a = 15.4966(13)$, $b = 12.7398(7)$, $c = 24.914(2)$ Å, $\beta = 91.214(1)^\circ$, $V = 4917.5(6)$ Å³, $Z = 4$, $F(000)$ 2158, $d_{\text{calc}} = 1.400$ g cm⁻³, $\mu = 0.742$ mm⁻¹. 35247 reflections were collected, 8400 unique [$R(\text{int}) = 0.1040$] of

which 5281 were observed [$I > 2.0\sigma(I)$]. At convergence, $R_1 = 0.0640$, $wR_2 = 0.1289$ [$I > 2.0\sigma(I)$] and $R_1 = 0.1182$, $wR_2 = 0.1537$ (all data), for 555 parameters.

CCDC reference numbers 264509–264511 for **2b**, **4b** and **5b**, respectively.

See <http://dx.doi.org/10.1039/b503004h> for crystallographic data in CIF or other electronic format.

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