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Multimetallic complexes and functionalized nanoparticles based on unsymmetrical dithiocarbamate ligands with allyl and propargyl functionality

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Supporting Information (consisting of crystallographic data and anisotropic displacement ellipsoid plots for the structures of **6a** and **11**) are available on the WWW under http://.

Keywords: nickel, ruthenium, dithiocarbamate, sulfur donors

Abstract

The new, unsymmetrical dithiocarbamate ligands, $KS_2CN(CH_2CH=CH_2)Me$ and $KS_2CN(CH_2C{\equiv}CH)Me$ are formed from the respective amines on reaction with KOH and carbon disulfide. The homoleptic complexes $[Ni\{S_2CN(CH_2CH=CH_2)Me\}_2]$ and $[M\{S_2CN(CH_2C{\equiv}CH)Me\}_2]$ (M = Ni, Pd, Pt) are formed on reaction with suitable metal precursors. Conversion between the two pendant functionalities was confirmed by hydrogenation of $[Ni\{S_2CN(CH_2C{\equiv}CH)Me\}_2]$ to yield $[Ni\{S_2CN(CH_2CH=CH_2)Me\}_2]$. The monodithiocarbamate compounds of group 8, 10 and 11 metals, $[Ru\{S_2CN(CH_2CH=CH_2)Me\}(dppm)_2]+$, $[Ru(CH=CHC_6H_4Me\text{-}4)\{S_2CN(CH_2CH=CH_2)Me\}(CO)(PPh_3)_2]$, $[Ni\{S_2CN(CH_2CH=CH_2)Me\}(dppp)]+$ and $[Au\{S_2CN(CH_2CH=CH_2)Me\}(PPh_3)]$ were formed successfully. Using $KS_2CN(CH_2C{\equiv}CH)Me$, the complex $[Ru\{S_2CN(CH_2C{\equiv}CH)Me\}(dppm)_2]^+$ was obtained from *cis*-$[RuCl_2(dppm)_2]$. One palladium example, $[Pd\{S_2CN(CH_2C{\equiv}CH)Me\}(PPh_3)_2]^+$, was also isolated in low yield. However, under the typical conditions employed, a rearrangement reaction prevented isolation of further group 10 propargyl-dithiocarbamate products. Over the extended reaction time required, $Me(HC{\equiv}CCH_2)NCS_2^-$ was found to undergo a remarkable, atom-efficient cyclisation to form the thiazolidine-2-thione, $H_2C=CCH_2N(Me)C(=S)S$, hin high yield, with $MeC=CHN(Me)C(=S)S$ as the minor product. The reactivity of the pendant triple bonds in $[Ni\{S_2CN(CH_2C{\equiv}CH)Me\}_2]$ was probed in the reaction with $[RuH(CO)(S_2P(OEt)_2)(PPh_3)_2]$ to form the trimetallic example $[Ni\{S_2CN(Me)CH_2CH=CHRu(CO)(S_2P(OEt)_2)(PPh_3)_2\}_2]$, while the copper(I) catalyzed reaction with benzylazide yielded the triazole product, $[Ni\{S_2CN(Me)CH_2(C_2HN_3)Bz\}_2]$. $KS_2CN(CH_2C{\equiv}CH)Me$ was also used to prepare the gold nanoparticles, $Au@S_2CN(CH_2C{\equiv}CH)Me$. Structural studies are reported for $[Ru(CH=CHC_6H_4Me\text{-}4)\{S_2CN(CH_2CH=CH_2)Me\}(CO)(PPh_3)_2]$ and $[Ru\{S_2CN(CH_2C{\equiv}CH)Me\}(dppm)_2]PF_6$.

Introduction

Since their discovery over 100 years ago,[1] dithiocarbamate complexes (MS_2CNR_2) have been widely used in a variety of applications, ranging from analytical science to medicine.[2] However, their peerless ability as a chelate, which has led to complexes being reported for the complete d-block elements in all common oxidation states, has largely eclipsed the potential for modifying the substituents of the NR_2 unit, with some notable exceptions.[3] Our recent research[4] has concentrated on this aspect, which has led to the construction of multimetallic assemblies through the manipulation of the donors attached to the backbone. The presence of versatile and reactive functionality in these positions has allowed the coordinated dithiocarbamate to be a center of reactivity in the molecule.

In the context of the ability to generate multimetallic systems in a stepwise, controlled manner, the presence of functionality that remains unaffected by the introduction of the first metal in the system is important. This allows a second metal to be added to form a heterobimetallic system.[5] The incorporation of pendant alkyne functionality has been shown to achieve this aim in complexes of the pentynoate ligand,[6] where reaction at the oxygen donors takes place initially before a second metal is introduced through interaction with the alkyne moiety. This obviates the need for protection/deprotection strategies which complicate some approaches to heterobimetallic assemblies.

The reaction of coordinated ligands bearing allyl substituents has recently been demonstrated. For example, complexes of the diallyldithiocarbamate ligand, $L_nMS_2CN(CH_2CH{=}CH_2)_2$ (M = Ru, Ni, Pd, Pt, Au) have been shown to undergo ring-closing metathesis readily, in contrast to diallyamine itself.[7]

In order to extend these investigations further, this report exploits the frequently overlooked class of unsymmetrical dithiocarbamate ligands. The ligands in Figure 1 have not been reported previously, yet combine a characteristic spectroscopic feature (the NMe group) with pendant alkene or alkyne functionality.

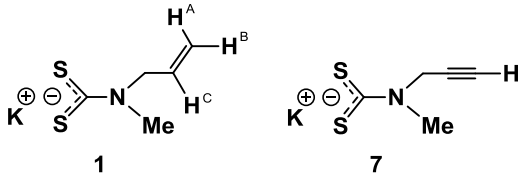


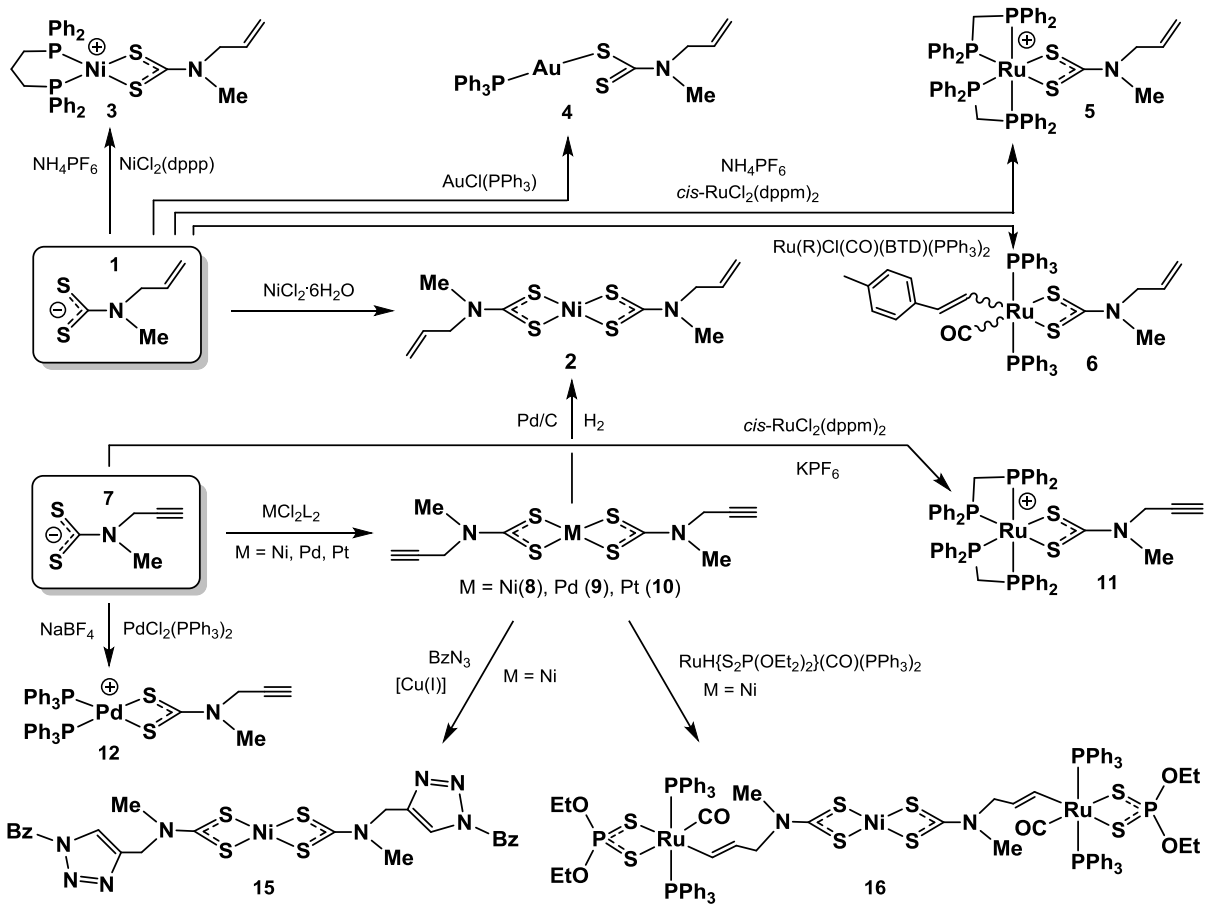
Figure 1. The unsymmetrical dithiocarbamates used in this work (showing allyl proton environments).

This approach allows the incorporation of the unsaturated unit within the coordination sphere of a metal, paving the way for further reactions to be carried out using the alkene or alkyne, both to extend the molecule through the backbone of the dithiocarbamate ligand, and to allow the addition of further metal units. While much of this reactivity proceeded as planned, an unexpected cyclisation reaction was also encountered, which is significant in the context of atom-efficient heterocycle formation.

Results and Discussion

Molecular complexes

N-methylallylamine and *N*-methylpropargylamine are commercially available and are commonly used precursors for a variety of products.[8,9] Despite the plethora of dithiocarbamate ligands prepared from secondary amines,[2] to the best of our knowledge, no reports exist of the corresponding dithiocarbamates of these particular amines. Reaction of $HN(Me)CH=CH_2$ with carbon disulfide and potassium hydroxide yielded the unsymmetrical dithiocarbamate ligand, $KS_2CN(CH_2CH=CH_2)Me$ (**1**), which was not isolated but used *in situ* for complexation to metal precursors. Nickel dithiocarbamates were historically among the first dithiocarbamates to be prepared[1,2] and their straightforward synthesis and purification has led to them being used as a convenient means with which to characterize the attached dithiocarbamate ligand. Reaction of hydrated nickel(II) chloride with two equivalents of **1** (Scheme 1) led to the formation of the green product $[Ni\{S_2CN(CH_2CH=CH_2)Me\}_2]$ (**2**). ^1H NMR analysis revealed a singlet at 3.14 ppm attributed to the methyl protons, while resonances at 4.20 (NCH_2), 5.77 (CCH=) and 5.30 ($=CH_2$) ppm were attributed to the protons of the allyl unit. The chemical shifts of these resonances were found to be similar to those observed for the related diallyldithiocarbamate complex $[Ni\{S_2CN(CH_2CH=CH_2)_2\}_2]$.[7b,c] Confirmation of the presence of the CS_2 unit was provided by a singlet at 207.5 ppm in the $^{13}C\{^1H\}$ NMR spectrum. The overall formulation was confirmed by a molecular ion in the mass spectrum (electrospray, positive mode) at *m/z* 351.



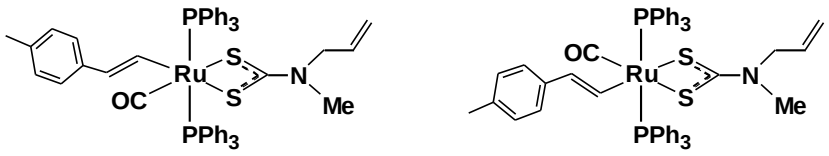
Scheme 1. Preparation of unsymmetrical dithiocarbamate complexes.
L = NCMe or NCPh, BTD = 2,1,3-benzothiadiazole, R = CH=CHC$_6$H$_4$Me-4.

In order to move beyond homoleptic examples, monodithiocarbamate compounds of group 8, 10 and 11 metals were prepared. The orange diphosphine precursor, [NiCl$_2$(dppp)] (dppp = 1,3-bis(diphenylphosphino)propane), reacted with **1** in the presence of NH_4PF_6 to yield [Ni{S$_2$CN(CH$_2$CH=CH$_2$)Me}(dppp)]PF$_6$ (**3**) in good yield. Apart from the presence of a new singlet at 12.9 ppm in the $^{31}P\{^1H\}$ NMR spectrum, similar features for the methylallyldithiocarbamate ligand were observed to those observed for **2** on analysis by NMR spectroscopy.

In a similar fashion, the gold complex [Au{S$_2$CN(CH$_2$CH=CH$_2$)Me}(PPh$_3$)] (**4**) was prepared from the reaction of **1** with [AuCl(PPh$_3$)]. Due to the well-established propensity for gold(I) complexes to adopt a linear geometry, bidentate coordination of dithiocarbamate ligands is not typically observed, though an anisobidentate mode (one short Au-S distance and one much longer Au-S interaction) is sometimes found in structurally characterized

examples.[7a] ^{1}H NMR analysis of **4** revealed resonances in similar positions to those observed for compound **2**, while the overall composition was confirmed with a molecular ion at *m/z* 606 in the mass spectrum (electrospray, positive mode).

Two ruthenium examples were prepared, with the first containing two diphosphine ligands. [Ru{$S_2CN(CH_2CH=CH_2)Me$}$(dppm)_2$]PF_6 (**5**), was formed in 95% yield from the *in situ* generation and subsequent reaction of **1** with *cis*-[$RuCl_2(dppm)_2$]. The majority of dithiocarbamate ligands are symmetrical, ruling out the formation of isomers (apart from optical isomers, which are possible for **5** but are not discernible spectroscopically). However, when employing dithiocarbamates prepared from secondary amines with different substituents, isomers are possible due to the restricted rotation around the C-N bond. Previous studies have examined this rotational barrier using NMR methods and estimations have varied between 65 and 88 kJ mol^{-1} for this process at 298K.[10] The unwanted generation of isomers may be a factor in explaining the relative paucity of unsymmetrical dithiocarbamates reported in the literature.[2] The symmetrical nature of complexes **2 - 5** prevent any isomerism being observed. However, in order to probe this aspect, the complex [Ru($CH=CHC_6H_4Me$-4){$S_2CN(CH_2CH=CH_2)Me$}$(CO)(PPh_3)_2$] (**6**) was prepared from the versatile precursor, [Ru($CH=CHC_6H_4Me$-4)$Cl(CO)(BTD)(PPh_3)_2$] (BTD = 2,1,3-benzothiadiazole). Alkenyl complexes have proved versatile reaction partners for 1,1-dithio ligands,[11] leading to octahedral complexes with a mutually *trans* arrangement of phosphines. The $^{31}P\{^{1}H\}$ NMR spectrum of **6** contained two closely-spaced singlets at 39.47 and 39.51 ppm, suggesting the presence of two very similar species. Duplicate resonances in approximately a 1:1 ratio for the NCH_3 protons of the methylallyldithiocarbamate ligand (2.40 and 2.61 ppm) confirmed this observation. The resonances attributed to the NCH_2 protons were also visible as two doublets at 3.48 and 3.75 ppm (J_{HH} = 5.4 Hz). The resonances for the alkenyl ligands were largely unaffected by the different orientation of the dithiocarbamate ligand apart from the closest proton (Hα), which appeared as an ill-defined multiplet at 7.73 ppm. The two isomers present were thus formulated as shown in Figure 2.



6a **6b**

Figure 2. Two isomers of [Ru(CH=CHC$_6$H$_4$Me-4){S$_2$CN(CH$_2$CH=CH$_2$)Me}(CO)(PPh$_3$)$_2$] (**6**).

The overall formulation of **6** was confirmed by an abundant molecular ion in the electrospray (+ve ion) mass spectrum at *m/z* = 917 and good agreement of elemental analysis with calculated values. Single crystals of **6** were grown and a structural study undertaken (Fig. 3). This revealed the presence of only one isomer (**6a**), however, selective crystallization to isolate only one isomer failed when attempted on a larger scale. Further details on the structural determination are provided in the Structural Discussion section.

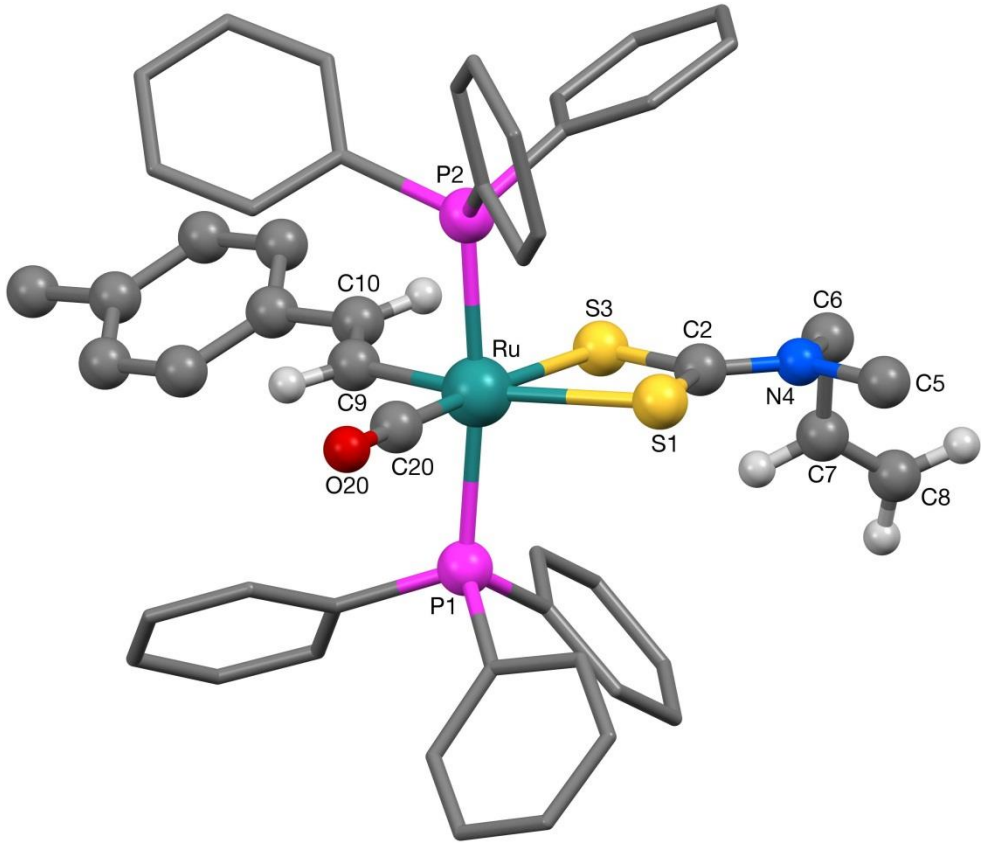


Fig. 3. The crystal structure of **6a**. Selected bond lengths (Å) and angles (°); Ru–S(1) 2.5229(4), Ru–S(3) 2.4471(4), Ru–P(1) 2.3863(4), Ru–P(2) 2.3638(4), Ru–C(9) 2.0763(16), Ru–C(20) 1.8379(16), S(1)–C(2) 1.7134(17), C(2)–S(3) 1.7011(18), C(2)–N(4) 1.334(2), C(7)–C(8) 1.256(4), C(9)–C(10) 1.338(2), S(1)–Ru–S(3) 70.124(14), S(1)–C(2)–S(3) 113.51(9).

The same protocol used to prepare **1** was employed to yield $KS_2CN(CH_2C{\equiv}CH)Me$ (**7**) from *N*-methylpropargylamine. As for **1**, and in previous studies of similar ligands,[7] this species was not isolated and was instead used *in situ* for the subsequent reactions with metal precursors. The first complex prepared was the analogue of **2**, $[Ni\{S_2CN(CH_2C{\equiv}CH)Me\}_2]$ (**8**). The chemical shifts of the resonances for the NMe (3.33 ppm) and NCH_2 (4.46 ppm) protons in the ^1H NMR spectrum were in similar positions to those observed for **2**, while the acetylenic protons gave rise to a resonance at 2.46 ppm, showing a J_{HH} coupling of 2.5 Hz. The $^{13}C\{^1H\}$ NMR resonance for the CS_2 unit was observed at 203.1 ppm.

Analogues of the heavier congeners of group 10 were also prepared, $[M\{S_2CN(CH_2C{\equiv}CH)Me\}_2]$ (M = Pd (**9**), Pt (**10**)), though in lower yield. Spectroscopic data for these complexes were found to be almost identical to those recorded for **8**.

Treatment of *cis*-[$RuCl_2(dppm)_2$] with **7** in the presence of KPF_6 led to the formation of [$Ru\{S_2CN(CH_2C{\equiv}CH)Me\}(dppm)_2]PF_6$ (**11**). Spectroscopic features for the dithiocarbamate ligand were again similar to those observed for **8** – **10**. The product was found to be crystalline, allowing crystals to be grown suitable for a structural study (Fig. 4). Further details are provided in the Structural Discussion section.

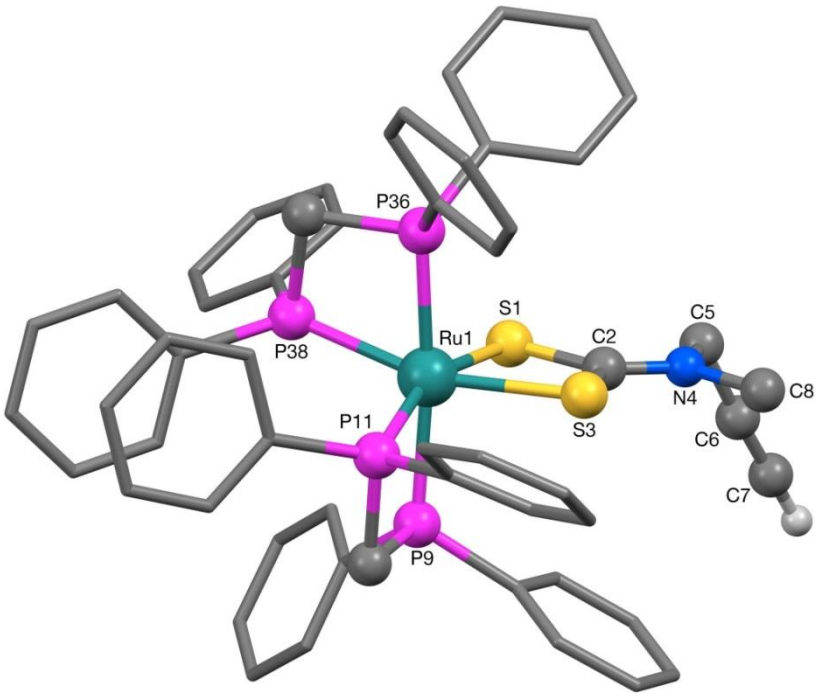
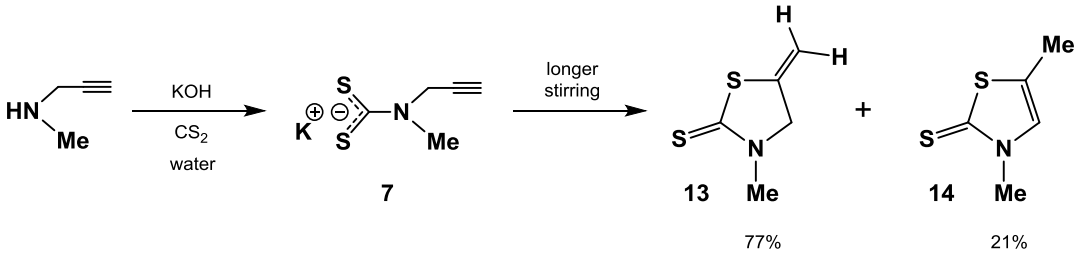


Fig. 4. The structure of the cation present in the crystals of **11**. Selected bond lengths (Å) and angles (°); Ru(1)–S(1) 2.4309(6), Ru(1)–S(3) 2.4286(6), Ru(1)–P(9) 2.3246(6), Ru(1)–P(11) 2.3157(5), Ru(1)–P(36) 2.3497(6), Ru(1)–P(38) 2.3355(6), S(1)–C(2) 1.712(3), C(2)–S(3) 1.704(3), C(2)–N(4) 1.329(4), C(6)–C(7) 1.200(6), S(1)–Ru(1)–S(3) 71.55(2), S(1)–C(2)–S(3) 112.48(15).

Using the same route developed for **11**, but employing $NaBF_4$ as the counterion source, the palladium complex, [$Pd\{S_2CN(CH_2C{\equiv}CH)Me\}(PPh_3)_2]BF_4$ (**12**), was prepared. The yield was modest (37%) and substantial amounts of the starting material were recovered for reasons which only became clear when the internal reactivity of **7** was uncovered.

Unlike the reaction of **1** with [$NiCl_2(dppp)$] to generate [$Ni\{S_2CN(CH_2CH{=}CH_2)Me\}(dppp)]PF_6$ (**3**), treatment of **7** with [$NiCl_2(L_2)$] (L_2 = dppe, dppp, dppf) led to symmetrization of the product to yield a mixture of species including

[Ni{$S_2CN(CH_2C{\equiv}CH)Me\}_2$] (**8**). ^{1}H NMR analysis of these reactions revealed some additional resonances at 3.30, 4.78, 5.14 and 5.26 ppm in the ratio 3:2:1:1. This side product was found to form in larger quantities on leaving $HN(Me)CH_2C{\equiv}CH$ to react with carbon disulfide over longer periods in the presence of base. Based on these data and additional characterization by electrospray (+ve mode) mass spectrometry (*m/z* = 146) and elemental analysis, this product was formulated as the cyclic product, $H_2C{=}CCH_2N(Me)C(=S)S$ (**13**). Optimization of the procedure (Scheme 2) allowed **13** to be isolated in 77% yield and separated from another more minor product, formulated as $MeC{=}CHN(Me)C(=S)S$ (**14**).



Scheme 2. Preparation of cyclisation products from **7**.

This represents a 100% atom efficient and high yielding route to thiazolidine-2-thiones from the propargylamine and carbon disulfide. This compares well to leading literature routes, such as the iodocyclization of allyl amines, which generates two moles of HI and proceeds in yields of 46-75%.[12] The extension of this route to other propargylamine substrates falls outside the scope of this project but could provide a valuable additional route to such heterocycles. While this reaction is an unexpected and interesting observation, it does limit the utility of **7** as a reagent. However, the successful formation of [Ni{$S_2CN(CH_2C{\equiv}CH)Me\}_2$] (**8**) allowed the reactivity of the pendant alkyne unit to be explored while coordinated to the nickel center.

Hydrogenation of **8** using standard conditions (palladium on carbon catalyst, hydrogen gas) yielded [Ni{$S_2CN(CH_2CH{=}CH_2)Me\}_2$] (**2**) in 92% yield, representing the conversion of alkyne to alkene functionality within the coordination sphere of a metal. Initial attempts using Lindlar catalyst protocols failed to achieve any conversion (though the same batch of catalyst readily converted 1-octyne to 1-octene). This indicated that the reactivity of the pendant alkyne was still somewhat divergent from a terminal triple bond in a typical organic setting. A common theme of earlier work in the group has been extension of the coordinated dithiocarbamate unit and this was explored here through the reaction in methanol of **8** with benzylazide in the presence of the catalyst [CuI(IAd)] (IAd = 1,3-

di(adamantyl)imidazol-2-ylidene)[13] (10 mol%, 5 mol% per alkyne unit) under standard 'click' chemistry conditions. The resulting triazole product, [Ni{$S_2CN(Me)CH_2(C_2HN_3)Bz$}$_2$] (**15**) gave rise to characteristic resonances for such triazoles at 5.53 (benzyl-CH_2) and 7.63 (triazole-CH) ppm in the ^{1}H NMR spectrum, alongside resonances at 3.18 (NMe) and 4.81 (NCH_2) ppm for the dithiocarbamate substituents. The overall formulation was confirmed by mass spectrometry and elemental analysis.

We have recently shown that the complex [$RuH(CO)(S_2P(OEt)_2)(PPh_3)_2$}] is a versatile precursor to vinyl complexes of the form [$Ru(CH=CHR)(CO)(S_2P(OEt)_2)(PPh_3)_2$}] through spontaneous insertion of alkynes into the Ru-H bond.[14] This approach was thus exploited to prepare trimetallic complexes through the reaction of **8** with two equivalents of [$RuH(CO)(S_2P(OEt)_2)(PPh_3)_2$] to yield [Ni{$S_2CN(Me)CH_2CH=CHRu(CO)(S_2P(OEt)_2)(PPh_3)_2$}$_2$] (**16**), as shown in Scheme 1. Resonances were observed at 32.0 (PPh_3) and 94.7 (PS_2) ppm in the ^{31}P{^{1}H} NMR spectrum, which were shifted substantially from those found in the hydride precursor. New resonances were also observed in the ^{1}H NMR spectrum at 6.97 (d, Hα, J_{HH} = 15.3 Hz) and 4.38 (m, Hβ) for the vinyl ligand, while the NMe and NCH_2 protons resonated at 2.28 and 3.43 ppm. The overall formulation was confirmed by mass spectrometry and elemental analysis.

Nanoparticle functionalization

Dithiocarbamates have recently been established as good alternatives to the ubiquitous thiolate units for the stabilization of gold nanoparticles.[15] In our previous investigations, we have demonstrated how functionalized dithiocarbamates can be used to cover the surface of nanoparticles using the same methodology applied to molecular systems.[4d-f,5b] The subsequent manipulation of the surface functionality has been illustrated through the successful ring-closing metathesis of immobilized diallydithiocarbamate units.[7a]

Using the method developed by Turkevich[16] and further refined subsequently,[17] citrate coated nanoparticles were prepared and the surface units displaced with $KS_2CN(CH_2C{\equiv}CH)Me$ to yield a black product, $Au@S_2CN(CH_2C{\equiv}CH)Me$ (**NP1**). This was washed thoroughly with water to remove excess citrate and dithiocarbamate ligands followed by washing with diethyl ether to remove any **13** formed. The nanoparticles proved soluble in

chlorinated solvents allowing characterization by ^{1}H NMR spectroscopy. This revealed broad resonances at 2.45 (≡CH), 3.59 (NMe) and 4.78 (NCH_2) ppm, which were slightly displaced and broadened compared to those observed for the precursor ligand. Infrared spectroscopy confirmed the absence of absorptions due to citrate surface units and showed similar features for **NP1** as observed for the free ligand, including the $\nu_{C\equiv C}$ absorption at 2120 cm^{-1}. Transmission Electron Microscopy (TEM) showed nanoparticles with diameter 4.8 ± 1.0 nm (Fig. 5).

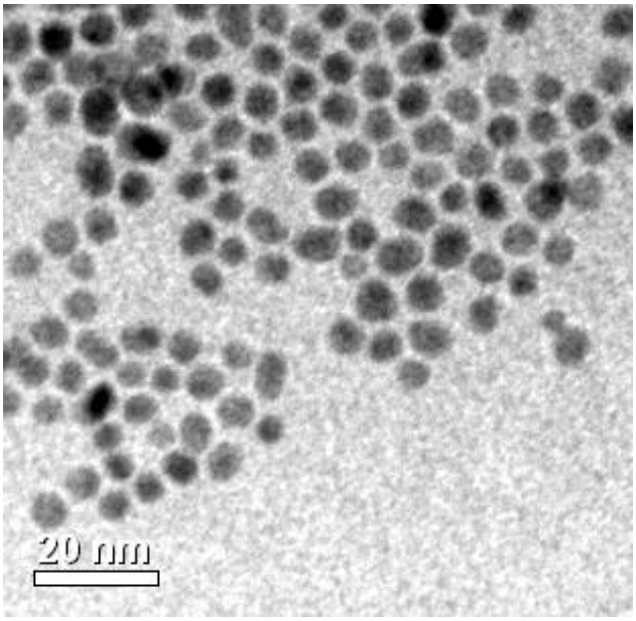


Fig. 5. TEM image of Au@$S_2CN(CH_2C\equiv CH)Me$ (**NP1**).

Analysis by Energy Dispersive X-Ray Spectroscopy (EDS) revealed the presence of gold and sulfur, while nitrogen could not be differentiated from other light elements, such as carbon. As has been noted previously,[7a] the absence of traces of potassium suggests the charge on the dithiocarbamate surface units is balanced by localized positive charge at the surface gold positions. Thermogravimetric analysis (TGA) was used to provide further information on the mass contributed by the surface units. A reduction in mass of 28.6% was observed on heating a 2.5 mg sample of **NP1** from 30 °C to 700 °C at a rate of 10 °C per minute to leave a residue of gold metal. This is consistent with a previous report by Angurell and Rossell for nanoparticles functionalized with mixed thiolate functionality.[18]

Structural Section

The structures of complexes **6a** and **11** both have distorted octahedral arrangements at the ruthenium center with *cis*-interligand angles in the ranges 70.124(14) – 103.73(5)° for **6a** and 71.55(2) – 104.05(2)° for **11**; in both cases, the smallest value corresponds to the bite angle of the dithiocarbamate ligand. In **6a**, the Ru–S(1) and Ru–S(3) bond lengths [2.5229(4) and 2.4471(4) Å respectively] differ by ca. 0.08 Å, indicating a slight asymmetry of the 1,1-dithio chelate caused (at least partly) by the greater *trans* influence of the vinyl unit compared to that of the carbonyl ligand. The corresponding bond distances in **11** (which has chemically equivalent phosphine donors in the *trans* positions) are essentially the same as each other, differing by less than 0.01 Å [Ru(1)–S(1) 2.4309(6), Ru(1)–S(3) 2.4286(6) Å], and are slightly shorter than seen in **6a**. The S–Ru–S and S–C–S angles in **6a** [70.124(14) and 113.51(9)° respectively] are both typical for ruthenium(II) dithiocarbamate complexes[4c,i] and compare well to the corresponding features in the structure of **11** [71.55(2) and 112.48(15)°, respectively]. In both structures, clear multiple bond character is evident in the shortened C(2)–N(4) distance of 1.334(2) [**6a**] and 1.329(4) Å [**11**], which lie much closer to the average C=N distance of 1.29 Å than to C-N single bond lengths (1.47 Å) from the literature.[19] The pendant alkene unit in **6a** displays a C(7)–C(8) bond length of 1.256(4) Å, which is short for a $RCH=CH_2$ double bond, which on average is 1.299 Å.[19] The terminal alkyne in **11** displays a bond distance of C(6)–C(7) of 1.200(6) Å, which is slightly longer than average for C-C≡CH (1.174 Å).[19]

Conclusions

The potential to extend the functionality of a metal complex after coordination of a flexible and reactive ligand is a powerful way to add complexity and further properties to the system. Unlike many phosphorus, oxygen and nitrogen chelates, dithiocarbamates offer great complex stability while accommodating metal centers in both high and low oxidation states. The work described here illustrates that dithiocarbamate ligands bearing reactive pendant functionality can provide a flexible platform for functional group transformations, including the generation of bimetallic and heterotrimetallic complexes. This is achieved without the need for protection/deprotection strategies through careful consideration of the reactivity of the alkene or alkyne functional groups compared to that of the sulfur donors. In addition, the

potential for employing this approach to the surface functionalization of metal nanoparticles has been demonstrated. Of even greater significance to heterocycle chemists, is the new, 100% atom efficient and high yielding route to thiazolidine-2-thiones starting from just the propargylamine and carbon disulfide in the presence of base.

Experimental Section

General Comments. Unless otherwise stated, all experiments were carried out in air and the complexes obtained appear stable towards the atmosphere, whether in solution or in the solid state. Reagents and solvents were used as received from commercial sources. Petroleum ether is the fraction boiling in the 40–60 °C range. The following complexes were prepared as described elsewhere: $[NiCl_2(dppp)]$,[20] $[RuHCl(CO)(PPh_3)_3]$,[21] $[RuHCl(CO)(BTD)(PPh_3)_2]$,[22] *cis*-$[RuCl_2(dppm)_2]$,[23] $[AuCl(PPh_3)]$,[24] $[Ru(CH{=}CHC_6H_4Me\text{-}4)Cl(CO)(BTD)(PPh_3)_2]$,[25] [Cu(I)(IAd)],[13] $[RuH(CO)(S_2P(OEt)_2)(PPh_3)_2\}]$[14,26] and *cis*-$[PdCl_2(PPh_3)_2]$,[27]. Electrospray (ES) and Fast Atom Bombardment (FAB) mass data were obtained using Micromass LCT Premier and Autospec Q instruments, respectively. Infrared data were obtained using a Perkin-Elmer Spectrum 100 FT-IR spectrometer and characteristic triphenylphosphine-associated infrared data are not reported. NMR spectroscopy was performed at 25 °C using Varian Mercury 300 and Bruker AV400 spectrometers in $CDCl_3$ unless stated otherwise. All coupling constants are in Hertz. Resonances in the $^{31}P\{^1H\}$ NMR spectrum due to the hexafluorophosphate counteranion were observed where the formulation indicates but are not included below. Elemental analysis data were obtained from London Metropolitan University. The procedures given provide materials of sufficient purity for synthetic and spectroscopic purposes. TEM images and EDS data were obtained using a JEOL 2010 high-resolution TEM (80-200 kV) equipped with an Oxford Instruments INCA EDS 80mm X-Max detector system. Thermogravimetric analysis was performed on a Perkin Elmer Pyris 1 Thermogravimetric Analyzer, using a platinum sample holder.

$KS_2CN(CH_2CH{=}CH_2)Me$ (1)

N-methylallylamine (1.00 mL, 10.4 mmol) and CS_2 (0.75 mL, 12.5 mmol) were stirred in the presence of KOH (643 mg, 11.5 mmol) in water (40 mL) for 30 minutes. Assuming complete conversion, this solution was used for the subsequent additions to the metal precursors.

[Ni{$S_2CN(CH_2CH=CH_2)Me$}$_2$] (2)

a) A solution of [$NiCl_2{\cdot}6H_2O$] (200 mg, 0.841 mmol) in acetone (20 mL) and dichloromethane (10 mL) was treated with 3 equivalents of $KS_2CN(CH_2CH=CH_2)Me$ (**1**) and the reaction stirred for 30 mins. All solvent was removed (rotary evaporator) and the residue dissolved in the minimum volume of dichloromethane and filtered through diatomaceous earth (Celite) to remove excess ligand. All solvent was again removed by rotary evaporation and petroleum ether (30 mL) added and the solid triturated ultrasonically. The dark green product was washed with water (10 mL), petroleum ether (10 mL) and dried under vacuum. Yield: 237 mg (80%). b) A solution of **8** (26 mg, 0.075 mmol) in ethyl acetate (10 mL) was treated with 5 mg of (10% Pd on carbon) and hydrogen gas was passed through the solution for 4 h at room temperature. The solution was filtered through Celite and the solvent removed (rotary evaporator) to yield the dark green product. Yield: 24 mg (92%). IR (solid state): 1641, 1515, 1382, 1252, 1209, 1143, 1075, 987, 929, 679 cm^{-1}. ^{1}H NMR ($CDCl_3$): 3.14 (s, 6H, NMe); 4.20 (d, 4H, NCH_2, J_{HH} = 4.8 Hz); 5.30 (m, 4H, $=CH^{AB}$); 5.77 (m, 2H, $=CH^{C}$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 207.5 (s, CS_2); 129.8 (s, $NCCH_2$); 119.6 (s, $=CH_2$); 53.3 (s, NCH_3); 35.9 (s, NCH_2) ppm. MS (ES +ve) *m/z* (abundance) = 351 (20) $[M]^+$. Analysis: Calculated for $C_{10}H_{16}N_2NiS_4$ (M_w = 351.2): C 34.2%, H 4.6%, N 8.0%; Found: C 34.3%, H 4.5%, N 7.9%.

[Ni{$S_2CN(CH_2CH=CH_2)Me$}(dppp)]PF_6 (3)

A solution of [$NiCl_2$(dppp)] (300 mg, 0.553 mmol) in acetone (20 mL) and dichloromethane (10 mL) was treated with 1.5 equivalents of $KS_2CN(CH_2CH=CH_2)Me$ (**1**) and NH_4PF_6 (181 mg, 1.110 mmol) in water (5 mL) and the reaction stirred for 30 mins. All solvent was removed (rotary evaporator) and the residue dissolved in the minimum volume of dichloromethane and filtered through diatomaceous earth (Celite) to remove KCl, excess NH_4PF_6 and ligand. All solvent was again removed using a rotary evaporator and petroleum ether (30 mL) added and the solid triturated ultrasonically. The orange product was washed with water (10 mL), petroleum ether (10 mL) and dried under vacuum. Yield: 295 mg (70%). IR (solid state): 1538, 1435, 1403, 1367, 1215, 1100, 973, 833 (ν_{PF}), 746, 693, 665, cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 12.9 (s, dppp). ^{1}H NMR ($CDCl_3$): 2.17 (m, 2H, dppp-CH_2); 2.67 (m, 4H, dppp-PCH_2); 3.12 (s, 3H, NMe); 4.18 (d, 2H, NCH_2, J_{HH} = 6.2 Hz); 5.30 (m, 2H, $=CH^{AB}$); 5.65 (m, 1H, $=CH^{C}$); 7.40 – 7.63 (m, 20H, C_6H_5) ppm. MS (ES +ve) *m/z*

(abundance) = 616 (100) $[M]^+$. Analysis: Calculated for $C_{32}H_{34}F_6NNiP_3S_2$ (M_w = 761.06): C 50.4%, H 4.5%, N 1.8%; Found: C 50.4%, H 4.6%, N 1.9%.

[Au{$S_2CN(CH_2CH=CH_2)Me$}(PPh_3)] (4)

A solution of [AuCl(PPh_3)] (300 mg, 0.606 mmol) in acetone (20 mL) and dichloromethane (10 mL) was treated with 1.5 equivalents of $KS_2CN(CH_2CH=CH_2)Me$ (**1**) and the reaction stirred for 30 mins. All solvent was removed (rotary evaporator) and the residue dissolved in the minimum volume of dichloromethane and filtered through diatomaceous earth (Celite) to remove KCl and excess ligand. All solvent was again removed (rotary evaporator) and petroleum ether (30 mL) added and the solid triturated ultrasonically. The yellow product was washed with water (10 mL), petroleum ether (10 mL) and dried under vacuum. Yield: 231 mg (63%). IR (solid state): 1584, 1475, 1434, 1379, 1261, 1205, 1098, 975, 910, 745, 990 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 36.2 (s, PPh_3). ^1H NMR ($CDCl_3$): 3.45 (s, 3H, NMe); 4.62 (d, 2H, NCH_2, J_{HH} = 5.8 Hz); 5.26, 5.29 (m x 2, 2 x 1H, $=CH^{AB}$); 5.96 (m, 1H, $=CH^{C}$); 7.44 – 7.53, 7.61 – 7.66 (m x 2, 15H, C_6H_5) ppm. MS (ES +ve) *m/z* (abundance) = 606 (10) $[M]^+$. Analysis: Calculated for $C_{23}H_{23}AuNPS_2$ (M_w = 605.07): C 45.6%, H 3.8%, N 2.3%; Found: C 45.6%, H 3.8%, N 2.3%.

[Ru{$S_2CN(CH_2CH=CH_2)Me$}($dppm)_2$]PF_6 (5)

A solution of $KS_2CN(CH_2CH=CH_2)Me$ (**1**) in water was prepared as described above and two equivalents (0.638 mmol) was added to a solution of *cis*-[$RuCl_2(dppm)_2$] (300 mg, 0.319 mmol) in acetone (20 mL) and dichloromethane (10 mL). This was followed by addition of NH_4PF_6 (104 mg, 0.638 mmol) in water (5 mL) before stirring the reaction for 30 mins. All solvent was removed by rotary evaporation and the residue dissolved in the minimum volume of dichloromethane and filtered through diatomaceous earth (Celite) to remove KCl and excess ligand. All solvent was again removed (rotary evaporator) and diethyl ether (30 mL) added and the solid triturated ultrasonically. The pale yellow product was washed with water (10 mL), diethyl ether (10 mL) and dried under vacuum. Yield: 350 mg (94%). IR (solid state): 1483, 1434, 1398, 1096, 998, 928, 831 (ν_{PF}), 740, 723, 693, 666, 616 cm^{-1}. ^1H NMR ($CDCl_3$): 2.93 (s, 3H, NMe); 4.06 (m, 2H, NCH_2); 4.60, 4.96 (m x 2, 2 x 2H, PCH_2P); 5.30 (d, 2H, $=CH^{AB}$); 5.58 (m, 1H, $=CH^{C}$); 6.53, 6.96, 7.10, 7.18 - 7.41, 7.65 (m x 5, 40H, C_6H_5) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): –18.8, –5.4 (t x 2, dppm, J_{PP} = 34.1 Hz). MS (ES +ve) *m/z*

(abundance) = 1016 (100) $[M]^+$. Analysis: Calculated for $C_{55}H_{52}F_6NP_5RuS_2$ (M_w = 1161.12): C 56.9%, H 4.5%, N 1.2%; Found: C 56.5%, H 4.3%, N 1.6%.

[Ru(CH=CHC$_6$H$_4$Me-4){S$_2$CN(CH$_2$CH=CH$_2$)Me}(CO)(PPh$_3$)$_2$] (6)

Using the same procedure as employed for the preparation of **4**, [Ru(CH=CHC$_6$H$_4$Me-4)Cl(CO)(BTD)(PPh$_3$)$_2$] (300 mg, 0.319 mmol) gave a pale yellow product. Yield: 202 mg (69%). IR (solid state): 1090 (ν_{CO}), 1710, 1643, 1548, 1410, 1277, 1230, 1127, 981, 968, 935, 920, 827 cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.24 (s, 6H, CCH_3); 2.40, 2.61 (s x 2, 2 x 3H, NMe isomers A and B); 3.48, 3.75 (d x 2, 2 x 2H, NCH_2 isomers A and B, J_{HH} = 5.4 Hz); 4.83 (t, 2 x 1H, =CH^A isomers A and B, J_{HAHC} = 16.7 Hz, J_{HAHB} = unresolved); 5.02 (dd, 2 x 1H, =CH^B isomers A and B, J_{HBHC} = 11.3 Hz, J_{HBHA} = 1.2 Hz); 5.24, 5.32 (m x 2, 2 x 1H, =CH^C isomers A and B); 5.61 (d, 2H, Hβ, J_{HH} = 16.6 Hz); 6.42, 6.83 (AB, 8H, C_6H_4, J_{AB} = 7.9 Hz); 7.31, 7.58 (m x 2, 60H, C_6H_5); 7.73 (m, 2H, Hα) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): 39.47, 39.51 (s x 2, isomers A and B, PPh_3) ppm. MS (ES +ve) *m/z* (abundance) = 917 (5) $[M]^+$; 800 (22) [M – alkenyl]$^+$. Analysis: Calculated for $C_{51}H_{47}NOP_2RuS_2$ (M_w = 917.16): C 66.8%, H 5.2%, N 1.5%; Found: C 66.7%, H 5.1%, N 1.6%.

KS$_2$CN(CH$_2$C≡CH)Me (7)

N-methylpropargylamine (84 μL, 1.0 mmol) and CS_2 (72 μL, 1.2 mmol) were stirred in the presence of KOH (67 mg, 1.20 mmol) in water (5 mL) for 5 minutes in an ice bath. This solution was used immediately (in slight excess) for the subsequent additions to the metal precursors.

[Ni{S$_2$CN(CH$_2$C≡CH)Me}$_2$] (8)

An aqueous solution (5 mL) of **7** (1.0 mmol) was added to an aqueous solution (5 mL) of $NiCl_2{\cdot}6H_2O$ (119 mg, 0.501 mmol) and the reaction was stirred for 3 hours. All solvent was removed using a rotary evaporator and the residue dissolved in dichloromethane and filtered through Celite to remove KCl. The solvent volume was concentrated to *ca.* 2 mL, diluted with ethanol (10 mL) and crystallized in an ice bath. The green product was filtered, washed with petroleum ether (10 mL) and dried under vacuum. Yield: 107 mg (62%). IR (solid state): 3261, 2123 ($\nu_{C\equiv C}$), 1518, 1440, 1412, 1396, 1338, 1254, 1201, 1095, 991, 959, 938, 876, 685, 657 cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.46 (t, 1H, C≡CH, J_{HH} = 2.5 Hz); 3.33 (s, 3H, CH_3); 4.46 (d, 2H, NCH_2, J_{HH} = 2.5 Hz) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): 203.1 (s, CS_2); 75.1 (s, *C*≡CH); 74.2

(s, (s, ≡CH); 39.5 (s, NCH_3); 35.7 (s, NCH_2) ppm. MS (ES +ve) *m/z* (abundance) = 346 (14) $[M]^+$. Analysis: Calculated for $C_{10}H_{12}N_2NiS_4$ (M_W = 347.17): C 34.6%, H 3.5%, N 8.1%; Found: C 34.7%, H 3.4%, N 8.1%.

[Pd{$S_2CN(CH_2C{\equiv}CH)Me$}$_2$] (9)

The same procedure was followed as described for the synthesis of **8** using $[PdCl_2(py)_2]$ (24 mg, 0.072 mmol) and **7** (0.143 mmol) to provide a yellow product. Yield: 15 mg (53%). IR (solid state): 3259, 2122 ($\nu_{C\equiv C}$), 1515, 1439, 1412, 1395, 1336, 1254, 1200, 1094, 988, 955, 938, 876, 685, 657 cm^{-1}. ^1H NMR ($CDCl_3$): 2.49 (t, 1H, C≡CH, J_{HH} = 2.5 Hz); 3.33 (s, 3H, CH_3); 4.52 (d, 2H, NCH_2, J_{HH} = 2.5 Hz) ppm. MS (ES +ve) *m/z* (abundance) = 396 (19) $[M]^+$. Analysis: Calculated for $C_{10}H_{12}N_2PdS_4$ (M_W = 394.90): C 30.4%, H 3.1%, N 7.1%; Found: C 30.5%, H 3.1%, N 7.2%.

[Pt{$S_2CN(CH_2C{\equiv}CH)Me$}$_2$] (10)

The same procedure was followed as described for the synthesis of **8** using $[PtCl_2(NCPh)_2]$ (30 mg, 0.064 mmol) and **7** (0.130 mmol) to provide a bright yellow product. Yield: 18 mg (58%). IR (solid state): 3258, 2122 ($\nu_{C\equiv C}$), 1523, 1441, 1414, 1393, 1334, 1310, 1253, 1199, 1095, 988, 955, 938, 877, 790, 687, 656 cm^{-1}. ^1H NMR ($CDCl_3$): 2.50 (t, 1H, C≡CH, J_{HH} = 2.4 Hz); 3.30 (s, 3H, CH_3); 4.42 (d, 2H, NCH_2, J_{HH} = 2.4 Hz) ppm. MS (ES +ve) *m/z* (abundance) = 483 (28) $[M]^+$. Analysis: Calculated for $C_{10}H_{12}N_2PtS_4$ (M_W = 483.56): C 24.8%, H 2.5%, N 5.8%; Found: C 24.7%, H 2.4%, N 5.7%.

[Ru{$S_2CN(CH_2C{\equiv}CH)Me$}(dppm)$_2$]PF_6 (11)

A solution of $HN(CH_2C{\equiv}CH)Me$ (10 μL, 0.12 mmol) in dichloromethane (2 mL) was cooled in an ice bath and triethylamine (21 μL, 0.15 mmol) added. After stirring for 5 mins, carbon disulfide (10 μL, 0.17 mmol) was added and the reaction stirred for a further 20 mins. A solution of *cis*-$[RuCl_2(dppm)_2]$ (98 mg, 0.10 mmol) in a mixture of dichloromethane (3 mL) and methanol (6 mL) was added followed by KPF_6 (31 mg, 0.17 mmol) in water (1 mL) and the reaction was stirred for 45 mins. All solvent was removed (rotary evaporator) and the crude product dissolved in the minimum volume of dichloromethane and filtered through Celite. Ethanol (20 mL) was added and the orange product was obtained by rotary evaporation. This was washed with ethanol (10 mL), hexane (10 mL) and dried under vacuum. Yield: 42 mg (35%). IR (solid state): 2122 ($\nu_{C\equiv C}$), 1484, 1434, 1189, 1097, 999,

834, 727, 694 cm^{-1}. ^{1}H NMR (CD_2Cl_2): 2.51 (t, 1H, C≡CH, J_{HH} = 2.3 Hz); 3.08 (s, 3H, CH_3); 4.12 (dd, 1H, NCH_2, J_{HH} = 17.6, 2.3 Hz); 4.49 (m, 2H, PCH_2P); 4.51 (dd, 1H, NCH_2, J_{HH} = 17.6, 2.3 Hz); 4.96 (m, 2H, PCH_2P); 6.50, 7.00, 7.11 (m x 3, 3 x 4H, C_6H_5); 7.25 – 7.50 (m, 24H, C_6H_5); 7.69 (m, 4H, C_6H_5). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): –4.7 (t, dppm, J_{PP} = 33.5 Hz), –18.9 (td, dppm, J_{PP} = 33.5, 12.4 Hz). MS (ES +ve) *m/z* (abundance) = 1014 (100) $[M]^+$. Analysis: Calculated for $C_{55}H_{50}F_6NP_5RuS_2$ (M_W = 1159.05): C 57.0%, H 4.4%, N 1.2%; Found: C 57.3%, H 4.4%, N 1.3%.

$[Pd\{S_2CN(CH_2C{\equiv}CH)Me\}(PPh_3)_2]BF_4$ (12)

N-methylpropargylamine (12 μL, 0.14 mmol) was mixed with dichloromethane (2 mL) and placed in an ice bath. Triethylamine (24 μL, 0.17 mmol) was added and the mixture stirred for 5 mins. Carbon disulfide (10 μL, 0.17 mmol) was added and the mixture stirred for a further 15 mins. The resulting dithiocarbamate was added to a solution of *cis*-$[PdCl_2(PPh_3)_2]$ (94 mg, 0.13 mmol) and $NaBF_4$ (26 mg, 0.24 mmol) in dichloromethane (30 mL) and methanol (10 mL). After stirring at room temperature for 2 h all solvent was removed using a rotary evaporator and the residue dissolved in the minimum volume of dichloromethane and passed through a plug of Celite. Isopropanol (30 mL) was added to the filtrate which was then concentrated by rotary evaporation and cooled in an ice bath to yield precipitation of the desired compound as a pale yellow solid. Yield: 43 mg (37% yield). A further slightly less pure crop (contaminated by around 5% starting material) could be obtained by leaving the filtrate in the freezer overnight. IR (solid state): 2172 ($\nu_{C\equiv C}$), 1969, 1906, 1813, 1672, 1531, 1480, 1435, 1094, 998, 751, 689 cm^{-1}. ^{1}H NMR (CD_2Cl_2): 2.54 (t, 1H, C≡CH, J_{HH} = 2.5 Hz); 3.31 (s, 3H, CH_3); 4.47 (d, 2H, NCH_2, J_{HH} = 2.5 Hz); 7.33 – 7.53 (m, 30H, C_6H_5) ppm. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): 30.4 (s, PPh_3) ppm. MS (ES +ve) *m/z* (abundance) = 774 (100) $[M]^+$. Analysis: Calculated for $C_{41}H_{36}BF_4NP_2PdS_2$ (M_W = 862.04): C 57.1%, H 4.3%, N 1.6%; Found: C 57.0%, H 4.3%, N 1.6%.

$H_2C{=}CCH_2N(Me)C(=S)S$ (13)

An aqueous solution (20 mL) of *N*-methylpropargylamine (84 μL, 1.00 mmol) and KOH (56 mg, 1.00 mmol) was stirred for 5 minutes. Carbon disulfide (72 μL, 1.20 mmol) was added to the solution and the reaction was stirred for 1 hour. Additional water (10 mL) was added to the solution and the white precipitate was filtered and dried under vacuum. Yield: 112 mg (77%). IR (solid state): 2914, 1755, 1625, 1501, 1432, 1406, 1388, 1286, 1228, 1182, 1094,

1021, 872 cm^{-1}. ^1H NMR ($CDCl_3$): 3.30 (s, 3H, CH_3); 4.78 (t, 2H, NCH_2, J_{HH} = 2.6 Hz); 5.14, 5.26 (m x 2, 2 x 1H, $=CH_2$) ppm. MS (ES +ve) *m/z* (abundance) = 146 (100) $[M]^+$. Analysis: Calculated for $C_5H_7NS_2$ (M_W = 145.25): C 41.4%, H 4.9%, N 9.6%; Found: C 41.3%, H 4.8%, N 9.5%.

MeC=CHN(Me)C(=S)S (14)

The aqueous filtrate from the synthesis of **13** was evaporated under reduced pressure to obtain a yellow oil. Yield: 30 mg (21%). IR (solid state): 3091, 2940, 1600, 1439, 1420, 1353, 1332, 1216, 1157, 1105, 1046, 932, 781 cm^{-1}. ^1H NMR ($CDCl_3$): 2.19 (s, 3H, CH_3); 3.62 (s, 3H, CH_3); 6.75 (s, 1H, =CH) ppm. MS (ES +ve) *m/z* (abundance) = 146 (100) $[M]^+$. Analysis: Calculated for $C_5H_7NS_2$ (M_W = 145.25): C 41.4%, H 4.9%, N 9.6%; Found: C 41.1%, H 4.7%, N 9.6%.

$[Ni\{S_2CN(Me)CH_2(C_2HN_3)Bz\}_2]$ (15)

Benzyl azide (24 µL, 0.19 mmol) and **8** (30 mg, 0.086 mmol) were dissolved in methanol (20 mL) and CuI(IAd) (4.5 mg, 0.009 mmol) was added and the reaction stirred overnight. The resulting dark green precipitate was filtered and dissolved in dichloromethane (10 mL) and filtered through Celite. All solvent was removed (rotary evaporator) and diethyl ether (20 mL) added. Ultrasonic trituration provided a green product, which was washed with diethyl ether (5 mL), petroleum ether (5 mL) and dried under vacuum. Yield: 33 mg (63%). ^1H NMR ($CDCl_3$): 3.18 (s, 3H, CH_3); 4.81 (s, 2H, NCH_2); 5.53 (s, 2H, benzyl-CH_2); 7.30, 7.40 (m x 2, 5H, C_6H_5); 7.63 (s, 1H, triazole-CH). MS (ES +ve) *m/z* (abundance) = 613 (5) $[M]^+$. Analysis: Calculated for $C_{24}H_{26}N_8NiS_4$ (M_W = 613.48): C 47.0%, H 4.3%, N 18.3%; Found: C 46.9%, H 4.3%, N 18.0%.

$[Ni\{S_2CN(Me)CH_2CH=CHRu(CO)(S_2P(OEt)_2)(PPh_3)_2\}_2]$ (16)

A dichloromethane solution (25 mL) of **8** (10.4 mg, 0.030 mmol) and $[RuH\{S_2P(OEt)_2\}(CO)(PPh_3)_2]$ (50 mg, 0.060 mmol) was stirred for 4 hours. The solution volume was concentrated and diethyl ether (10 mL) added. After crystallization in an ice bath, a brown solid was filtered, washed with cold diethyl ether (10 mL) and cold petroleum ether (10 mL) and dried under vacuum. Yield: 33 mg (54%). IR (solid state): 3052, 1909 (ν_{CO}), 1480, 1432, 1390, 740, 690 cm^{-1}. ^1H NMR (CD_2Cl_2): 0.88 (t, 12H, OCH_2, J_{HH} = 7.1 Hz); 2.33 (s, 6H, NCH_3); 2.90 - 3.15 (m, 8H, $OCCH_3\}_2$); 3.45 (d, 4H, NCH_2); 4.38 (m, 2H, Hβ); 6.97 (d, 2H, Hα, J_{HH} = 15.3 Hz, J_{HP} unresolved); 7.34 - 7.62 (m, 60H, C_6H_5) ppm.

$^{31}P\{^{1}H\}$ NMR: 32.0 (s, PPh_3), 94.7 (s, PS_2) ppm. MS (FAB) *m/z* (abundance) = 1044 (24) [M – $S_2CN(Me)CH_2CH{=}CHRu(CO)(S_2P(OEt)_2)(PPh_3)_2]^+$. Analysis: Calculated for $C_{92}H_{94}N_2NiO_6P_6Ru_2S_8$ (M_W = 2026.94): C 54.5%, H 4.7%, N 1.4%; Found: C 54.6%, H 4.6%, N 1.4%.

Au@$S_2CN(CH_2C{\equiv}CH)Me$ (NP1)

An aqueous solution (200 mL) of $HAuCl_4{\cdot}xH_2O$ (230 mg, 0.677 mmol) was brought to reflux. An aqueous solution (200 mL) of trisodium citrate dihydrate (1570 mg, 5.34 mmol) was added and the solution was removed from the heat and stirred in an ice bath for 40 minutes. The solution changed from yellow to black as nanoparticles formed. In a separate flask, an aqueous solution (200 mL) of freshly prepared **7** (2.64 mmol) was immediately added dropwise to the nanoparticle solution. The solution was stirred at room temperature for five hours and then stored at 5 °C for 18 hours to allow the nanoparticles to settle. The water was decanted, and the nanoparticles were washed with water (5 x 120 mL). All water was then removed (under vacuum) and the black powder triturated in diethyl ether (4 x 50 ml), collected and dried under vacuum. Yield: 50 mg (41%). IR (solid state): 2120 ($\nu_{C\equiv C}$), 1740, 1626, 1469, 1371, 1199, 1078, 1019, 935, 815 cm^{-1}. ^{1}H NMR (CD_2Cl_2): 2.45 (s(br), 1H, ≡CH); 3.59 (s(br), 3H, NMe); 4.78 (s(br), 2H) ppm. TEM: Analysis of 300 nanoparticles gave a size of 4.8 ± 1.0 nm. EDS: Indicated the presence of gold and sulfur. TGA: 28.6% surface units, 71.4% gold.

Crystallography

Crystals of compounds **6a** and **11** were grown by slow diffusion of ethanol into a dichloromethane solution of the complex in each case. Table 1 provides a summary of the crystallographic data for compounds 6a and 11. Data were collected using Oxford Diffraction Xcalibur 3 (**6a**) and Xcalibur PX Ultra A (**11**) diffractometers, and the structures were refined based on F^2 using the SHELXTL and SHELX-97 program systems.[28] CCDC 963408 to 963409.

Table 1. Crystallographic Data for compounds **6a** and **11**.

data	**6a**	**11**
Chemical formula	$C_{51}H_{47}NOP_2$	$[C_{55}H_{50}NP_4RuS_2](PF_6)$
solvent	CH_2Cl_2	$0.5(CH_2Cl_2)$
fw	1001.95	1201.46
T (°C)	–100	–100
space group	P–1 (no. 2)	$P2_1/c$ (no. 14)
a (Å)	12.0925(3)	17.13911(11)
b (Å)	13.2486(3)	11.81289(6)
c (Å)	17.1306(4)	27.19952(16)
α (deg)	91.4086(18)	—
β (deg)	108.979(2)	94.8134(5)
γ (deg)	111.961(2)	—
V (Å^3)	2373.28(11)	5487.46(5)
Z	2	4
ρ_{calcd} (g cm^{-3})	1.402	1.454
λ (Å)	0.71073	1.54184
μ (mm^{-1})	0.637	5.340
R_1(obs) [a]	0.0320	0.0335
wR_2(all) [b]	0.0804	0.0898

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

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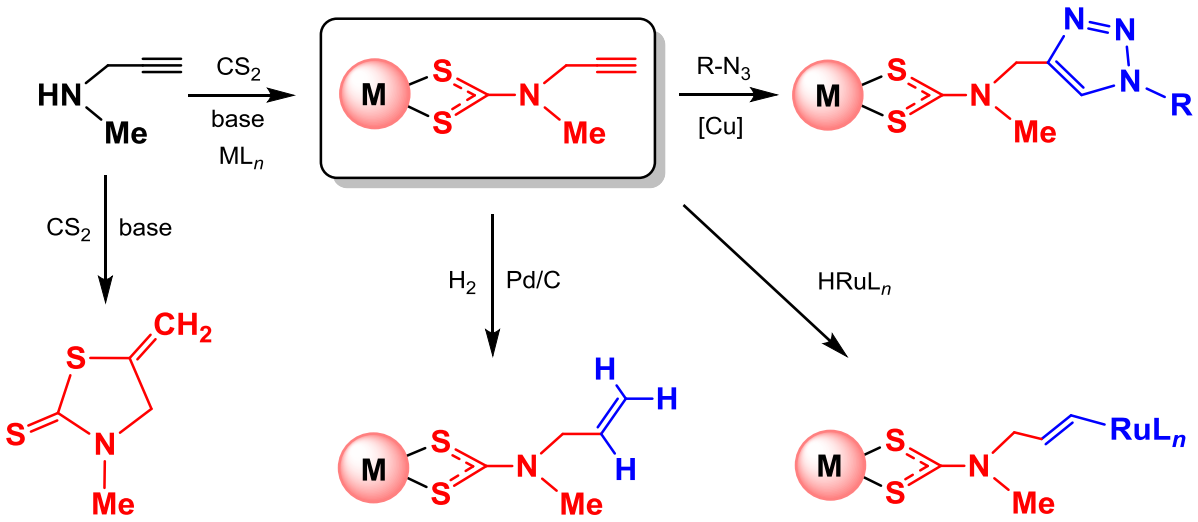
For table of contents use:

Multimetallic complexes and functionalized nanoparticles based on unsymmetrical dithiocarbamate ligands with allyl and propargyl functionality

Venesia L. Hurtubise, James M. McArdle, Saira Naeem, Anita Toscani, Andrew J. P. White, Nicholas J. Long* and James D. E. T. Wilton-Ely*



Unsymmetrical dithiocarbamate ligands prove to be versatile starting points for the preparation of both multimetallic complexes and surface-functionalized gold nanoparticles. The ligands provide a platform for functional group transformations of the pendant alkene or alkyne functionality, while cyclisation of the propargyl derivative provides an atom-efficient and high-yielding route to thiazolidine-2-thiones.

Supporting Information

The X-ray crystal structure of 6a

The included dichloromethane solvent molecule in the structure of **6a** was found to be disordered. Three orientations were identified, of *ca*. 41, 36 and 23% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and all of the atoms were refined isotropically.

The X-ray crystal structure of 11

The C(45)- and C(57)-based phenyl rings in the structure of **11** were found to be disordered, and in each case two orientations were identified, of *ca*. 74:26 and 71:29% occupancy respectively. All four orientations were refined as optimised rigid bodies, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientations were refined anisotropically (the remainder were refined isotropically). The included dichloromethane solvent molecule was also found to be disordered. Two orientations were identified, of *ca*. 31 and 19% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (the remainder were refined isotropically); inspection of the thermal parameters suggested that the solvent was not more than about 50% occupancy in total.

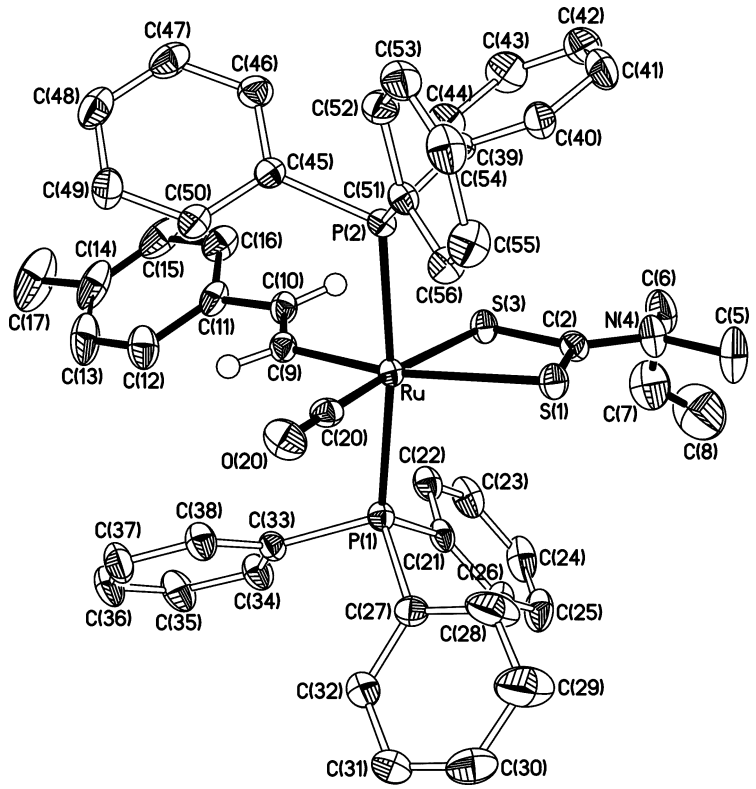


Fig. S1 The crystal structure of **6a** (50% probability ellipsoids).

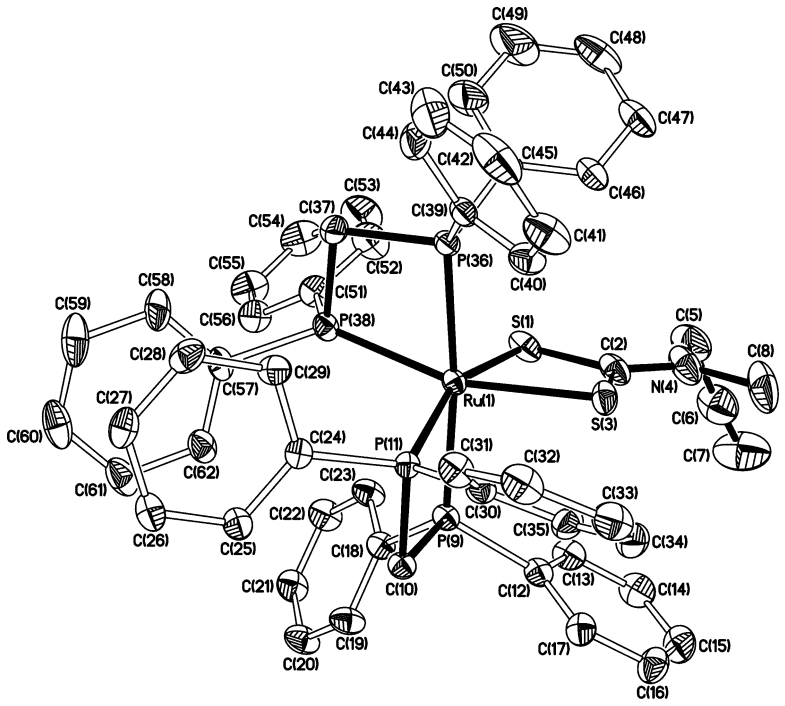
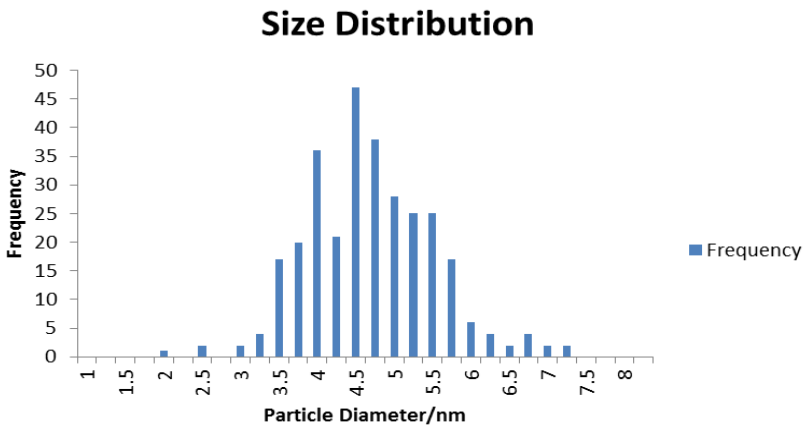


Fig. S2 The structure of the cation present in the crystals of **11** (30% probability ellipsoids).

Transmission Electron Microscopy (TEM)

The average size and size distribution of the nanoparticles (4.8 ± 1.0 nm) was determined using TEM.



Thermogravimetric analysis (TGA)

TGA was used to estimate the proportion of the mass attributable to the surface units. A sample of mass 2.488 mg of **NP1** was heated from 30 °C to 700 °C at a rate of 10 °C per minute (total points recorded in run: 4020). The reduction in mass was 28.6%, leaving gold metal as the only residue.