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Article

Multimetallic Assemblies Using Piperazine-Based Dithiocarbamate Building Blocks

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Treatment of *cis*-$[RuCl_2(dppm)_2]$ (dppm = bis(diphenylphosphino)methane) with dithiocarbamates, NaS_2CNR_2 (R = Me, Et) and $[H_2NC_5H_{10}][S_2CNC_5H_{10}]$, yields cations $[Ru(S_2CNR_2)_2(dppm)_2]^+$ and $[Ru(S_2CNC_5H_{10})_2(dppm)_2]^+$, respectively. The zwitterions $S_2CNC_4H_8NHR$ (R = Me, Et) react with the same metal complex in the presence of base to yield $[Ru(S_2CNC_4H_8NR)(dppm)_2]^+$. Piperazine or 2,6-dimethylpiperazine reacts with carbon disulfide to give the zwitterionic dithiocarbamate salts $H_2NC_4H_6(R_2\text{-}3,5)NCS_2$ (R = H; R = Me), which form the complexes $[Ru(S_2CNC_4H_6(R_2\text{-}3,5)NH_2)(dppm)_2]^{2+}$ on reaction with *cis*-$[RuCl_2(dppm)_2]$. Sequential treatment of $[Ru(S_2CNC_4H_8NH_2)(dppm)_2]^{2+}$ with triethylamine and carbon disulfide forms the versatile metalla-dithiocarbamate complex $[Ru(S_2CNC_4H_8NCS_2)(dppm)_2]$ which reacts readily with *cis*-$[RuCl_2(dppm)_2]$ to yield $[\{Ru(dppm)_2\}_2\text{-}(S_2CNC_4H_8NCS_2)]$. Reaction of $[Ru(S_2CNC_4H_8NCS_2)(dppm)_2]$ with $[Os(CH{=}CHC_6H_4Me\text{-}4)Cl(CO)(BTD)(PPh_3)_2]$ (BTD = 2,1,3-benzothiadiazole), $[Pd(C_6H_4CH_2NMe_2)Cl]_2$, $[PtCl_2(PEt_3)_2]$, and $[NiCl_2(dppp)]$ (dppp = 1,3-bis(diphenylphosphino)propane) results in the heterobimetallic complexes $[(dppm)_2Ru(S_2CNC_4H_8NCS_2)ML_n)]^{m+}$ ($ML_n = Os(CH{=}CH\text{-}C_6H_4Me\text{-}4)(CO)(PPh_3)_2]^+$, $m = 1$; $ML_n = Pd(C,N\text{-}C_6H_4CH_2NMe_2)$, $m = 1$; $ML_n = Pt(PEt_3)_2$, $m = 2$; $ML_n = Ni(dppp)$, $m = 2$). Reaction of $[NiCl_2(dppp)]$ with $H_2NC_4H_8NCS_2$ yields the structurally characterized compound, $[Ni(S_2CNC_4H_8NH_2)(dppp)]^{2+}$, which reacts with base, CS_2, and *cis*-$[RuCl_2(dppm)_2]$ to provide an alternative route to $[(dppm)_2Ru(S_2CNC_4H_8NCS_2)Ni(dppp)]^+$. A further metalla-dithiocarbamate based on cobalt, $[CpCo(S_2CNC_4H_8NH_2)(PPh_3)]^{2+}$, is formed by treatment of $CpCoI_2(CO)$ with $S_2CNC_4H_8NH_2$ followed by PPh_3. Further reaction with NEt_3, CS_2, and *cis*-$[RuCl_2(dppm)_2]$ yields $[(Ph_3P)CpCo(S_2CNC_4H_8NCS_2)Ru(dppm)_2]^{2+}$. Heterotrimetallic species of the form $[\{(dppm)_2Ru(S_2CNC_4H_8NCS_2)\}_2M]^{2+}$ result from the reaction of $[Ru(S_2CNC_4H_8NCS_2)(dppm)_2]$ and $M(OAc)_2$ (where M = Ni, Cu, Zn). Reaction of $[Ru(S_2CNC_4H_8NCS_2)(dppm)_2]$ with $Co(acac)_3$ and $LaCl_3$ results in the formation of the compounds $[\{(dppm)_2Ru(S_2CNC_4H_8NCS_2)\}_3Co]^{3+}$ and $[\{(dppm)_2Ru(S_2CNC_4H_8NCS_2)\}_3La]^{3+}$, respectively. The electrochemical behavior of selected examples is also reported.

Introduction

All transition metals form complexes with dithiocarbamate ligands,[1] and the stabilization such coordination affords has led to the development of a wide range of applications in areas as diverse as materials science, medicine, and agriculture. Given this versatility, their well-defined architecture, and the extensive metal-centered electrochemistry shown by these complexes,[2] it is surprising that they have found little use in the rapidly expanding area of supramolecular design. Recent work has started to address this issue through the preparation of a range of fascinating new supramolecular architectures based on multifunctional dithiocarbamate ligands, which often show intriguing structure-redox properties.[3] It is clear from this work that dithiocarbamates have far greater potential in supramolecular and materials chemistry than that currently utilized. This has led us to focus our efforts on the development of multidentate dithiocarbamate ligands for the synthesis of multimetallic arrays. These arrays could be one,

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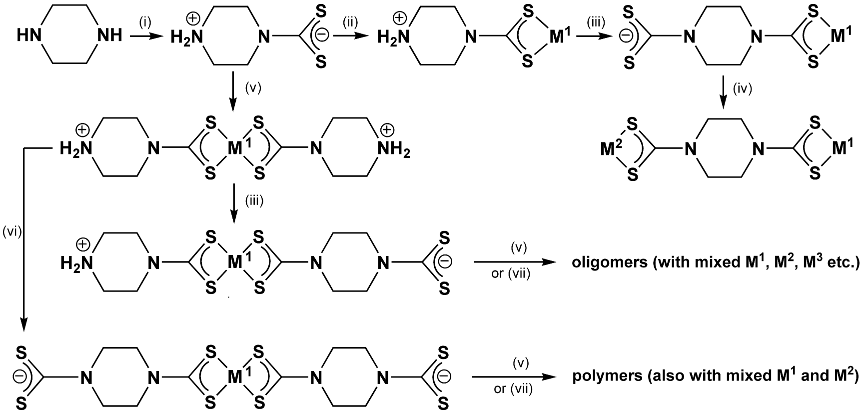
Scheme 1. (i) CS_2; (ii) M^1X; (iii) $2NEt_3$, CS_2; (iv) M^2X; (v) M^1X_2; (vi) $4NEt_3$, $2CS_2$; (vii) M^2X_2



two, or three-dimensional in nature, the dimensionality being easily controlled as a function of the properties of both the metal and the ligand. We envisage that these materials will show novel physical properties in their own right leading, among other possibilities, to their use as precursors to the synthesis of well-defined nanoparticulates in a manner developed extensively by O'Brien and co-workers.[4]

A simple strategy for the synthesis of multimetallic wires is outlined below (Scheme 1), based on a molecule containing two secondary amine centers. Such species react with CS_2 to afford a zwitterionic product[5] whereby one of the amines acts as a nucleophile and the second as a base. Importantly, only negligible amounts of the symmetrical double salt $[S_2CNC_4H_8NCS_2][H_2NC_4H_8NH_2]$ are formed. This behavior underpins the methodology described here as it allows one end of the amine to be extended selectively upon reaction with carbon disulfide. Treatment of the zwitterion, $H_2NC_4H_8NCS_2$ (**1**), with a metal complex results in the formation of a new metal-amine compound, which in turn can react with further CS_2 to generate a new metal-containing dithiocarbamate (metalla-dithiocarbamate). In this manner multimetallic arrays can be constructed in a modular, stepwise fashion. This report expands on our preliminary results,[6] to demonstrate how this approach can be extended to include the preparation of materials containing between one and four metals.

A number of transition metal and main group complexes of the ligands $H_2NC_4H_8NCS_2$ and $[S_2CNC_4H_8NCS_2]^{2-}$ are known.[1,7] However, these species are confined to symmetrical complexes or mononuclear examples. This report explores the untapped potential for the preparation of (hetero)multimetallic compounds by the method outlined above.

Scheme 2. (i) $[H_2NC_5H_{10}][S_2CNC_5H_{10}]$, $NaBF_4$ or $[RHNC_4H_8CS_2]$ (R = Me, Et), $NaBF_4$

X = CH_2 (**6**), NMe (**7**), NEt (**8**)

Results and Discussion

Synthesis of Model Ruthenium Dithiocarbamate Complexes. The ruthenium(II) complex *cis*-$[RuCl_2(dppm)_2]$[8] was chosen to provide a *cis*-$Ru(dppm)_2$ moiety as our initial metal fragment. This choice was based on our observation that *cis*-$[RuCl_2(dppm)_2]$ reacts cleanly with a wide range of dithiocarbamate salts, $R_2NCS_2^-$ (NR_2 = NMe_2, NEt_2, NC_5H_{10} (**3**)[9,10]) to afford the cations $[Ru(S_2CNR_2)(dppm)_2]^+$ in high yield (Scheme 2). Furthermore, the zwitterions $S_2CNC_4H_6(R_2\text{-}3,5)NH_2$ (R = H (**1**), Me (**2**)), $S_2CNC_4H_8NHMe$ (**4**), and $S_2CNC_4H_8NHEt$ (**5**) also react, but to give dicationic

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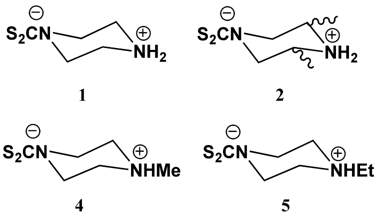
Chart 1. Zwitterionic Ligands Used to Generate the Complexes



products, $[Ru(S_2CNC_4H_6R_2NH_2)(dppm)_2]^{2+}$, or monocations, $[Ru(S_2CNC_4H_8NR)(dppm)_2]^+$ (R = Me, Et), when the reaction is carried out in the presence of base (Chart 1). These complexes are easily characterized by a range of spectroscopic techniques, of which ^{31}P NMR spectroscopy proves particularly useful.

Robinson and co-workers reported that *cis*-$[RuCl_2(dppm)_2]$ reacts with dithiocarbamates of zinc, cadmium, mercury, and lead to form $[Ru(S_2CNEt_2)(dppm)_2]_2[MCl_4]$ (M = Zn, Cd, Hg, Pb).[11] A partial crystal structure and some spectroscopic and microanalytical data were also included in the report. To gather complete spectroscopic and analytical data on these model species, the complexes $[Ru(S_2CNMe_2)(dppm)_2]BF_4$ and $[Ru(S_2CNEt_2)(dppm)_2]BF_4$ were prepared from *cis*-$[RuCl_2(dppm)_2]$ and the hydrates of NaS_2CNR_2 (R = Me, Et) in the presence of $NaBF_4$ (data provided in the Supporting Information). The cyclic secondary amine, piperidine, reacts readily with CS_2 in water to yield $[H_2NC_5H_{10}][S_2CNC_5H_{10}]$.[9] Treatment of *cis*-$[RuCl_2(dppm)_2]$ with this salt in a mixture of dichloromethane and ethanol (in the presence of $NaBF_4$) results in the formation of the corresponding piperidine dithiocarbamate compound, $[Ru(S_2CNC_5H_{10})(dppm)_2]BF_4$ (**6**). Two multiplet resonances are seen in the ^1H NMR spectrum for the piperidine protons at 1.46 and 3.58 ppm. Elemental analysis and a molecular ion at *m*/*z* 1031 confirmed the overall composition. Reaction of 1-methylpiperzine or 1-ethylpiperzine with CS_2 in the presence of base provides the zwitterions $[RHNC_4H_8CS_2]$ (R = Me, Et), which react with *cis*-$[RuCl_2(dppm)_2]$ and base to give the dications $[Ru(S_2CNC_4H_8NR)(dppm)_2]^+$ (R = Me (**7**), Et (**8**)). The NMe group in **7** gave rise to a singlet in the ^1H NMR spectrum at 2.54 ppm while the NEt moiety in **8** was identified from typical triplet and quartet resonances at 1.11 and 2.47 ppm, respectively ($J_{HH} = 7.1$ Hz).

Treatment of 1 equiv of *cis*-$[RuCl_2(dppm)_2]$ with zwitterion $S_2CNC_4H_8NH_2$, followed by an excess of $NaBF_4$ affords the colorless dication $[(dppm)_2Ru(S_2CNC_4H_8NH_2)][BF_4]_2$ (**9**) in high yield. The presence of the dithiocarbamate ligand was evidenced by two multiplets at 3.04 and 3.88 ppm (NC_4H_8N) not present in the *cis*-$[RuCl_2(dppm)_2]$ starting material along with a broad singlet at 2.35 ppm for the NH_2 protons. Two triplets were observed in the ^{31}P NMR spectrum at −3.8 and −17.3 ppm showing coupling of 34.4 Hz. Mass spectrometry (FAB) provided information on the overall composition of the cation with a molecular ion at *m*/*z* 1030. The formulation as a BF_4^- double salt was supported by a broad ν_{BF} band in the solid state infrared spectrum (nujol) and elemental analysis.

Addition of carbon disulfide to 2,6-dimethylpiperazine (used as obtained commercially) led to the corresponding analogue of **1**, $H_2NC_4H_6(Me_2\text{-}3,5)NCS_2$ (**2**). It is probable that the dithiocarbamate moiety is formed at the sterically less hindered end of the 2,6-dimethylpiperazine ring. The greater complexity of the ^1H NMR spectra of this ligand and its complexes reflects the effect of the methyl substituents on the proton environments, rendering them chiral, as well as subject to conformational isomerism. Three environments were observed for the piperazine protons in the ^1H NMR spectrum at 2.76, 3.00, and 5.57 ppm with the methyl groups appearing as a doublet at 1.07 ($J_{HH} = 6.5$ Hz) ppm. No clear differentiation between the possible isomers was possible from the NMR spectrum. Elemental analysis and mass spectrometry confirmed the overall composition. The reaction of **2** with *cis*-$[RuCl_2(dppm)_2]$ provides $[(dppm)_2Ru(S_2CNC_4H_6(Me_2\text{-}3,5)NH_2)]$ (**10**), which gave rise to five distinct resonances for the axial and equatorial protons of the piperazine ring along with an apparent triplet (overlapping doublets) at 1.14 ($J_{HH} = 6.3$ Hz) for the methyl groups.

Homo- and Heterobimetallic Dithiocarbamate Complexes. The generation of $[(dppm)_2Ru(S_2CNC_4H_8NCS_2)]$ (**11**) from **9** was carried out in situ by sequential addition of 2 equiv of base and CS_2. Compound **11** is the key building block for the subsequent chemistry and can be considered to be a metalla-dithiocarbamate. To demonstrate its utility in the formation of dinuclear species, this compound was treated with a second equivalent of *cis*-$[RuCl_2(dppm)_2]$ to afford (after salt metathesis) the binuclear complex $[(dppm)_2Ru(S_2CNC_4H_8NCS_2)Ru(dppm)_2][BF_4]_2$ (**12**). The same complex is also produced in a one-step reaction upon addition of the double salt $Na_2[S_2CNC_4H_8NCS_2]$ (formed from piperazine, excess NaOH and CS_2) to 2 equiv of *cis*-$[RuCl_2(dppm)_2]$ followed by salt metathesis. Because of the symmetrical nature of the complex, doublets were seen for the axial and equatorial protons in the chair formation of the piperazine at 3.51 and 3.62 ppm ($J_{HH} = 9.5$ Hz). This conformation was confirmed by a crystallographic study of **12** communicated previously.[6]

The bridging dithiocarbamate mode found in **12** is not unique; Shaver and co-workers having prepared a related diruthenium complex, $[Cp(PPh_3)Ru(S_2CNC_6H_4NCS_2)Ru(PPh_3)Cp]$, from the unusual reaction of 2 equiv of $[CpRu(PPh_3)_2SH]$ with *para*-phenylenediisothiocyanate.[7f] A number of non-transition metal complexes, particularly of tin, have also been reported, in which the piperazine bis(dithiocarbamate) bridging ligand has been crystallographically characterized.[7g−j] A fascinating example based on gold has also been recently reported, in which the piperazine bis(dithiocarbamate) ligand adopts a boat conformation, spanning a ring of 16 gold centers.[7k]

The clear advantage of the stepwise activation of the zwitterionic ligand **1** is the ready accessibility of heterobimetallic complexes. This is demonstrated by the reaction of **9** with base and CS_2 (to generate **11**) followed by addition of 1 equiv of the osmium vinyl complex $[Os(CH{=}CHC_6H_4Me\text{-}4)Cl(CO)(BTD)(PPh_3)_2]$. The product is $[(dppm)_2Ru(S_2CN\text{-}$

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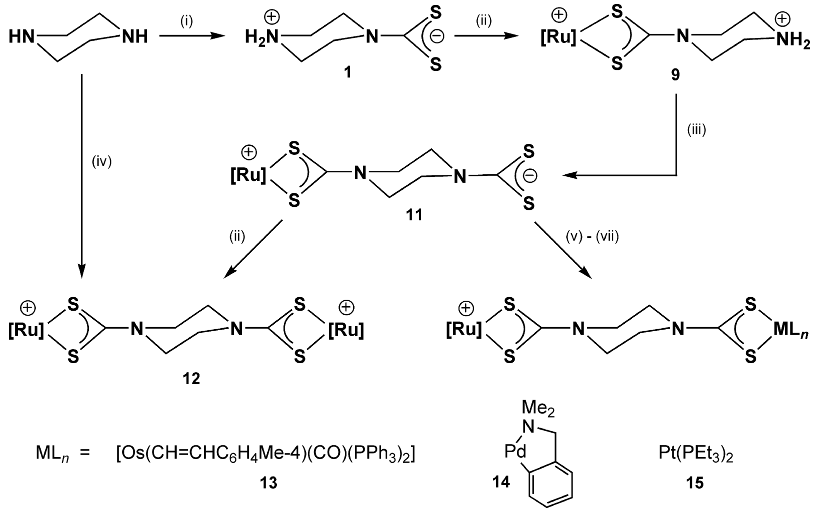
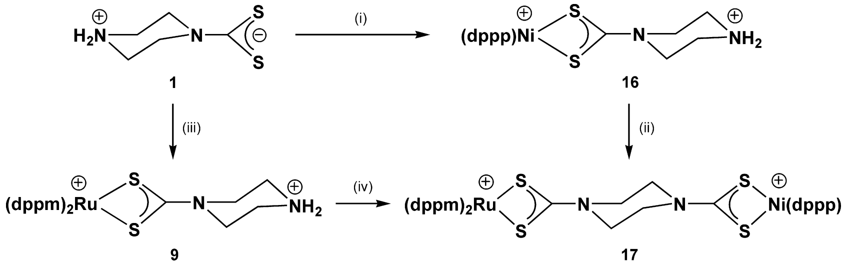
[11] Exarchos, G.; Robinson, S. D.; Steed, J. W. *Polyhedron* **2001**, *20*, 2951–2963.

Scheme 3. [M] = Ru(dppm)$_2$; (i) CS$_2$; (ii) *cis*-[RuCl$_2$(dppm)$_2$], 2NaBF$_4$; (iii) 2NEt$_3$, CS$_2$; (iv) 2NEt$_3$, 2CS$_2$; 2*cis*-[RuCl$_2$(dppm)$_2$]; (v) [Os(CH=CHR)Cl(CO)(BTD)L$_2$] (BTD = 2,1,3-benzothiadiazole); (vi) [Pd(*C,N*-C$_6$H$_4$CH$_2$NMe$_2$)Cl]$_2$; (vii) [PtCl$_2$(PEt$_3$)$_2$]



Scheme 4. (i) [NiCl$_2$(dppp)], 2NaBF$_4$; (ii) 2NEt$_3$, CS$_2$, *cis*-[RuCl$_2$(dppm)$_2$]; (iii) *cis*-[RuCl$_2$(dppm)$_2$], 2NaBF$_4$; (iv) 2NEt$_3$, CS$_2$, [NiCl$_2$(dppp)]



C$_4$H$_8$NCS$_2$)Os(CH=CHC$_6$H$_4$Me-4)(CO)(PPh$_3$)$_2$]BF$_4$ (**13**), formed by displacement of chloride and the labile 2,1,3-benzothiadiazole (BTD) ligand (Scheme 3). A new singlet is observed in the ^{31}P NMR at 9.3 ppm for the *trans* bis(triphenylphosphine) unit in addition to typical resonances for the dppm ligands. The ^{1}H NMR spectrum also clearly shows the presence of resonances characteristic of the vinyl ligand at 2.21 (s, CH$_3$) and 5.59 (d, Hβ), 6.36, 6.81 (AB system, C$_6$H$_4$), and 8.28 (dt, Hα) ppm. Elemental analysis and an abundant molecular ion at *m*/*z* 1967 further support the above formulation of the Ru−Os bimetallic complex.

The cyclometalated dimer, [PdCl(*C,N*-C$_6$H$_4$CH$_2$NMe$_2$)]$_2$, reacts with 2 equiv of **11** (generated in situ) to yield a colorless compound, [(dppm)$_2$Ru(S$_2$CNC$_4$H$_8$NCS$_2$)Pd(*C,N*-C$_6$H$_4$CH$_2$NMe$_2$)]$^+$ (**14**), which was identified from its ^{1}H NMR spectrum. The NMe$_2$ group and methylene bridge in the compound give rise to singlets shifted from those in the precursor to 2.92 and 4.01 ppm, respectively. The aryl resonances for the palladium-bonded ligand are obscured by those of the dppm ligands. Platinum bis(phosphine) units can also be introduced through replacement of the chloride ligands in the complex [PtCl$_2$(PEt$_3$)$_2$] by the metalladithiocarbamate **11**. The product, [(dppm)$_2$Ru(S$_2$CNC$_4$H$_8$NCS$_2$)Pt(PEt$_3$)$_2$](BF$_4$)$_2$ (**15**), shows new resonances in the ^{31}P NMR spectra for the phosphines bonded to the Ru and Pt centers. In the latter, ^{195}Pt satellites are observed showing a J_{PtP} coupling of 3116.5 Hz.

To broaden the range of metalla-dithiocarbamate species available, the suitability of the nickel complex [NiCl$_2$(dppp)] (dppp = 1,3-bis(diphenylphosphino)propane) was investigated. This species reacts similarly to *cis*-RuCl$_2$(dppm)$_2$ through displacement of both chloride ligands by the piperazine dithiocarbamate ligand, **1**. This reaction was carried out in the presence of excess NaBF$_4$ to provide [Ni(S$_2$CNC$_4$H$_8$NH$_2$)(dppp)](BF$_4$)$_2$ (**16**) in 70% yield (Scheme 4). A single resonance was observed in the ^{31}P NMR spectrum at 13.8 ppm and five broadened multiplets seen in the ^{1}H NMR spectrum for the dppp ligand and the protons of the C$_4$H$_8$NH$_2$ moiety. A molecular ion was observed at *m*/*z* = 631. The elemental analysis obtained was in good agreement with a chloroform monosolvate (confirmed by integration of the ^{1}H NMR spectrum). Crystals were grown from slow diffusion of diethyl ether into a dichloromethane solution of the complex and a structural study undertaken. However, this was found to be the deprotonated monocation (**16a**, Figure 1). The loss of the proton must occur during the crystallization process as the material used to grow crystals did not analyze to be the formulation in the structure **16a**.

The structural study also revealed that rather than the complex crystallizing solely as the BF$_4^-$ salt, the structure contains a combination of chloride counter-anions and tetrafluoroborate counteranions (the former presumably originating from the chlorinated solvents used during crystallization). The chloride ions are in the cleft between two pairs of molecules occupying a position on the improper 4-fold axis (Figure 1). There is disorder of the piperazine ring, such that it is present in both chair conformations in a 50:50 ratio.

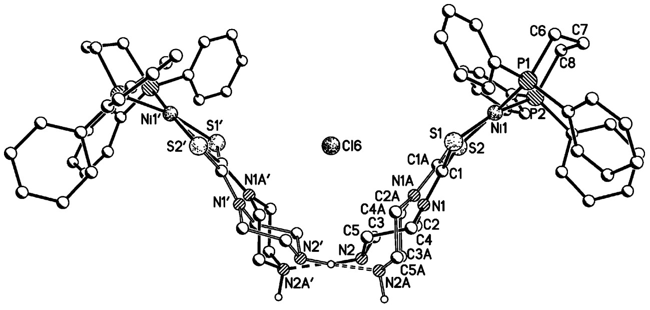


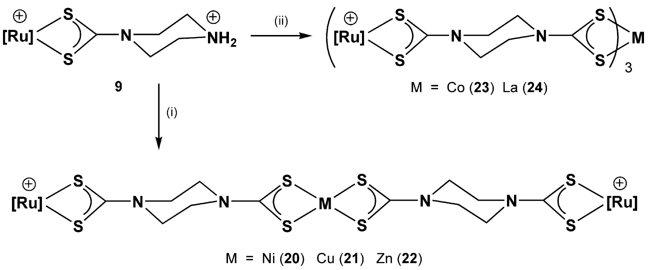
Figure 1. Molecular structure of the cation in compound **16a**. Selected bond distances (Å) and angles (deg): Ni1−P1 = 2.1679(18), Ni1−P2 = 2.1733(18), Ni1−S1 = 2.2009(18), Ni1−S2 = 2.1995(19), S1−C1 = 1.75(2), S2−C1 = 1.74(2), N1−C1 = 1.30(3), P1−Ni1−P2 = 95.53(7), P1−Ni1−S1 = 91.89(7), P2−Ni1−S2 = 92.85(7), S2−Ni1−S1 = 79.68(7), S2−C1−S1 = 107.8(13).

These two disordered components of the piperazine moiety are paired such that there are hydrogen bonds connecting molecules related by the 2-fold rotation implicit in the improper axis. The 4-fold improper rotation also generates a second hydrogen bonded pair of molecules, creating a pocket occupied by the chloride, which is approximately 3.6 Å from the center of the piperazine rings (Supporting Information). In addition to the chloride, the charge is balanced by tetrafluoroborate counteranions, giving the overall formula [**16a**]$(BF_4)_{0.75}(Cl)_{0.25}\cdot 0.5CHCl_3\cdot 0.5CH_2Cl_2$ when the site multiplicities are taken into account. The geometry around the nickel center is square planar with limited deformation from the plane and the diphosphine ligand is accommodated well because of the flexibility of the propylene bridge. A useful structure for comparison purposes is the complex $[Ni(S_2CNC_6H_{12})(dppf)]ClO_4$.[12] This structure displays a similar distorted square-planar coordination around the metal center, and the Ni−S, S−C, C−N bond lengths correlate closely to those found in **16a**.

Treating a dichloromethane solution of **16** with triethylamine followed by carbon disulfide and then 1 equiv of *cis*-$[RuCl_2(dppm)_2]$ led to formation of the Ni−Ru bimetallic dication, $[(dppm)_2Ru(S_2CNC_4H_8NCS_2)Ni(dppp)](BF_4)_2$ (**17**). Characteristic triplets for the dppm ligands were observed in the ^{31}P NMR spectrum at −4.1 and −16.8 ppm (J_{PP} = 34.9 Hz) along with a singlet at 13.7 ppm (dppp). The same product was prepared starting from **9** through treatment with base, CS_2, and then $[NiCl_2(dppp)]$, thus illustrating the versatility of the methodology employed (Scheme 4).

Metalla-dithiocarbamates based on other metal fragments are also readily accessible. Treatment of $[CpCoI_2(CO)]$ with $S_2CNC_4H_8NH_2$ followed by PPh_3 (and NH_4PF_6) leads to the formation of $[CpCo(S_2CNC_4H_8NH_2)(PPh_3)](PF_6)_2$ (**18**). Deprotonation with triethylamine in the presence of carbon disulfide followed by addition of 1 equiv of *cis*-$[RuCl_2(dppm)_2]$ yields $[(Ph_3P)CpCo(S_2CNC_4H_8NCS_2)Ru(dppm)_2](PF_6)_2$ (**19**). A singlet (45.7 ppm) and two triplets (−5.4 and −17.7 ppm) in the ^{31}P NMR spectrum provided the initial evidence for the formulation, which was further supported by ^1H NMR spectroscopy, mass spectrometry, and elemental analysis.

Scheme 5. [M] = $Ru(dppm)_2$; (i) $2NEt_3$, CS_2, $^1/_2[M(OAc)_2]$ (M = Ni or Cu); (ii) $2NEt_3$, CS_2, $^1/_3[Co(acac)_3]$ or $^1/_3[LaCl_3]$



Multimetallic Dithiocarbamate Complexes. In the cases described above, the added metal center binds only a single dithiocarbamate ligand, however, this approach can easily be extended to include trimetallic species. This is achieved using complexes that have two binding sites for bidentate dithiocarbamate ligands. To illustrate this, the complexes $[\{(dppm)_2Ru(S_2CNC_4H_8NCS_2)\}_2M][BF_4]_2$ (M = Ni (**20**), Cu (**21**), Zn (**22**); Scheme 5) were prepared from reaction of complex **11** (2 equiv), generated in situ with nickel, copper, and zinc acetate, respectively. These examples illustrate the facility of incorporating diamagnetic and paramagnetic centers with well-defined and well-understood redox properties into these arrays. Complexes **20** and **21** share many spectroscopic features and, from the data available, appear to be isostructural. Two triplets are observed at −4.2 and −16.8 ppm (J_{PP} = 34.5 Hz) in the ^{31}P NMR spectrum, and a series of well-defined multiplets are observed for both the piperazine and methylene (dppm) protons. The presence of the nickel center is indicated by a molecular ion in the FAB-MS spectrum at *m*/*z* = 2271 and microanalytical data. For the copper example (**21**), the paramagnetic nature of the Cu(II) center leads to broadening of the resonances for the methylene bridges of the diphosphines (^{31}P NMR resonances not affected) at 4.61 and 4.96 ppm and the disappearance of the piperazine protons. Again, mass spectrometry (FAB-MS) is necessary to determine the presence of the copper with a peak corresponding to the molecular ion at *m*/*z* = 2271. Data for the zinc complex, $[\{(dppm)_2Ru(S_2CNC_4H_8NCS_2)\}_2Zn][BF_4]_2$ (**22**), were also found to be similar with elemental analysis and a peak corresponding to $[M + BF_4]^+$ at *m*/*z* = 2366 proving the most diagnostic.

Having prepared linear bi- and trimetallic species, two metal ions that are known to coordinate three dithiocarbamate ligands were selected to construct tetrametallic species. Three equivalents of $[Ru(S_2CNC_4H_8NCS_2)(dppm)_2]$ (**11**) were generated in situ, and $[Co(acac)_3]$ was added as a solid. The green product, $[\{(dppm)_2Ru(S_2CNC_4H_8NCS_2)\}_3Co][BF_4]_3$ (**23**), gave rise to multiplets at 3.66 and 3.79 ppm for the piperazine protons in the ^1H NMR spectrum and a further pair of multiplets corresponding to the methylene bridges of the dppm ligands. Because of the large molecular mass of the material, mass spectrometry data were difficult to obtain; however, a substantial ion peak for the loss of one metalla-dithiocarbamate unit was observed at *m*/*z* = 2272. Lanthanum also forms six-coordinate dithiocarbamate com-

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[12] Pastorek, R.; Kamenicek, J.; Pavlicek, M.; Husarek, J.; Sindelar, Z.; Zak, Z. *J. Coord. Chem.* **2002**, *55*, 1301–1308.

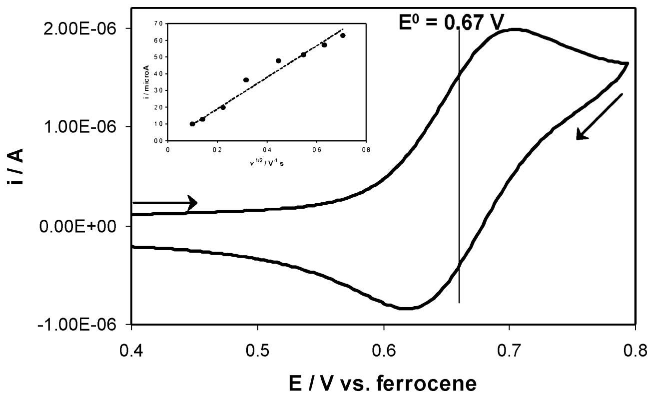

Figure 2. CV of 0.5 mM of complex **9** in 0.1 M TBAClO$_4$ in DCM at 50 mV s^{-1}, Pt electrode, $A = 0.03141$ cm^2. Inset shows plot of peak oxidation current vs square root of scan rate.

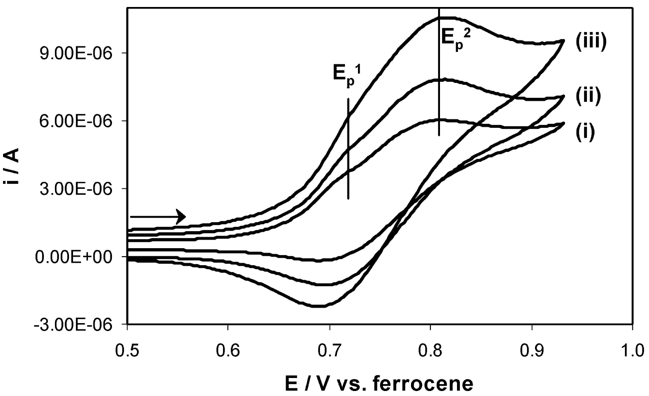

Figure 3. CVs of 0.8 mM of complex **12** in 0.1 M TBAClO$_4$ in DCM at (i) 50 mV s^{-1}; (ii) 100 mV s^{-1}; (iii) 200 mV s^{-1}. Pt electrode; area 0.03141 cm^2.

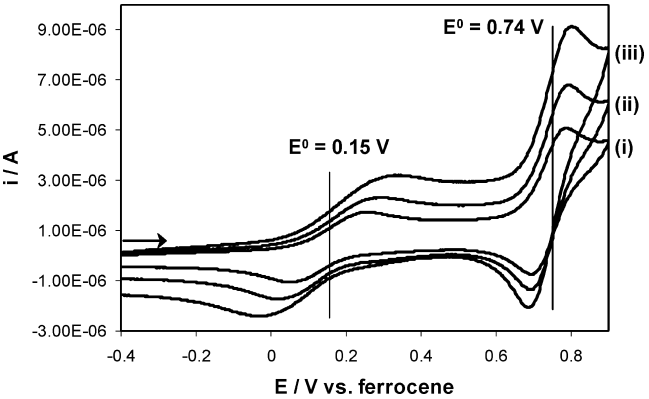

Figure 4. CVs of 0.66 mM of [{(dppm)$_2$Ru(S$_2$CNC$_4$H$_8$NCS$_2$)}$_2$Cu](BF$_4$)$_2$ (**21**) in 0.1 M TBAClO$_4$ in DCM at a Pt working electrode, area = 0.03141 cm^2 at (i) 50 mV s^{-1}; (ii) 100 mV s^{-1}; (iii) 200 mV s^{-1}.

pounds,[13] and so this metal was chosen to prepare a representative complex of the lanthanides. An aqueous solution of LaCl$_3$ was used to prepare [{(dppm)$_2$Ru(S$_2$CNC$_4$H$_8$NCS$_2$)}$_3$La][BF$_4$]$_3$ (**24**) in a similar manner to **23**. The FAB mass spectrum also exhibited a peak corresponding to loss of a (dppm)$_2$Ru(S$_2$CNC$_4$H$_8$NCS$_2$) unit at $m/z = 2353$. The overall composition was further supported by elemental analysis. While all the compounds described above show well-defined triplets in their ^{31}P NMR spectra, complex **24** displays two triplet resonances at −16.6 and −17.3 ppm along with a peak due to two superimposed resonances at −4.0 ppm. There are four possible pairs of optical isomers for the MRu$_3$ compounds **23** (M = Co) and **24** (M = La) because of all four metal centers being chiral. The two pairs of resonances observed for **24** would indicate that two isomers with sufficiently different chemical shifts can be differentiated in the ^{31}P NMR spectrum for this compound. In contrast to the case for the lanthanum complex, there is an absence of clear additional peaks or shoulders in the ^{31}P NMR spectra of the cobalt complex (**23**) suggesting that the isomers are not identifiable spectroscopically (similar chemical shift).

Electrochemistry. Dithiocarbamate ligands have established a reputation for supporting metal-based electrochemistry.[2] Although the piperazine bis(dithiocarbamate) spacer linking the metal centers is not conjugated, limited communication might be expected between the metals centers, the electrochemistry of selected complexes was investigated to establish the degree to which the metal centers might interact.[14] The diversity of ruthenium dithiocarbamate chemistry and the reliability of the Ru(II)/Ru(III) couple have led to many of these compounds being used as the focus of electrochemical investigations, although that is not the aim here.

The cyclic voltammogram (CV) for [Ru(S$_2$CNC$_4$H$_8$NH$_2$)(dppm)$_2$](BF$_4$)$_2$ (**9**) is shown in Figure 4, where a reversible one-electron oxidation corresponding to the Ru^{2+}/Ru^{3+} couple is observed. $E^{0\prime}$ for the couple is 0.67 V versus ferrocene and peak positions were found to be independent of scan rate. Peak currents for the oxidation and reduction peaks are equal in magnitude and show a linear dependence with square root of scan rate ($\nu^{1/2}$), indicative of a reversible, diffusion-controlled electron transfer, as shown in the inset to Figure 2.

Figure 3 shows CVs for [{Ru(dppm)$_2$}$_2$(S$_2$CNC$_4$H$_8$NCS$_2$)](BF$_4$)$_2$ (**12**) at 50, 100, and 200 mV s^{-1}. The forward scan consists of an oxidation peak with $E_p^2 = 0.81$ V versus ferrocene, with a shoulder to the lower potential side at E_p^1. The relative heights of the shoulder and peak suggest two overlapping one-electron oxidation processes. The reverse peak cannot be resolved into separate peaks. Peak positions are independent of scan rate over a range 10−500 mV s^{-1}. The electrochemical response is stable with repeated cycling and no additional features associated with the monomeric species appear, indicating the complex is stable to oxidation within this potential range.

The presence of overlapping oxidation peaks is indicative of a multistep charge transfer reaction with a degree of interaction between the Ru^{2+} centers[14,15] resulting in oxidation of the second Ru^{2+} center being more difficult than oxidation of the first. Such redox couplings can be due to inductive effects, electron hopping, or delocalization through a bridging ligand, but in this case is most likely to be due to electrostatic repulsion between the metal sites.

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Figure 4 shows CVs for 0.66 mM solutions of $[\{(dppm)_2Ru(S_2CNC_4H_8NCS_2)\}_2Cu](BF_4)_2$(**21**) at scan rates of 50, 100, and 200 mV s^{-1}. A couple is observed centered at 0.15 V (versus ferrocene) followed by an additional couple at $E^{0\prime} = 0.74$ V versus ferrocene that can be attributed to the oxidation and reduction of the two ruthenium centers. The monomeric $[Cu(S_2CNC_4H_8NH_2)_2](BF_4)_2$ complex was found to undergo a reversible one-electron oxidation and reduction at 0.04 V versus ferrocene (see Supporting Information) corresponding to a Cu(II) to Cu(III) oxidation. The 0.15 V couple in Figure 4 is therefore assigned to the Cu(II)/Cu(III) oxidation and reduction. However, in contrast to the electrochemistry for the monomer, the peak separation between the oxidation and reduction peaks increases with increasing scan rate, indicating sluggish electron transfer kinetics between the copper metal center and the electrode. The thermodynamic and kinetic constraints on electron transfer for the copper center within the complex may be attributed to a combination of steric factors (i.e., the bulkiness of the complex and the central position of the copper) and electrostatic considerations (i.e., the close proximity of two positively charged Ru^{2+} centers). The positions of the Ru^{2+} peaks are similar to those in Figure 3, for complex **12**, but there is a single oxidation and reduction peak, and two overlapping peaks cannot be observed at any scan rate. The positions of these peaks are independent of scan rate, and the height of the oxidation peak is between that of a one and two electron transfer indicating that the two Ru^{2+} centers undergo oxidation effectively simultaneously and at a very similar potential. In contrast to complex **12**, there is minimal electrostatic interaction between the centers as they are separated by a larger distance. The copper center appears to have little influence on the electron transfer at the ruthenium centers. Data on copper bis(dithiocarbamates) have been cited as an example of the remarkable ability of the ligand to stabilize unusually high oxidation states, such as Cu(III).[2] The complex is very stable to repeated cycling, and no features corresponding to the monomeric Ru form (complex **9**) are observed indicating that the complex remains stable to dissociation over this potential range.

The electrochemistry of complexes **12** and **21** suggests that reversible oxidation and reduction of metal centers can take place without decomposition or rearrangement of the complex. However, where a metal center undergoes a change in geometry with a change in oxidation state this may not always be the case (see Supporting Information for discussion of complex **20**). In the examples above, the metal centers undergo oxidation relatively independently of each other, with any interaction being purely electrostatic. There is no indication of communication between metal centers facilitating the electron transfer process, which is not unexpected considering the lack of conjugation in the piperazine bis(dithiocarbamate) linker.

Conclusion

The system described here utilizes the properties of a piperazine-based dithiocarbamate (**1**) to construct complex, multimetallic materials in a controlled, stepwise manner. Given the vast range of elements that are known to coordinate dithiocarbamate ligands and the diversity of their geometries, this approach has great potential for supramolecular assemblies incorporating a wide range of metal centers whose properties (e.g., redox, CVD, host−guest chemistry) can be tailored. Our current work is directed toward the functionalization of two- and three-dimensional gold substrates and the use of heterometallic polymeric materials for the deposition of layers via chemical vapor deposition.

Experimental Section

General Procedures. All manipulations were carried out under aerobic conditions using commercially available solvents and reagents as received. Infrared and NMR spectroscopy was carried out at 25 °C using Shimadzu FTIR 8700 (KBr plates with nujol or in CH_2Cl_2 solution) and Bruker AMX-300 (^1H: 299.87 MHz, ^{31}P: 121.39 MHz) or AMX-400 (^1H: 400.14 MHz, ^{31}P: 161.97 MHz) spectrometers respectively. Unless otherwise stated, $CDCl_3$ was used as solvent for all NMR spectra. In ^{31}P NMR spectra of hexafluorophosphate salts, the resonance due to the counteranion was observed in all cases at the same chemical shift and so has been omitted from the data reported below. Solid state CPMAS NMR spectra were obtained on a Varian CMX MSL 200 spectrometer. Infrared spectroscopic features due to the bis(diphenylphosphino)methane ligands have been omitted to aid clarity. FAB-MS spectra (nitrobenzyl alcohol matrices) were measured using a VG 70-SB magnetic sector mass spectrometer or obtained from the EPSRC National Mass Spectrometry Service Centre, University of Wales Swansea. Elemental analyses were performed at University College London. The complexes *cis*-$[RuCl_2(dppm)_2]$,[9] $[Os(CH{=}CHC_6H_4CH_3\text{-}4)Cl(CO)(BTD)(PPh_3)_2]$,[16] $[Pd(C,N\text{-}C_6H_4CH_2NMe_2)Cl]_2$,[17] *cis*-$[PtCl_2(PEt_3)_2]$,[18] and $[NiCl_2(dppp)]$[19] were prepared according to published procedures. All other materials were obtained commercially. The electrochemical behavior of selected dithiocarbamate complexes was investigated using cyclic voltammetry in dichloromethane (DCM) with 0.1 M tetrabutylammonium perchlorate ($TBAClO_4$) as the background electrolyte. Measurements were taken with a PSTAT 10 potentiostat (Autolab, Ecochemie) and a three electrode cell comprising a platinum disk working electrode (area = 0.03141 cm^2), a platinum wire coil counter electrode, and a silver wire quasi-reference electrode. All potentials are reported with respect to the reversible ferrocene/ferrocenium couple at 0.57 V versus Ag. CVs were carried at different scan rates, ν of 10−500 mV s^{-1}.

Synthesis of $[S_2CNC_4H_8NH_2]$ (1). Piperazine (2000 mg, 0.023 mol) was dissolved in water (30 mL) and carbon disulfide (1760 mg, 0.023 mol) was added with stirring causing precipitation of a pale green product after 20 min. This was filtered and washed with water (5 mL) and dried under vacuum. Yield: 3620 mg (97%). IR (KBr/nujol): 1601, 1580, 1265, 1227, 1207, 1134, 1119, 1015, 966, 897 cm^{-1}. ^1H NMR (D_2O): 2.88 (m, $H_2CNH_2CH_2$, 4H), 4.30 (s, NH_2, 2H), 4.31 (m, $H_2CN(CS_2)CH_2$, 4H) ppm. MS (EI) *m*/*z* (abundance %) = 162 (49) $[M]^+$. Analysis: Calcd for $C_5H_{10}N_2S_2$: C, 37.0; H, 6.2; N, 17.3%. Found: C, 37.4; H, 6.5; N, 17.5%.

Synthesis of $[S_2CNC_4H_6(Me_2\text{-}3,5)NH_2]$ (2). Method as for compound **1** but using 2,6-dimethylpiperazine (500 mg, 4.38 mmol)

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and carbon disulfide (334 mg, 4.39 mmol) to yield 430 mg (52%). IR (KBr disk): 1549, 1450, 1394, 1367, 1285, 1232, 1178, 1146, 1097, 1045, 989, 947 cm^{-1}. ^{1}H NMR (D_2O): 1.07 (d, 2 × CH_3, J_{HH} = 6.5 Hz, 6H], 2.76 (t, CH_{ax}, 2H, J_{HH} = 12.3 Hz), 3.00 (m, CH_{ax}, 2H), 5.57 (d, CH_{eq}, 2H, J_{HH} = 14.1 Hz) ppm. MS (EI) *m/z* (abundance %) = 190 (100) [M]$^+$. Analysis: Calcd for $C_7H_{14}N_2S_2$: C, 44.2; H, 7.4; N, 14.7%. Found: C, 44.0; H, 7.3; N, 14.7%.

Synthesis of [$S_2CNC_5H_{10}$][$H_2NC_5H_{10}$] (3). Piperidine (1000 mg, 0.012 mol) was dissolved in water (15 mL), and carbon disulfide (900 mg, 0.012 mmol) was added. The reaction was stirred for 2 h. Chloroform (50 mL) was added and, after vigorous stirring, the aqueous layer discarded. Reduction in solvent volume led to precipitation of an off-white product. This was dried under vacuum. Yield: 910 mg (62%). IR (KBr/nujol): 1277, 1240, 1219, 1157, 1124, 1022, 1001 *ν*.$_{CS}$), 972, 949, 883, 866, 853 cm^{-1}. ^{1}H NMR: 1.56 (m, ($S_2CNC_5H_{10}$)H^{3-5} + ($H_2NC_5H_{10}$)H,$^{3-5}$ 12H), 3.26 (t, ($H_2NC_5H_{10}$)H,^{2,6} 4H, J_{HH} = 5.66 Hz), 4.32 (t, ($S_2CNC_5H_{10}$)H,^{2,6} 4H, J_{HH} = 4.97 Hz), 8.89 (s(br), NH_2, 2H) ppm. ^{13}C NMR: 208.5 (s, CS_2), 51.9 (s, ($S_2CNC_5H_{10}$)$C^{2,6}$), 45.0 (s, ($H_2NC_5H_{10}$)$C^{2,6}$), 22.7, 26.1 (s × 2, ($S_2CNC_5H_{10}$)$C^{3,5}$ + ($H_2NC_5H_{10}$)$C^{3,5}$), 22.5, 24.4 (s × 2, ($S_2CNC_5H_{10}$)C^4 + ($H_2NC_5H_{10}$)C^4) ppm. MS (CI -ve) *m/z* (abundance %) = 160 (100) [$S_2CNC_5H_{10}$]$^-$. (FAB) *m/z* (abundance %) = 247 (8) [$S_2CNC_5H_{10}$][$H_2NC_5H_{10}$]. Analysis: Calcd for $C_{11}H_{22}N_2S_2$: C, 53.6; H, 9.0; N, 11.4%. Found: C, 53.4; H, 9.1; N, 11.2%.

Synthesis of [$S_2CNC_4H_8NHMe$] (4). A suspension of 1-methylpiperazine (1000 mg, 9.98 mmol) and KOH (560 mg, 9.98 mmol) was stirred in methanol (60 mL) for 30 min. Carbon disulfide (760 mg, 9.98 mmol) was added dropwise to give a yellow solution. The reaction was stirred for 24 h, and the yellow precipitate filtered and washed with water (50 mL) and methanol (50 mL) and dried. Yield: 500 mg (28%). IR (KBr disk): 1555, 1470, 1413, 1367, 1356, 1307, 1263, 1188, 1139, 1093, 1070, 1029, 970, 912 cm^{-1}. ^{1}H NMR: insufficiently soluble. ^{13}C CPMAS NMR: 215.4 (s, CS_2), 55.8, 54.1 (s × 2, NCH_2, probably due to presence of two crystallographically independent molecules in unit cell), 47.4 (s, NCH_2), 41.3 (s, CH_3) ppm. MS (ES -ve): 175 [M − H]$^+$. Analysis: Calcd for $C_6H_{12}N_2S_2$: C, 40.9; H, 6.9; N, 15.9%. Found: C, 40.8; H, 7.0; N, 15.7%.

Synthesis of [$S_2CNC_4H_8NHEt$] (5). As for **3** but using 1-ethylpiperazine (1000 mg, 8.76 mol), KOH (500 mg, 8.91 mmol) and carbon disulfide (670 mg, 8.80 mmol) to yield 530 mg of colorless product (32%). IR (KBr disk): 1445, 1375, 1313, 1263, 1205, 1182, 1139, 1122, 1085, 1029, 984, 918 cm^{-1}. ^{1}H NMR: insufficiently soluble. ^{13}C CPMAS NMR: 215.3 (s, CS_2), 54.1, 51.0, 47.4 (s × 3, NCH_2 + CH_2Me), 11.7 (s, CH_3) ppm. MS (ES -ve): 189 [M − H]$^+$. Analysis: Calcd for $C_7H_{14}N_2S_2$: C, 44.2; H, 7.4; N, 14.7%. Found: C, 44.0; H, 7.6; N, 14.5%.

Synthesis of [Ru($S_2CNC_5H_{10}$)(dppm)$_2$]BF_4 (6). *cis*-[$RuCl_2$(dppm)$_2$] (100 mg, 0.106 mmol) and [$S_2CNC_5H_{10}$][$H_2NC_5H_{10}$] (39 mg, 0.158 mmol) were suspended in a mixture of dichloromethane (10 mL) and ethanol (10 mL) and an aqueous solution (5 mL) of $NaBF_4$ (23 mg, 0.210 mmol) added. The reaction was stirred for 1 h and then all solvent was removed. The residue was taken up in a minimum volume of dichloromethane and filtered through diatomaceous earth. Ethanol (20 mL) was added, and the solvent volume reduced until precipitation was complete. The pale yellow product was filtered and washed with water (5 mL), ethanol (10 mL), and hexane (10 mL). Yield: 102 mg (86%). IR (KBr/nujol): 1321, 1246, 1192, 1057 (ν_{BF}), 999 (ν_{CS}) cm^{-1}. ^{31}P NMR: −17.8, −4.2 (t × 2, dppm, J_{PP} = 34.0 Hz) ppm. ^{1}H NMR: 1.46, 3.58 (m × 2, NC_5H_{10}, 10H), 4.61, 4.95 (m × 2, PCH_2P, 2 × 2H), 6.52, 6.93, 7.01, 7.16, 7.34, 7.61 (m × 6, PC_6H_5, 40H) ppm. MS (FAB) *m/z* (abundance %) = 1031 (100) [M]$^+$. Analysis: Calcd for $C_{56}H_{54}BF_4NP_4RuS_2$: C, 60.2; H, 4.9; N, 1.3%. Found: C, 60.3; H, 5.0; N, 1.4%.

Synthesis of [Ru($S_2CNC_4H_8NMe$)(dppm)$_2$]BF_4 (7). 1-Methylpiperazine (15 mg, 0.150 mmol) and KOH (8.5 mg, 0.152 mmol) were stirred in methanol (60 mL) for 30 min, and then CS_2 (11.5 mg, 0.151 mmol) was added to form $S_2CNC_4H_8NMe$ in situ. A dichloromethane solution (20 mL) of *cis*-[$RuCl_2$(dppm)$_2$] (100 mg, 0.106 mmol) was added along with an aqueous solution (5 mL) of $NaBF_4$ (35 mg, 0.318 mmol) added. The reaction was stirred for 30 min. Reduction of solvent volume under reduced pressure yielded a gray-white product, which was filtered and washed with water (5 mL), ethanol (10 mL), and hexane (10 mL). Yield: 110 mg (92%). IR (KBr/nujol): 1290, 1242, 1057 (ν_{BF}), 999 (ν_{CS}) cm^{-1}. ^{31}P NMR: −17.5, −3.9 (t × 2, dppm, J_{PP} = 34.5 Hz) ppm. ^{1}H NMR: 2.54 (s, CH_3, 3H), 2.59, 2.67, 3.62, 3.72 (m × 4, NC_4H_8N, 4 × 2H), 4.58, 5.01 (m × 2, PCH_2P, 2 × 2H), 6.51, 6.92, 7.00, 7.16, 7.29, 7.58 (m × 6, C_6H_5, 40H). MS (FAB) *m/z* (abundance %) = 1045 (48) [M]$^+$. Analysis: Calcd for $C_{56}H_{55}BF_4N_2P_4RuS_2 \cdot 0.5CH_2Cl_2$: C, 57.8; H, 4.8; N, 2.4%. Found: C, 57.9; H, 4.8; N, 2.2%.

Synthesis of [Ru($S_2CNC_4H_8NEt$)(dppm)$_2$]BF_4 (8). Prepared by the same procedure as for **7** using 1-ethylpiperazine (17 mg, 0.149 mmol), KOH (8.5 mg, 0.152 mmol), CS_2 (11.5 mg, 0.151 mmol), and *cis*-[$RuCl_2$(dppm)$_2$] (100 mg, 0.106 mmol) with an excess of $NaBF_4$ (35 mg, 0.318 mmol) to yield 110 mg (91%) of a gray-white product. IR (KBr/nujol): 1238, 1057 (ν_{BF}), 999 (ν_{CS}) cm^{-1}. ^{31}P NMR: −17.7, −4.0 (t × 2, dppm, J_{PP} = 34.5 Hz) ppm. ^{1}H NMR: 1.11 (t, $CH_2C\underline{H}_3$, 3H, J_{HH} = 7.2 Hz), 2.33, 2.40 (m × 2, NC_4H_8N, 2 × 2H), 2.47 (q, $C\underline{H}_2CH_3$, 2H, J_{HH} = 7.2 Hz), 3.58, 3.67 (m × 2, NC_4H_8N, 2 × 2H), 4.61, 4.99 (m × 2, PCH_2P, 2 × 2H), 6.53, 6.92, 6.99, 7.15, 7.32, 7.61 (m × 6, C_6H_5, 40H). MS (FAB) *m/z* (abundance %) = 1059 (100) [M]$^+$. Analysis: Calcd for $C_{57}H_{57}BF_4N_2P_4RuS_2 \cdot 0.5CH_2Cl_2$: C, 58.1; H, 4.9; N, 2.4%. Found: C, 58.2; H, 5.0; N, 2.4%.

Synthesis of [Ru($S_2CNC_4H_8NH_2$)(dppm)$_2$](BF_4)$_2$ (9). The zwitterion $S_2CNC_4H_8NH_2$ (155 mg, 0.955 mmol) and $NaBF_4$ (210 mg, 1.913 mmol) were suspended in methanol (20 mL), and *cis*-[$RuCl_2$(dppm)$_2$] (600 mg, 0.638 mmol) was added as a dichloromethane (10 mL) solution. The reaction was heated to reflux for 10 min and then stirred for 2 h. All solvent was removed, and the residue was taken up in a minimum amount of dichloromethane and filtered through diatomaceous earth. Addition of ethanol (30 mL) and reduction of solvent volume by rotary evaporation yielded the colorless product (565 mg, 73%). IR (KBr/nujol): 1312, 1269, 1236, 1190, 1161, 1057 (ν_{BF}), 999 (ν_{CS}), 849 cm^{-1}. ^{31}P NMR: −3.8, −17.3 (t × 2, dppm, J_{PP} = 34.4 Hz) ppm. ^{1}H NMR: (NH_2, 2H, not observed), 3.04, 3.88 (m × 2, NC_4H_8N, 2 × 4H), 4.53, 4.91 (m × 2, PCH_2P, 2 × 2H), 6.48−7.57 (m × 6, C_6H_5, 40H) ppm. MS (FAB) *m/z* (abundance %) = 1030 (100) [M]$^+$, 870 (1) [M − $S_2CNC_4H_8NH_2$]$^+$, 646 (8) [M − dppm]$^+$. Analysis: Calcd for $C_{55}H_{54}B_2F_8N_2P_4RuS_2$: C, 54.8; H, 4.5; N, 2.3%. Found: C, 54.6; H, 4.5; N, 2.5%

Synthesis of [Ru($S_2CNC_4H_6$(Me_2-3,5)NH_2)(dppm)$_2$](BF_4)$_2$ (10). As for **9** but using $S_2CNC_4H_6$(Me_2-2,6)NH_2 (**2**, 30 mg, 0.158 mmol), $NaBF_4$ (35 mg, 0.319 mmol), and *cis*-[$RuCl_2$(dppm)$_2$] (100 mg, 0.106 mmol) to provide a pale yellow product (90 mg, 69%). IR (KBr/nujol): 1319, 1242, 1190, 1059 (ν_{BF}), 999 (ν_{CS}) cm^{-1}. ^{31}P NMR: −17.9, −3.9 (m × 2, dppm) ppm. ^{1}H NMR: 1.14 (t, 2 × CH_3, 6H, J_{HH} = 6.3 Hz), 1.97 (s(br), NH_2, 2H), 2.25, 2.45 (t × 2, CH_{ax}, 2 × 1H, J_{HH} = 11.6 Hz), 2.58, 2.78 (m × 2, CHMe, 2 × 1H), 4.38 (t(br), CH_{eq}, 2H, J_{HH} = 14.5 Hz), 4.60, 4.96 (m × 2, PCH_2P, 2 × 2H), 6.53−7.61 (m, C_6H_5, 40H) ppm. MS (FAB) *m/z* (abundance %) = 1059 (100) $[M]^+$. Analysis: Calcd for $C_{57}H_{58}B_2F_8N_2P_4RuS_2$: C, 55.5; H, 4.7; N, 2.3%. Found: C, 55.6; H, 4.8; N, 2.2%.

Synthesis of $[Ru(S_2CNC_4H_8NCS_2)(dppm)_2]$ (11). $[Ru(S_2CNC_4H_8NH_2)(dppm)_2](BF_4)_2$ (**9**; 100 mg, 0.083 mmol) was dissolved in dichloromethane (20 mL) and triethylamine (3 drops, excess) and carbon disulfide (7 mg, 0.092 mmol) added. The reaction was stirred for 1 h. Ethanol (30 mL) was added, and the solvent volume concentrated under reduced pressure until precipitation of the pale yellow solid was complete. The product was washed with water (15 mL) and ethanol (30 mL) and dried. The product can be further purified by crystallization from chloroform-ethanol mixtures. Yield: 74 mg (86%). IR (KBr/nujol): 1279, 1217, 1050, 1030, 997 (ν_{CS}), 920 cm^{-1}. ^{31}P NMR: −18.9, −5.2 (t × 2, dppm, J_{PP} = 34.3 Hz) ppm. ^1H NMR: 2.74, 3.58 (m × 2, NC_4H_8N, 2 × 4 H), 4.50, 4.85 (m × 2, PCH_2P, 2 × 2 H), 6.45, 6.85, 6.94, 7.23, 7.29, 7.52 (m × 6, C_6H_5, 40 H) ppm. MS (ES) *m/z* (abundance %) = 1031 (28) $[M - CS_2]^+$, 647 (10) $[M - dppm - CS_2]^+$. Analysis: Calcd for $C_{56}H_{52}N_2P_4RuS_2 \cdot 2CHCl_3$: C, 51.8; H, 4.1; N, 2.1%. Found: C, 51.4; H, 4.1; N, 1.7%.

Synthesis of $[\{Ru(dppm)_2\}_2(S_2CNC_4H_8NCS_2)][BF_4]_2$ (12). (a) A solution of HNC_4H_8NH (9 mg, 0.105 mmol) in methanol (10 mL) was treated with triethylamine (5 drops, excess) and stirred for 10 min. Carbon disulfide (3 drops, excess) was then added and stirring continued for a further 10 min. A dichloromethane solution (10 mL) of *cis*-$[RuCl_2(dppm)_2]$ (200 mg, 0.213 mmol) was added followed by a solution of $NaBF_4$ (47 g, 0.428 mmol) in water (1 mL) and methanol (5 mL). The reaction was stirred for 1 h and then all solvent removed. The residue was taken up in a minimum volume of dichloromethane and filtered through diatomaceous earth. Diethyl ether (30 mL) was added to precipitate the pale yellow product. This was filtered and washed with water (5 mL), diethylether (10 mL), and hexane (10 mL). Yield: 163 mg (72%). (b) $[Ru(S_2CNC_4H_8NH_2)(dppm)_2](BF_4)_2$ (**9**, 50 mg, 0.042 mmol) was dissolved in dichloromethane (10 mL) and methanol (5 mL) and triethylamine (3 drops, excess) added. The reaction was stirred for 10 min and then carbon disulfide (2 drops, excess) added. A dichloromethane solution (10 mL) of *cis*-$[RuCl_2(dppm)_2]$ (39 mg, 0.042 mmol) was added followed by a solution of $NaBF_4$ (9 mg, 0.082 mmol) in water (1 mL) and methanol (5 mL). Stirring was continued for 1 h after which all solvent was removed. The residue was taken up in a minimum volume of dichloromethane and filtered through diatomaceous earth. Diethyl ether (30 mL) was added to precipitate the pale yellow product. This was filtered and washed with water (5 mL), diethylether (10 mL), and hexane (10 mL). Yield: 69 mg (76%). IR (KBr/nujol): 1310, 1278, 1219, 1057 (ν_{BF}), 997 (ν_{CS}) cm^{-1}. ^{31}P NMR: −16.8, −4.1 (t × 2, dppm, J_{PP} = 34.2 Hz) ppm. ^1H NMR: 3.51, 3.62 (d × 2, ax/eq-NC_4H_8N, 4H, J_{HH} = 9.5 Hz), 4.56, 4.91 (m × 2, PCH_2P, 2 × 2H), 6.50, 6.93, 7.03, 7.26, 7.38, 7.63 (m × 6, C_6H_5, 80H) ppm. MS (FAB) *m/z* (abundance %) = 2063 (22) $[M + BF_4]^+$, 1976 (12) $[M]^+$. Analysis: Calcd for $C_{106}H_{96}B_2F_8N_2P_8Ru_2S_4 \cdot CH_2Cl_2$: C, 57.5; H, 4.4; N, 1.3%. Found: C, 57.3; H, 4.6; N, 1.3%.

Synthesis of $[(dppm)_2Ru(S_2CNC_4H_8NCS_2)Os(CH{=}CHC_6H_4\text{-}Me\text{-}4)(CO)(PPh_3)_2]BF_4$ (13). $[Ru(S_2CNC_4H_8NH_2)(dppm)_2](BF_4)_2$ (**9**, 100 mg, 0.083 mmol) was dissolved in dichloromethane (10 mL) and treated with NEt_3 (5 drops, excess) and stirred for 5 min. Carbon disulfide (3 drops, excess) was added, and the reaction stirred for 5 min to generate $[Ru(S_2CNC_4H_8NCS_2)(dppm)_2]$ in situ. $[Os(CH{=}CHC_6H_4Me\text{-}4)Cl(CO)(BTD)(PPh_3)_2]$ (86 mg, 0.083 mmol) was added as a dichloromethane solution (10 mL), and the reaction was stirred for 1 h. All solvent was removed, and the residue was taken up in a minimum amount of dichloromethane and filtered through diatomaceous earth. Addition of ethanol (30 mL) and reduction of solvent volume by rotary evaporation yielded the product as a pale orange powder, which was washed with ethanol (10 mL) and hexane (10 mL). Yield: 121 mg (71%). IR (KBr/nujol): 1898 (ν_{CO}), 1614, 1310, 1217, 1188, 1057 (ν_{BF}), 918, 847 cm^{-1}. ^{31}P NMR: −17.1, −4.4 (t × 2, dppm, J_{PP} = 34.4 Hz), 9.3 (s, PPh_3) ppm. ^1H NMR: 2.21 (s, CH_3, 3H), 2.78−3.33 (m(br), NC_4H_8N, 8H), 4.64, 4.97 (m × 2, PCH_2P, 2 × 2H), 5.59 (d, Hβ, 1H, J_{HH} = 17.1 Hz), 6.36, 6.81 ($(AB)_2$, C_6H_4, 4H, J_{AB} = 8.0 Hz), 6.52, 6.93, 6.96, 7.26, 7.61 (m × 5, C_6H_5, 70H), 8.28 (dt, Hα, 1H, J_{HH} = 17.1 Hz, J_{HP} = 2.6 Hz) ppm. MS (FAB) *m/z* (abundance %) = 1967 (38) $[M]^+$, 1705 (30) $[M - PPh_3]^+$, 1588 (28) $[M - \text{vinyl-}PPh_3]^+$. Analysis: Calcd for $C_{102}H_{91}BF_4N_2OOsP_6RuS_4 \cdot CH_2Cl_2$: C, 57.9; H, 4.4; N, 1.3%. Found: C, 57.7; H, 4.5; N, 1.3%.

Synthesis of $[(dppm)_2Ru(S_2CNC_4H_8NCS_2)Pd(C,N{-}C_6H_4CH_2NMe_2)]BF_4$ (14). $[Ru(S_2CNC_4H_8NH_2)(dppm)_2](BF_4)_2$ (**9**, 100 mg, 0.083 mmol) was dissolved in dichloromethane (10 mL) and treated with NEt_3 (5 drops, excess) and stirred for 5 min. Carbon disulfide (3 drops, excess) was added, and the reaction stirred for 5 min. $[PdCl(C,N\text{-}C_6H_4CH_2NMe_2)]_2$ (23 mg, 0.042 mmol) was added as a solution in dichloromethane (5 mL), and the reaction was stirred for 1 h. All solvent was removed, and the residue was taken up in a minimum amount of dichloromethane and filtered through diatomaceous earth. The crude product was redissolved in dichloromethane (5 mL), and diethylether (30 mL) added to precipitate the colorless product. This was washed with diethylether (10 mL) and dried. Yield: 106 mg (89%). IR (KBr/nujol): 1574, 1308, 1278, 1219, 1157, 1055 (ν_{BF}), 999 (ν_{CS}), 907, 849 cm^{-1}. ^{31}P NMR: −16.9, −4.2 (t × 2, dppm, J_{PP} = 34.2 Hz) ppm. ^1H NMR: 2.92 (s, NCH_3, 6H), 3.71, 3.79 (m × 2, NC_4H_8N, 8H), 4.01 (s, CCH_2, 2H), 4.64, 4.96 (m × 2, PCH_2P, 2 × 2H), 6.53, 6.94, 7.03, 7.17, 7.31, 7.62 (m × 6, 40H + 4H, C_6H_5 + C_6H_4) ppm. MS (FAB) *m/z* (abundance %) = 1346 (12) $[M]^+$. Analysis: Calcd for $C_{65}H_{64}BF_4N_3P_4PdRuS_4$: C, 54.5; H, 4.5; N, 2.9%. Found: C, 54.3; H, 4.9; N, 3.0%.

Synthesis of $[(dppm)_2Ru(S_2CNC_4H_8NCS_2)Pt(PEt_3)_2](BF_4)_2$ (15). $[Ru(S_2CNC_4H_8NH_2)(dppm)_2](BF_4)_2$ (**9**, 84 mg, 0.070 mmol) was dissolved in a mixture of dichloromethane (20 mL) and methanol (20 mL) treated with NEt_3 (3 drops, excess) and stirred for 5 min. Carbon disulfide (3 drops, excess) was added, and the reaction stirred for 5 min. $[PtCl_2(PEt_3)_2]$ (35 mg, 0.070 mmol) was added as a solution in dichloromethane (5 mL) and $[NH_4]BF_4$ (8 mg, 0.076 mmol) as a solution in methanol (10 mL). The reaction was stirred for 16 h. All solvent was removed, and the residue was taken up in a minimum amount of dichloromethane and filtered through diatomaceous earth. Diethylether (30 mL) was added to precipitate the colorless product, which was washed with diethylether (10 mL) and dried. Yield: 83 mg (69%). IR (KBr/nujol): 1309, 1280, 1225, 1056 (ν_{BF}), 999 (ν_{CS}) cm^{-1}. ^{31}P NMR: −17.9, −5.4 (t × 2, dppm, J_{PP} = 34.6 Hz), 5.7 (s, PEt_3, J_{PtP} = 3116.5 Hz) ppm. ^1H NMR: 1.10 (dt, $PCCH_3$, 18 H, J_{HP} = 17.3, J_{HH} = 7.0), 1.90 (m, PCH_2, 12 H), 3.78 (m(br), NC_4H_8N, 8 H), 4.49, 4.84 (m × 2, PCH_2P, 2 × 2 H), 6.42, 6.86, 6.97, 7.12, 7.25, 7.54 (m × 6, C_6H_5, 40 H) ppm. MS (FAB) *m/z* (abundance %) = 1624 (100) $[M + BF_4]^+$, 1536 (9) $[M]^+$. Analysis: Calcd for $C_{68}H_{82}B_2F_8N_2P_6PtRuS_4$: C, 47.7; H, 4.8; N, 1.3%. Found: C, 47.9; H, 4.7; N, 1.4%.

Synthesis of $[Ni(S_2CNC_4H_8NH_2)(dppp)](BF_4)_2$ (16). $[NiCl_2(dppp)]$ (100 mg, 0.185 mmol) and $S_2CNC_4H_8NH_2$ (**1**, 45 mg, 0.277 mmol) were suspended in a mixture of dichloromethane (10 mL) and methanol (10 mL) and an aqueous solution (5 mL) of $NaBF_4$ (41 g, 0.373 mmol) was added. The reaction was stirred for 2 h, and then all solvent was removed. The residue was taken up in a minimum amount of dichloromethane and filtered through diatomaceous earth. The crude product was redissolved in dichloromethane (5 mL), and diethylether (30 mL) added to precipitate the orange product. This was washed with diethylether (10 mL) and dried. Yield: 105 mg (70%). The complex can be recrystallized from chloroform and diethyl ether. IR (KBr/nujol): 1312, 1267, 1240, 1055 (ν_{BF}), 999 (ν_{CS}), 916, 831 cm^{-1}. ^{31}P NMR: 13.8 (s, dppp) ppm. ^{1}H NMR: 2.15, 2.60, 2.71, 3.02, 3.79 (m(br) × 5, $P(CH_2)_3P + NC_4H_8NH_2$, 16H), 7.39−7.62 (m, PC_6H_5, 20H) ppm. MS (FAB) *m/z* (abundance %) = 631 (30) [M]$^+$. Analysis: Calcd for $C_{32}H_{36}B_2F_8N_2NiP_2S_2\cdot CHCl_3$: C, 42.8; H, 4.0; N, 3.0%. Found: C, 43.0; H, 4.1; N, 3.2%.

Synthesis of [(dppm)$_2$Ru(S$_2$CNC$_4$H$_8$NCS$_2$)Ni(dppp)](BF$_4$)$_2$ (17). (a) $[Ru(S_2CNC_4H_8NH_2)(dppm)_2](BF_4)_2$ (**9**, 100 mg, 0.083 mmol) was dissolved in dichloromethane (10 mL) and treated with NEt_3 (5 drops, excess) and stirred for 5 min. Carbon disulfide (3 drops, excess) was added and the reaction stirred for 5 min. $[NiCl_2(dppp)]$ (45 mg, 0.083 mmol) was added as a solution in dichloromethane (5 mL), and the reaction was stirred for 1 h. All solvent was removed, and the residue was taken up in a minimum amount of dichloromethane and filtered through diatomaceous earth. The crude product was redissolved in dichloromethane (5 mL), and diethylether (30 mL) added to precipitate the brown product. This was washed with diethylether (10 mL) and dried. Yield: 84 mg (58%). **b)** $[Ni(S_2CNC_4H_8NH_2)(dppp)][BF_4]_2$ (**17**, 30 mg, 0.037 mmol) was dissolved in dichloromethane (10 mL) and treated with NEt_3 (3 drops, excess) and stirred for 5 min. Carbon disulfide (2 drops, excess) was added, and the reaction stirred for 5 min. *cis*-$[RuCl_2(dppm)_2]$ (35 mg, 0.037 mmol) was added as a solution in dichloromethane (5 mL), and the reaction was stirred for 1 h. All solvent was removed, and the residue was taken up in a minimum amount of dichloromethane and filtered through diatomaceous earth. The crude product was redissolved in dichloromethane (5 mL), and diethylether (30 mL) added to precipitate the brown product. This was washed with diethylether (10 mL) and dried. Yield: 38 mg (59%). IR (KBr/nujol): 1312, 1279, 1229, 1053 (ν_{BF}), 997 (ν_{CS}), 837 cm^{-1}. ^{31}P NMR: −16.8, −4.1 (t × 2, dppm, J_{PP} = 34.9 Hz), 13.7 (s, dppp) ppm. ^{1}H NMR: 1.8−2.6 (m, $(CH_2)_3$, 6H), 3.47, 3.65 (m × 2, NC_4H_8N, 8H), 4.51, 4.90 (m × 2, PCH_2P, 2 × 2H), 6.46, 6.91, 6.99, 7.26, 7.39, 7.59 (m × 6, 60H, C_6H_5) ppm. MS (FAB) *m/z* (abundance %) = 1576 (1) [M]$^+$, 1031 (2) [M − Ni(dppp) − CS_2]$^+$. Analysis: Calcd for $C_{83}H_{78}B_2F_8N_2NiP_6RuS_4$: C, 56.9; H, 4.5; N, 1.6%. Found: C, 57.1; H, 4.7; N, 1.5%.

Synthesis of [CpCo(S$_2$CNC$_4$H$_8$NH$_2$)(PPh$_3$)](PF$_6$)$_2$ (18). $[CoCpI_2(CO)]$ (500 mg, 1.232 mmol) was dissolved in acetone (20 mL) to which the zwitterion $S_2CNC_4H_8NH_2$ (219 mg, 1.350 mmol) was added as a solution in a mixture of acetone (20 mL) and methanol (20 mL). NH_4PF_6 (600 mg, 3.681 mmol) was added as a solution in methanol (15 mL). The reaction was stirred for 2 h. All solvent was removed, and the residue was suspended in ethanol (60 mL) and triphenylphosphine (355 mg, 1.354 mmol) added. The reaction was heated to reflux for 2 h, after which all solvent was removed and the residue taken up in a minimum amount of dichloromethane and filtered through diatomaceous earth. The crude product was redissolved in dichloromethane (10 mL), and diethylether (40 mL) added to precipitate the purple product. This was washed with diethylether (10 mL) and dried. Yield: 626 mg (61%). IR (KBr/nujol): 1309, 1260, 1145, 1093, 1015, 999 (υ_{C-S}), 839 (υ_{P-F}), 751, 695 cm^{-1}. ^{31}P NMR (CD_2Cl_2): 44.8 (s, PPh_3) ppm. ^{1}H NMR (CD_2Cl_2): 2.71, 2.87, 3.24, 3.64 (m × 4, NC_4H_8N, 4 × 2H), 5.33 (s, C_5H_5, 5H), 7.49−7.64 (m, C_6H_5, 15H) ppm. MS (ES) *m/z* (abundance %): 548 (100) [M]$^+$, 285 (35) [M − PPh_3]$^+$. Analysis: Calcd for $C_{28}H_{30}CoF_{12}N_2P_3S_2$: C, 40.1; H, 3.6; N, 3.3%. Found: C, 40.2; H, 3.5; N, 3.4%.

Synthesis of [(Ph$_3$P)CpCo(S$_2$CNC$_4$H$_8$NCS$_2$)Ru(dppm)$_2$](PF$_6$)$_2$ (19). $[Co(Cp)(S_2CNC_4H_8NH_2)(PPh_3)](PF_6)_2$ (**18**, 40 mg, 0.048 mmol) was dissolved in a mixture of dichloromethane (20 mL) and methanol (20 mL), treated with NEt_3 (3 drops, excess), and stirred for 5 min. Carbon disulfide (3 drops, excess) was added, and the reaction stirred for 5 min. *cis*-$[RuCl_2(dppm)_2]$ (45 mg, 0.048 mmol) was added as a solution in dichloromethane (5 mL). The reaction was stirred for 5 h. All solvent was removed, and the residue was taken up in a minimum amount of dichloromethane and filtered through diatomaceous earth. Ethanol (30 mL) was added, and the purple product precipitated under reduced pressure. This was washed with ethanol (10 mL), hexane (10 mL) and dried. Yield: 81 mg (96%). IR (KBr/nujol): 1307, 1278, 1223, 1093, 999 (υ_{CS}), 839 (υ_{P-F}), 723, 695 cm^{-1}. ^{31}P NMR: −17.7, −5.4 (m × 2, dppm), 45.7 (s, PPh_3) ppm. ^{1}H NMR: 2.95−3.84 (m (br), NC_4H_8N, 8H), 4.53, 4.94 (m × 2, PCH_2P, 2 × 2H), 5.40 (s, C_5H_5, 5H), 6.43−7.64 (m, C_6H_5, 55H) ppm. MS (FAB) *m/z* (abundance %): 1639 (1) [M + PF_6]$^+$, 1230 (25) [M − PPh_3]$^+$. Analysis: Calculated for $C_{79}H_{72}CoF_{12}N_2P_7RuS_4$: C, 53.2; H, 4.1; N, 1.6%. Found: C, 53.0; H, 4.2; N, 1.2%.

Synthesis of [{(dppm)$_2$Ru(S$_2$CNC$_4$H$_8$NCS$_2$)}$_2$Ni](BF$_4$)$_2$ (20). $[Ru(S_2CNC_4H_8NH_2)(dppm)_2](BF_4)_2$ (**9**, 100 mg, 0.083 mmol) was dissolved in dichloromethane (15 mL), and methanol (10 mL) added. This solution was treated with NEt_3 (5 drops, excess) and stirred for 5 min. Carbon disulfide (3 drops, excess) was added, and the reaction stirred for a further 5 min. $[Ni(OAc)_2]$ (7.3 mg, 0.041 mmol) was added as a solid, and the reaction was stirred for 1 h. All solvent was removed, and the residue was taken up in a minimum amount of dichloromethane and filtered through diatomaceous earth. The crude product was redissolved in dichloromethane (5 mL), and diethylether (30 mL) added to precipitate the brown product. This was washed with diethylether (10 mL) and dried. Yield: 69 mg (69%). IR (KBr/nujol): 1308, 1279, 1221, 1192, 1057 (ν_{BF}), 999 (ν_{CS}), 910, 849 cm^{-1}. ^{31}P NMR: −16.8, −4.2 (t × 2, dppm, J_{PP} = 34.5 Hz) ppm. ^{1}H NMR: 3.58 (m, NC_4H_8N, 16H), 4.64, 4.98 (m × 2, PCH_2P, 2 × 4H), 6.52, 6.94, 7.03, 7.18, 7.26, 7.38, 7.61 (m × 7, C_6H_5, 80H) ppm. MS (FAB) *m/z* (abundance %) = 2271 (9) [M]$^+$. Analysis: Calcd for $C_{112}H_{104}B_2F_8N_4NiP_8Ru_2S_8$: C, 55.0; H, 4.3; N, 2.3%. Found: C, 55.4; H, 4.2; N, 2.2%.

Synthesis of [{(dppm)$_2$Ru(S$_2$CNC$_4$H$_8$NCS$_2$)}$_2$Cu](BF$_4$)$_2$ (21). $[Ru(S_2CNC_4H_8NH_2)(dppm)_2](BF_4)_2$ (**9**, 100 mg, 0.083 mmol) was dissolved in dichloromethane (10 mL) and methanol (10 mL) added. This solution was treated with NEt_3 (5 drops, excess) and stirred for 5 min. Carbon disulfide (3 drops, excess) was added, and the reaction stirred for a further 5 min. $[Cu(OAc)_2]$ (7.5 mg, 0.041 mmol) was added as a solid, and the reaction was stirred for 1 h. All solvent was removed, and the residue was taken up in a minimum amount of dichloromethane and filtered through diatomaceous earth. Ethanol (30 mL) was added to and the solvent volume concentrated under reduced pressure to precipitate the brown product. This was washed with ethanol (10 mL) and hexane (20 mL) and dried. Yield: 62 mg (62%). IR (KBr/nujol): 1585, 1572, 1310, 1279, 1221, 1157, 1057 (ν_{BF}), 999 (ν_{CS}), 910, 849 cm^{-1}. ^{31}P NMR: −16.8, −4.2 (t × 2, dppm, J_{PP} = 34.3 Hz) ppm. ^{1}H NMR: (NC_4H_8N not observed due to paramagnetic Cu(II)), 4.61, 4.96 (s(br) × 2, PCH_2P, 2 × 4H), 6.52, 6.93, 7.03, 7.32, 7.62 (s(br) × 5, C_6H_5, 80H) ppm. MS (FAB) *m/z* (abundance %) = 2276 (3) [M]$^+$, 1509 (4) [M − $Ru(dppm)_2$]$^+$. Analysis: Calcd for $C_{112}H_{104}B_2CuF_8N_4P_8Ru_2S_8\cdot CH_2Cl_2$: C, 53.6; H, 4.2; N, 2.2%. Found: C, 53.4; H, 4.2; N, 2.2%.

[{(dppm)$_2$Ru(S$_2$CNC$_4$H$_8$NCS$_2$)}$_2$Zn](BF$_4$)$_2$ (22). $[Ru(S_2CNC_4H_8NH_2)(dppm)_2](BF_4)_2$ (**9**, 350 mg, 0.290 mmol) was dissolved in acetonitrile (60 mL), treated with NEt_3 (6 drops, excess), and stirred for 5 min. Carbon disulfide (4 drops, excess) was added, and the reaction stirred for 5 min. $[Zn(OAc)_2]$ (26.6 mg, 0.145 mmol) was added as a solution in warm acetonitrile (20 mL). The reaction was stirred at room temperature for 16 h. All solvent was removed, and the residue was taken up in a minimum amount of acetonitrile. The yellow-green product was precipitated by addition of a saturated aqueous solution of NH_4BF_4. This was collected by filtration, washed with water (10 mL), ethanol (10 mL), and hexane (10 mL), and dried. Yield: 326 mg (92%). IR (KBr/nujol): 1309, 1278, 1254, 1219, 1189, 1096, 1056 ($\upsilon_{\mathrm{B-F}}$), 999 ($\upsilon_{\mathrm{C-S}}$), 912 cm^{-1}. ^{31}P NMR: −18.3, −5.3 (t × 2, dppm, J_{PP} = 34.6 Hz) ppm. ^1H NMR: 3.45−3.99 (m, NC_4H_8N, 16H), 4.55, 4.93 (m × 2, PCH_2P, 2 × 4H), 6.50, 6.90, 7.00, 7.28, 7.60 (m × 5, C_6H_5, 80H) ppm. MS (FAB) *m/z* (abundance %): 2366 (2) $[M + BF_4]^+$, 2278 (2) $[M]^+$. Analysis: Calculated for $C_{112}H_{104}B_2F_8N_4P_8Ru_2S_8Zn$: C, 54.9; H, 4.3; N, 2.3%. Found: C, 55.0; H, 4.2; N, 2.2%.

Synthesis of $[\{(dppm)_2Ru(S_2CNC_4H_8NCS_2)\}_3Co](BF_4)_3$ (23). $[Ru(S_2CNC_4H_8NH_2)(dppm)_2](BF_4)_2$ (**9**, 100 mg, 0.083 mmol) was dissolved in dichloromethane (15 mL) and methanol (10 mL) added. This solution was treated with NEt_3 (5 drops, excess) and stirred for 5 min. Carbon disulfide (3 drops, excess) was added and the reaction stirred for a further 5 min. $Co(acac)_3$ (9.9 mg, 0.028 mmol) was added as a solid and the reaction was stirred for 1 h. All solvent was removed, and the residue was taken up in a minimum amount of dichloromethane and filtered through diatomaceous earth. The crude product was redissolved in dichloromethane (5 mL), and diethylether (30 mL) added to precipitate the green product. This was washed with diethylether (10 mL) and dried. Yield: 72 mg (71%). IR (KBr/nujol): 1310, 1279, 1221, 1159, 1096, 1058 (ν_{BF}), 999 (ν_{CS}), 914 cm^{-1}. ^{31}P NMR: −16.8, −3.9 (t × 2, dppm, J_{PP} = 34.5 Hz) ppm. ^1H NMR: 3.66, 3.79 (m × 2, NC_4H_8N, 24H), 4.52, 4.92 (m × 2, PCH_2P, 2 × 6H), 6.47, 6.95, 7.09, 7.35, 7.64 (m × 5, C_6H_5, 120H) ppm. MS (FAB) *m/z* (abundance %) = 2272 (12) $[M - S_2CNC_4H_8NCS_2Ru(dppm)_2]^+$. Analysis: Calcd for $C_{168}H_{156}B_3CoF_{12}N_6P_{12}Ru_3S_{12}\cdot 2CH_2Cl_2$: C, 53.8; H, 4.5; N, 2.2%. Found: C, 53.6; H, 4.2; N, 2.2%.

Synthesis of $[\{(dppm)_2Ru(S_2CNC_4H_8NCS_2)\}_3La](BF_4)_3$ (24). $[Ru(S_2CNC_4H_8NH_2)(dppm)_2](BF_4)_2$ (**9**, 100 mg, 0.083 mmol) was dissolved in dichloromethane (15 mL) and methanol (10 mL) added. This solution was treated with NEt_3 (5 drops, excess) and stirred for 5 min. Carbon disulfide (3 drops, excess) was added, and the reaction stirred for a further 5 min. $LaCl_3$ (6.8 mg, 0.028 mmol) was added as a solution in water (2 mL), and the reaction was stirred for 1 h. All solvent was removed, and the residue was taken up in a minimum amount of dichloromethane and filtered through diatomaceous earth. The crude product was redissolved in dichloromethane (5 mL) and diethylether (30 mL) added to precipitate the off-white product. This was washed with diethylether (10 mL) and dried. Yield: 59 mg (57%). IR (KBr/nujol): 1310, 1279, 1215, 1155, 1096, 1057 (ν_{BF}), 999 (ν_{CS}), 918 cm^{-1}. ^{31}P NMR: −17.3 (t, dppm, one isomer, J_{PP} = 34.8 Hz), −16.6 (t, dppm, other isomer, J_{PP} = 34.6 Hz), −4.0 (t × 2, dppm, both isomers, J_{PP} = ~ 35 Hz) ppm. ^1H NMR: 3.64, 3.79 (m × 2, NC_4H_8N, 24H), 4.57, 4.93 (m × 2, PCH_2P, 2 × 6H), 6.49, 6.91, 7.03, 7.15, 7.24, 7.35, 7.59 (m × 7, C_6H_5, 120H) ppm. MS (FAB) *m/z* (abundance %) = 2353 (8) $[M - S_2CNC_4H_8NCS_2Ru(dppm)_2]^+$. Analysis: Calcd for $C_{168}H_{156}B_3F_{12}LaN_6P_{12}Ru_3S_{12}$: C, 54.3; H, 4.2; N, 2.3%. Found: C, 53.7; H, 4.4; N, 2.2%.

Crystallography. Crystals of **16a** were grown by slow diffusion of diethylether into a chloroform solution of the complex. A single crystal was mounted on a glass fiber, and all geometric and intensity data were recorded from this sample on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 150 ± 2 K with an Oxford Cryosystems Cryostream N_2 open-flow cooling device.[20] Data reduction and integration were carried out with SAINT+ and absorption corrections applied using the program SADABS.[21] The structure was solved by direct methods with ShelXS[22] and developed using alternating cycles of full-matrix least-squares refinement and difference-Fourier synthesis.

Table 1. Crystal Data for Complex **16a**

	16a$\cdot 0.5(CHCl_3)0.5(CH_2Cl_2)$
chemical formula	$C_{33}H_{36.50}B_{0.75}Cl_{2.75}F_3N_2NiP_2S_2$
Fw	808.51
crystal system	tetragonal
crystal color	orange plate
crystal size (mm)	0.25 × 0.21 × 0.06
space group	$I\bar{4}$
a (Å)	24.5845(13)
b (Å)	24.5845(13)
c (Å)	12.6638(10)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	7654.0(8)
Z	8
D_{calcd} (g/cm^3)	1.405
T (K)	150(2)
μ(Mo Kα) (mm^{-1})	0.932
F(000)	3328
reflections collected	25910
unique reflns (R_{int})	7840 (0.0840)
R_1 ($I > 2\sigma(I)$)	0.0793
wR'_2 (all data)	0.1888

In general, non-hydrogen atoms were refined with anisotropic displacement parameters, the exceptions were the atoms that comprise the disordered piperazine moiety and the half-occupied boron (B1), where low occupancy (together with the diffuse electron density and close proximity of the disordered components for the piperazine), meant that refinement of anisotropic displacement parameters lead to unfeasible thermal ellipsoids. Restraints were also necessary to maintain a reasonable geometry for the piperazine. Hydrogen atoms were placed in calculated positions and their thermal parameters linked to those of the atoms to which they were attached using a riding model. The terminal N−H proton for the disordered piperazine could not be located in the difference map so was positioned based on the structure of the free ligand[23] which refined with appropriate restraints. The structure was modeled as containing one partially occupied BF_4^- ion (50%) with one chloride ion and one BF_4^- ion both located on the improper 4-fold rotation axis. In addition, the structure was found to contain both chloroform and dichloromethane in a 1:1 ratio disordered on the same site such that one CH_2Cl_2 proton appeared to be partially replaced with a chlorine atom. Structure solution and refinement used the SHELXTL PLUS V6.10 program package.[22] See Table 1 for selected crystal data.

Crystallographic data for the structure of complex [**16a**]$(BF_4)_{0.75}(Cl)_{0.25}\cdot 0.5CHCl_3\cdot 0.5CH_2Cl_2$ have been deposited with the Cambridge Crystallographic Data Centre, CCDC 677007. Copies of the data can be obtained free of charge on application to the

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Supporting Information Available: Crystallographic data in CIF file format, additional figures, and further experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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