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Functionalised dithiocarbamate complexes: Complexes based on indoline, indole and substituted piperazine backbones – X-ray crystal structure of $[Ni(S_2CNC_3H_6C_6H_4)_2]$

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ABSTRACT

A range of new nickel, copper and zinc bis(dithiocarbamate) complexes has been prepared from secondary amines with functionalised backbones. These include complexes derived from iso-indoline, tetrahydro-isoindoline, 1,2,3,4-tetrahydroisoquinoline and a number of functionalised piperazines. The crystal structure of $[Ni(S_2CNC_3H_6C_6H_4)_2]$ derived from 1,2,3,4-tetrahydroisoquinoline is reported.

1. Introduction

Dithiocarbamates are versatile ligands which have been shown to bind to all the transition elements supporting a wide range of oxidation states [1]. However, while dithiocarbamate complexes have been known for over a century, with many thousands having been prepared, the vast majority of these contain only simple alkyl substituents such as methyl and ethyl. A developing interest in the area of dithiocarbamate chemistry is the functionalization of the backbone such that new applications and interactions can be developed. This area is still in its early stages but already interesting potential applications have been noted including the functionalization of gold nanoparticles [2–7], the stepwise build-up of multimetallic arrays [5–10], the synthesis of dithiocarbamate-containing supramolecular systems which can be used for anion binding [11–17], the development of technetium radiopharmaceuticals [18–22] and efficient chelators for the treatment of acute cadmium intoxication [23–25].

In this contribution we extend some of our recent work in the area of functionalized dithiocarbamate complexes [26,27] and report the synthesis of some simple homoleptic dithiocarbamate complexes based on iso-indoline, iso-indole and functionalized 1-piperazine backbones. The aim of the work was initially to see if it was possible to prepare such complexes easy and efficiently, and then we hoped to investigate structural characteristics such as hydrogen-bonding, secondary amine coordination and π–π stacking using X-ray crystallography. We herein report that while such complexes are easy and efficiently prepared, the generation of high quality single crystals required for X-ray crystallography is much more of a challenge.

2. Results and discussion

Eight amines were utilised in this study (Chart 1). Tetrahydro-iso-quinoline (**A**) and the substituted piperazines (**E**–**G**) were purchased and used as supplied. Tetrahydro-isoindoline (**B**) [28] and isoindoline (**C**) [29] were prepared from the respective phthalimides upon reduction with $LiAlH_4$ and BH_3·thf respectively, while iso-indole was also prepared from o-xylene dibromide *via* the sulphonamide [30] (Scheme 1). Better yields were obtained by this latter route although the extra step makes it more time-consuming. 1-p-Tolylpiperazine (**D**) [31] was easily prepared as an ammonium salt upon heating bis(2-chloroethyl)amine [32] and p-toluidene in diglyme for 24 h, and diamine (**H**) [33] was similarly prepared from p-phenylenediamine (Scheme 2).

Dithiocarbamate salts of amines **A**–**G** were easily prepared upon slow addition of carbon disulfide to a methanol solution of equimolar amounts of KOH and the respective amine. No attempt was made to isolate or characterise these salts. Rather, addition of

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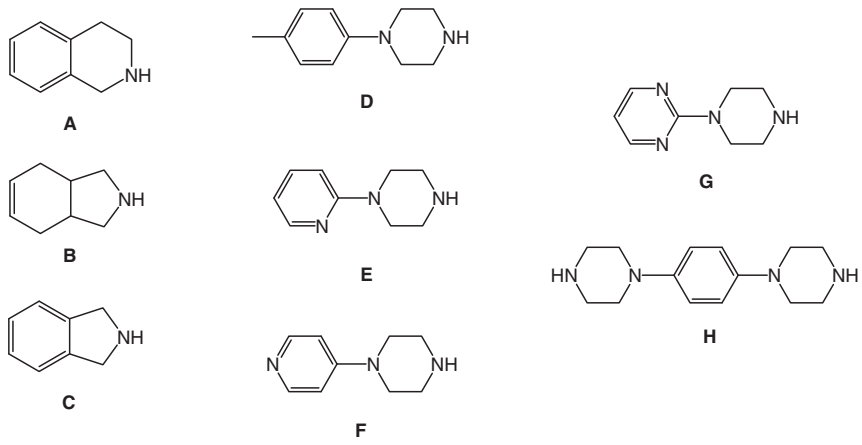
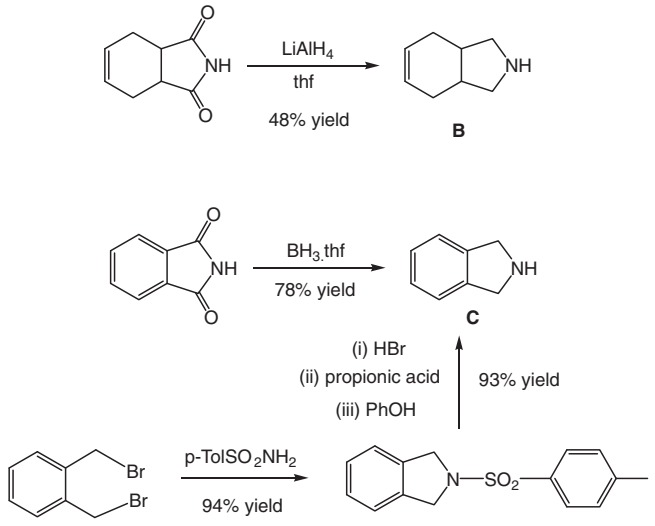


Chart 1.

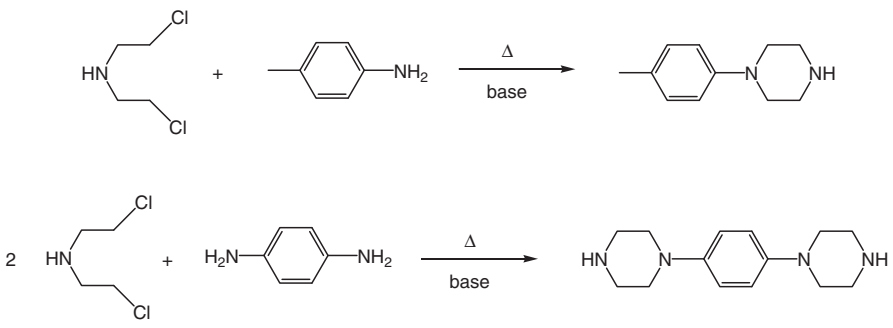


Scheme 1. Synthesis of tetrahydro-iso-indoline and iso-indoline.

the metal(II) acetates (M = Ni, Cu, Zn) resulted in the clean formation of the bis(dithiocarbamate) complexes which were isolated by filtration (Chart 2). Yields were typically between 50–90% and in general isolation and purification were straightforward. All complexes were characterised by IR spectroscopy and the majority gave satisfactory elemental analyses. We had hoped to look at the solid-state structures of many of these complexes in some detail in order to probe packing and intermolecular interactions but the recrystallisation of almost all proved problematic. For many, solubility in common organic solvents was poor. This was especially the case for complexes derived from isoindoline (**3**) and 4-pyridylpiperazine (**7**). This can be an issue with dithiocarbamate salts derived from dimethylamine, but generally as the backbone are extended solubility increases markedly [1]. The poor solubility of the majority of these complexes most likely relates to the very intermolecular interactions we had hoped to probe. A second issue was that many of the samples gave only very thin plates upon recrystallisation and these proved to be unsuitable for X-ray crystallography. We were able to obtain suitably sized single crystals of **1a**, the nickel complex derived from tetrahydro-isoquinoline and the results of this study are summarised in Fig. 1.

The complex is similar to other structurally characterised nickel bis(dithiocarbamate)complexes [1]. The metal atom lies on an inversion centre and is bound by two dithiocarbamate ligands in a square-planar array, the bite-angle of 79.02(5)° being typical. Thirteen atoms lie approximately in a plane and then the molecule folds about the C(2)–C(10) vector. The molecules pack in a herring-bone-type manner (Fig. 2) and there are a series of short intermolecular interactions. Most notable is the π-stacking of the arene components the distance between ring centroids being 3.659 Å with the shortest carbon–carbon contact of 3.350 Å between C(4) and C(6A). Other short intermolecular contacts include; S(1)–H(7A) 2.968 Å, C(7)–H(3A) 2.798 Å, C(1)–H(6A) 2.850 Å and H(2B)–H(2B′) 2.388 Å. While a number of tetrahydro-isoquinoline derived dithiocarbamate complexes have previously been reported [34–37] this is the first to be crystallographically characterised.

The nickel and zinc complexes, when sufficiently soluble in $CDCl_3$ or other commonly available deuterated solvents, were characterised by ^{1}H NMR spectroscopy. The spectrum of **1a** confirmed that the solid-state structure was maintained in solution. Together with a multiplet in the aromatic region there were three signals of equal intensity in the aliphatic region. A singlet at δ 4.86



Scheme 2. Synthesis of functionalised piperazines.

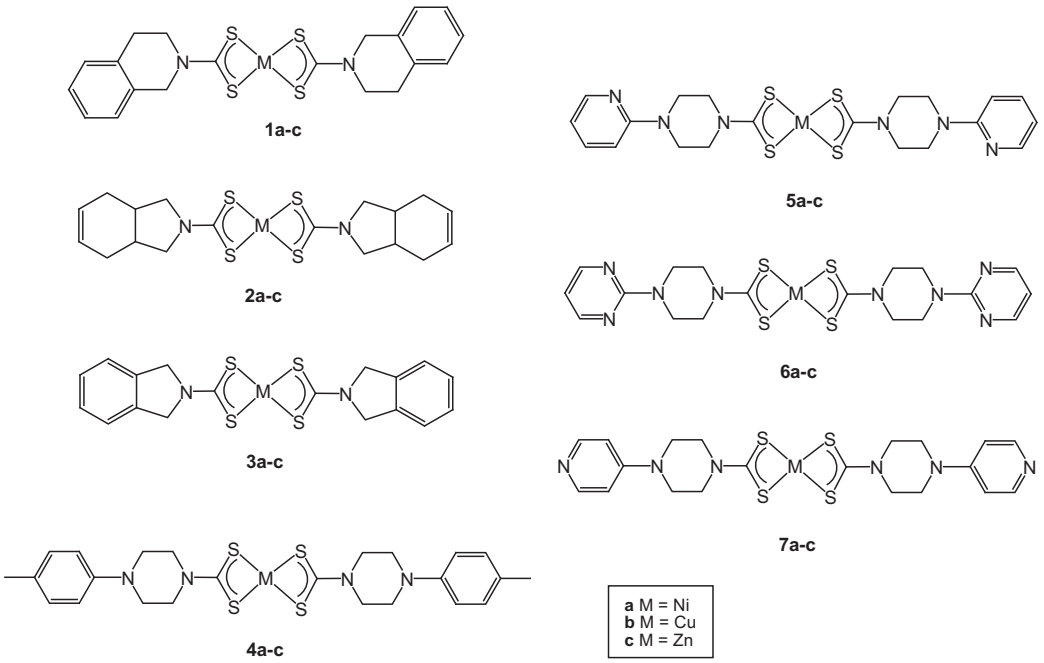


Chart 2.

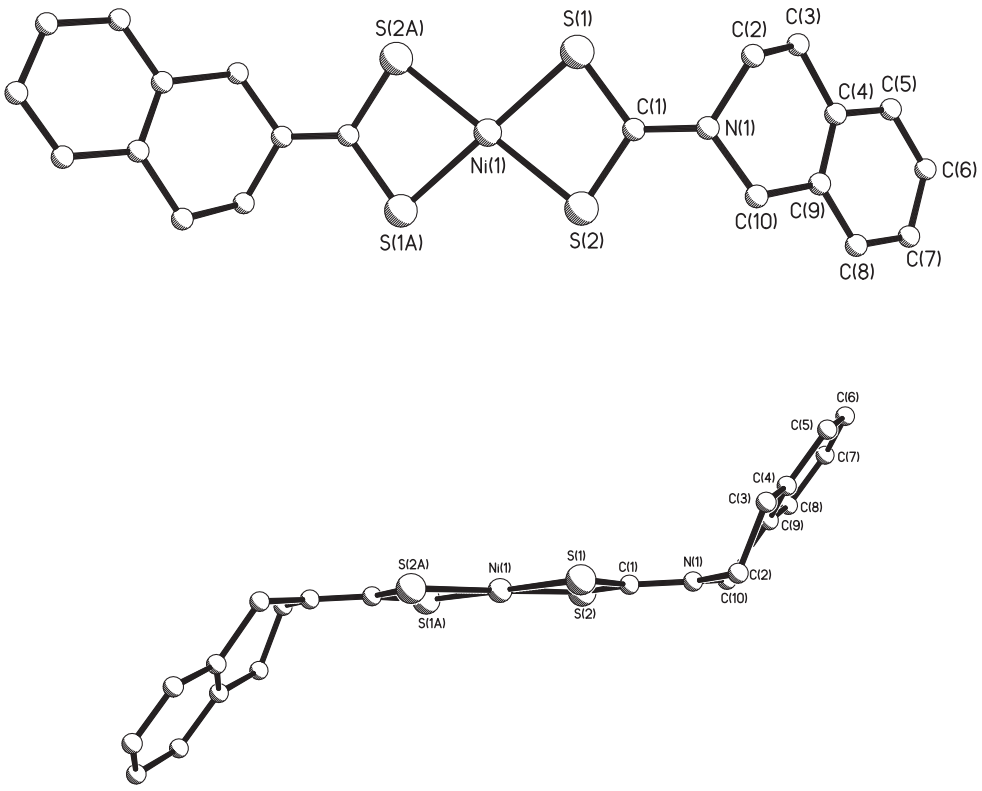


Fig. 1. Two views of the molecular structure of **1a** with selected bond lengths (Å) and angles (°); Ni(1)–S(1) 2.208(1), Ni(1)–S(2) 2.198(1), C(1)–N(1) 1.315(4), S(1)–Ni(1)–S(2) 79.02(5), S(1)–C(1)–S(2) 109.5(2), S(1)–Ni(1)–S(2A) 100.98(5).

is assigned to the nitrogen-bound methylene unit, and triplets at δ 3.96 and 2.95 (J 6.1 Hz) to the ethylene sub-unit; that shifted to lower-field being nitrogen-bound. The nickel tetrahydro-isoindoline complex **2a** was also readily characterised by ^{1}H NMR spectroscopy, the vinylic protons appearing as a singlet at δ 5.65 together with five equal intensity multiplets at δ 3.63, 3.40, 2.43, 2.25 and 1.85; the two at lower-field being assigned to those on carbons attached to nitrogen. The substituted piperazine complexes all show equal intensity multiplets in the aliphatic region associated with the methylene groups of the piperazine unit,

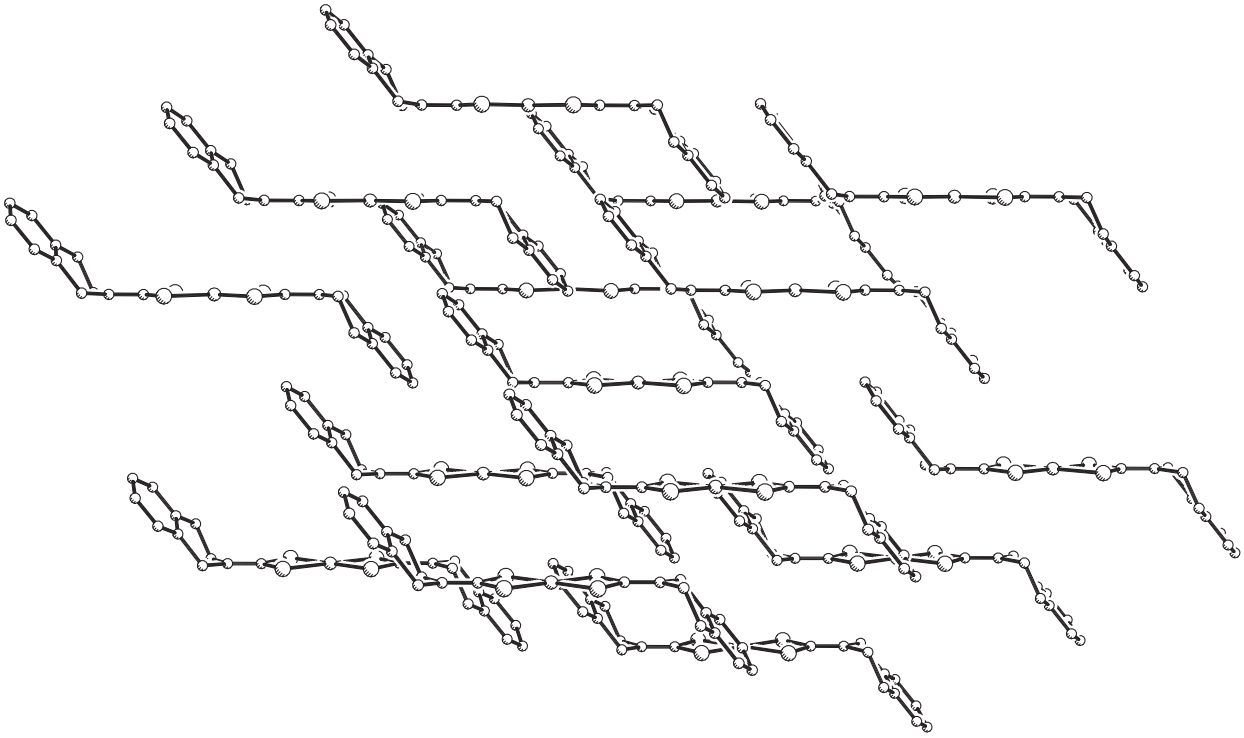
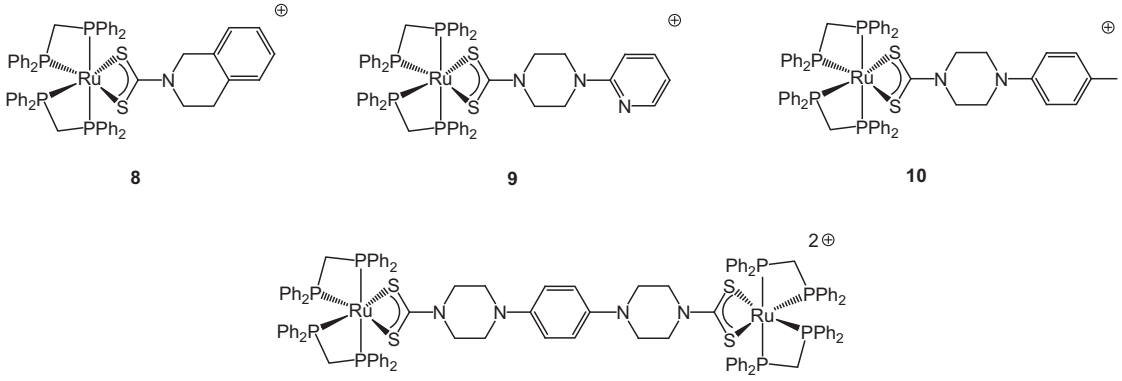


Fig. 2. Packing motiff for **1a** showing π-stacking between the arene rings.



8 **9** **10**

11

Chart 3.

together with signals in the aromatic region. For example, **5a** shows multiplets at δ 3.90 and 3.66 each integrating as eight protons, together with four equal intensity multiplets (each integrating to two protons) at δ 8.19, 7.53, 6.70 and 6.66.

We have previously used piperazine bis(dithiocarbamate) to link together metal centres in order to build-up multimetallic arrays [5–10]. The addition of simple metal salts to piperazine bis(dithiocarbamate), however, simply results in the rapid precipitation of solids that are presumably oligo- or polymeric. Their poor solubility in any solvent makes them difficult to characterise. In contrast, addition of two *cis*-[Ru(dppm)$_2$] (dppm = bis(diphenylphosphino)methane) moieties affords a soluble complex that we have fully characterised in both solution and the solid-state [8]. We thus sought to extend this metal-linking strategy to bis(dithiocarbamates) with longer organic backbones, which was the rational behind the synthesis of diamine **H**. Firstly, however, we chose three of the monoamines to attach a *cis*-[Ru(dppm)$_2$] moiety in order to confirm that this simple strategy would be likely to succeed.

Addition of a dichloromethane solution of *cis*-[RuCl$_2$(dppm)$_2$] to methanol solutions of the dithiocarbamate salts of **A**, **D** and **E**, followed by addition of a twofold excess of $NaBF_4$, resulted in the slow (*ca.* 20 min) deposition of cream precipitates which after washing and drying were found to be the tetrafluoroborate salts of **8**–**10** (Chart 3). These were readily characterised on the basis of their ^{31}P NMR spectra which in each case consisted of triplets at *ca.* −4.7 and −18.2 ppm, being consistent with the formation of the [*cis*-Ru(dppm)$_2$(dtc)]$^+$ cation [8,9]. The NMR spectra of **8** were more complicated than initially anticipated and showed temperature dependence. At room temperature, the ^{31}P NMR spectrum consists of three sharp triplet resonances together with a poorly resolved multiplet at −5.03 ppm. Upon warming to 55 °C, the three

triplets remain unchanged but the multiplet broadens considerably. The ^{1}H NMR spectrum also shows temperature dependence, most notably a triplet at δ 3.86 (J 5.6 Hz) in the room temperature spectrum is observed as a complex multiplet at 55 °C, while a broad multiplet at δ 4.94 resolves into two separate and better defined multiplets at the higher temperature. We associate these changes with restricted rotation about the nitrogen–carbon bond of the dithiocarbamate and/or the flipping of the six-membered NC_5 ring. The latter would appear most likely as this would equilibrate the methylene protons on each carbon atom in the ring while having little effect on the phosphorus environments.

In a similar manner, we attempted the synthesis of the bis(dithiocarbamate) salt of **H** and added two equivalents of *cis*-$[RuCl_2(dppm)_2]$ followed by a slight excess of $NaBF_4$. This lead to the slow deposition of a cream precipitates which was isolated in the usual manner. The ^{31}P NMR spectrum clearly showed the formation of a new dithiocarbamate complex **11**, and the ^{1}H NMR while being complex, was consistent with the proposed formulation. Unfortunately we were unable to obtain an analytically pure sample of this complex, possibly due to the inclusion of solvent.

3. Conclusions

This work has shown that while bis(dithiocarbamate) complexes with functionalised backbones are easily prepared their crystallisation can be more problematic. We were able to grow single crystals of **1a** and here a $\pi-\pi$ interaction was found, together with other short intermolecular interactions. It is likely that such interactions are found in most if not all of the complexes of this type but probing them in the absence of single crystals remains challenging.

4. Experimental

4.1. General methods

Amine syntheses were carried out under a nitrogen atmosphere using standard Schlenk-line techniques but all other reactions were carried out in air using standard bench reagents. NMR spectra were run on a Bruker AMX400 spectrometer and referenced internally to the residual solvent peak (^{1}H) or externally to $P(OMe)_3$ (^{31}P). Infrared spectra were run on a Nicolet 205 FT-IR spectrometer as KBr discs. Elemental analyses were performed at UCL. Isoindoline (**A**) and N-substituted piperazines **E**–**G** were purchased from Aldrich and used without further purification.

4.2. X-ray data collection and solution

Single crystals of **1a** were mounted on glass fibres and all geometric and intensity data were taken from these samples using a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 150 ± 2 K. Data reduction was carried out with SAINT PLUS and absorption correction applied using the programme SADABS. Structures were solved by direct methods and developed using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogens were placed in calculated positions (riding model). Structure solution used SHELXTL PLUS V6.10 program package. Crystallographic data for **1a**: green plate, dimensions 0.16 × 0.12 × 0.05 mm, triclinic, space group $P\bar{1}$, a = 7.019(4), b = 7.273(4), c = 10.462(6) Å, α = 78.675(9), β = 107.425(2), γ = 81.837(9)°, V = 499.7(5) Å^3, Z = 1, F(000) 246, D_{calc} = 1.579 g cm^{-3}, μ = 1.397 mm^{-1}. 4045 reflections were collected, 2209 unique [R_{int} = 0.0240] of which 1765 were observed [$I > 2\sigma(I)$]. At convergence, R_1 = 0.0485, wR_2 = 0.1236 [$I > 2\sigma(I)$] and R_1 = 0.0614, wR_2 = 0.1299 (all data), for 124 parameters.

4.3. Synthesis of amines

4.3.1. Tetrahydro-isoindoline (*B*)

A thf (40 ml) solution of 1,2,3,6-tertahydrophthalimide (3.93 g, 0.026 mmol) was added dropwise to a suspension of $LiAlH_4$ (1.48 g, 0.039 mmol) in thf (15 ml) so as to maintain a gentle reflux. After addition the mixture was refluxed for a further 35 h. After cooling to room temperature a mixture of thf (10 ml) and water (3 ml) was added dropwise in order to destroy excess $LiAlH_4$. Addition of diethyl ether (30 ml) resulted in formation of a precipitate. This was washed with water (3 × 15 ml) and then taken up in diethyl ether (3 × 15 ml). After drying with $MgSO_4$, removal of volatiles afforded **B** as an orange oil (1.50 g, 48%). ^{1}H NMR ($CDCl_3$) δ 5.63 (s, 2H), 2.98 (m, 2H), 2.14 (m, 4H), 1.86 (m, 2H).

4.3.2. Isoindoline (*C*)

A 1 M solution of BH_3·thf (100 ml) was added dropwise over *ca.* 30 min to a thf (10 ml) suspension of phthalimide (5.50 g, 0.037 mmol). During the addition the solution became yellow–orange. After addition the mixture was refluxed for 14 h. After cooling to 0 °C, methanol (10 ml) was added dropwise and after stirring for 20 min, 6 M HCl (10.5 ml) was slowly added. The resulting mixture was refluxed for 1 h and then after cooling to 0 °C, 6 M NaOH was slowly added until the pH was greater than 10. This solution was then extracted with diethyl ether (3 × 20 ml) and dried with $MgSO_4$. Removal of volatiles afforded **C** as an orange oil (3.44 g, 78%). ^{1}H NMR ($CDCl_3$) δ 7.22 (m 2H), 7.20 (m, 4H), 4.22 (s, 4H).

Alternatively; in a three-necked round-bottom flask equipped with a reflux condensor to a vigorously stirred suspension of NaH (60% dispersed in mineral oil, 2.34 g, 0.058 mmol) in dmf (60 ml) was added dropwise a dmf (35 ml) solution of p-toluenesulfonamide (10.0 g, 0.058 mmol). After the addition the mixture was stirred for a further 1 h and then heated at 65 °C for a further 1 h. To this was then added a dmf (85 ml) solution of o-xylenedibromide (6.17 g, 0.023 mmol) maintaining the temperature at 65 °C. After 3 h the mixture was cooled to room temperature and iced water was added. This was left overnight to give a light grey precipitate which was collected by filtration, washed with water and air dried to afford para-tosylisoindoline (6.0 g, 94%). ^{1}H NMR ($CDCl_3$) δ 7.76 (d, J 8.3, 2H), 7.32 (d, J 8.3, 2H), 7.23 (m, 2H), 7.17 (m, 2H), 4.61 (s, 4H), 2.40 (s, 3H). In a three-necked round-bottom flask equipped with a reflux condensor, p-tosyliso-indoline (1.20 g, 0.044 mmol), phenol (1.2 g), 48% HBr (9 ml) and propionic acid (1.5 ml) were added sequentially. The mixture was refluxed for 2 h. After cooling to room temperature it was transferred to a separating funnel and washed with diethyl ether (2 × 50 ml). The aqueous layer was then added dropwise to a NaOH solution (7.50 g in 20 ml H_2O) with vigorous stirring. The resulting solution was extracted with diethyl ether (5 × 30 ml) and dried with $MgSO_4$. Removal of volatiles afforded **C** as a brown oil (0.48 g, 93%).

4.3.3. 1-p-Tolylpiperazine (*D*)

In a three-necked round-bottom flask equipped with a reflux condensor p-toluidine (3.50 g, 0.033 mmol) and bis(2-chloroethyl)amine (5.89 g, 0.033 mmol) in diglyme (50 ml) were refluxed for 16 h. This produced a very dark orange solid. After cooling, methanol (*ca.* 100 ml) was added in order to dissolve all solids. Addition of diethyl ether (*ca.* 200 ml) led to the precipitation of 1-p-tolylpiperazine (**D**) as its ammonium salt. This was filtered, washed and dried to give the salt (5.96 g, 85%). A portion of this (2.01 g) was dissolved in 1.5 M sodium carbonate. After stirring for 1 h this was extracted with ethyl acetate (2 × 20 ml) and removal of volatiles afforded **D** as an oily orange solid (0.95 g,

67%). ^{1}H NMR ($CDCl_3$) δ 7.07 (d, *J* 7.7, 2H), 6.85 (d, *J* 7.7, 2H), 3.07 (m, 4H), 3.04 (m, 4H), 2.25 (s, 3H).

4.3.4. p-Phenylenebis(1-piperazine) (**H**)

In a three-necked round-bottom flask equipped with a reflux condensor p-phenylenediamine (4.00 g, 0.036 mmol) and bis(2-chloroethyl)amine (12.85 g, 0.072 mmol) in diglyme (100 ml) were refluxed for 16 h. This produced a dark brown solid. After cooling, methanol (*ca.* 200 ml) was added in order to dissolve all solids. Addition of diethyl ether (*ca.* 200 ml) led to the precipitation p-phenylenebis(1-piperazine) (**H**) as an ammonium salt. This was filtered, washed and dried to give the salt (9.20 g, *ca.* 80%). A portion of this (2.11 g) was dissolved in 2 M sodium hydroxide. After stirring for 1 h this was extracted with ethyl acetate (2 × 30 ml) and removal of volatiles afforded **H** as a dark oily solid (1.22 g, 75%). ^{1}H NMR ($CDCl_3$) δ 6.89 (s, 4H), 3.63 (m, 8H), 3.56 (m, 4H). *MS: m/z* 246 (M^+ 12%).

4.4. Synthesis of dithiocarbamate salts

Amines (5.0 mmol) were added to MeOH (30 ml) and KOH (0.28 g, 5.0 mmol) was added. This solution was left to stir for 5 min and CS_2 (0.38 g, 5.0 mmol) was added dropwise and left to stir for 1 h. This produced pale yellow solutions which were used for all further experiments.

4.5. Synthesis of nickel, copper and zinc complexes

Nickel acetate (0.62 g, 2.50 mmol) was added to the dithiocarbamate salts resulting in the immediate formation of a green precipitate. This was filtered and washed with water (3 × 15 ml), methanol (2 × 15 ml) and diethyl ether (2 × 10 ml). The solid was then air dried for 1 h and collected. Yields given below are based on the amount of this crude product. Recrystallisation was attempted for all complexes by the slow mixing of methanol into a saturated dichloromethane solution. Similar reactions and work-up were carried out using copper(II) acetate and zinc acetate.

1a *(0.83 g, 70%):* IR (KBr) 1523 (C=N), 982 (C–S) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.23–7.13 (m, 8H), 4.86 (s, 4H), 3.96 (t, *J* 6.1, 4H), 2.95 (t, *J* 6.1, 4H); *MS: m/z* 475 (M^+ 12%). *Anal.* Calc. for $Ni_1S_4N_2C_{20}H_{20}{\cdot}0.5CH_2Cl_2$: C, 48.21 (47.56); H, 4.04 (4.06); N, 5.34 (5.41).

2a *(0.74 g, 65%):* IR (KBr) 1512 (C=N), 982 (C–S) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.65 (s, 4H), 3.63 (m, 4H), 3.40 (m, 4H), 2.43 (m, 4H), 2.25 (m, 4H), 1.85 (m, 4H); *MS: m/z* 455 (M^+ 3%). *Anal.* Calc. for $Ni_1S_4N_2C_{18}H_{24}{\cdot}0.25CH_2Cl_2$: C, 46.23 (46.01); H, 5.25 (5.15); N, 5.86 (5.88).

3a *(0.90 g, 77%):* IR (KBr) 1505 (C=N), 985 (C–S) cm^{-1}. *Anal.* Calc. for $Ni_1S_4N_2C_{18}H_{16}$: C, 47.65 (48.33); H, 3.59 (3.61); N, 5.96 (6.26).

4a *(0.88 g, 63%):* IR (KBr) 1515 (C=N), 1019 (C–S) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.09 (d, *J* 8.2, 4H), 6.82 (d, *J* 8.2, 4H), 3.93 (m, 8H), 3.18 (m, 8H), 2.26 (s, 6H); *MS: m/z* 561 (M^+ 92%). *Anal.* Calc. for $Ni_1S_4N_4C_{24}H_{30}{\cdot}0.5CH_2Cl_2$: C, 49.59 (48.74); H, 5.38 (5.06); N, 9.08 (9.28).

5a *(0.82 g, 60%):* IR (KBr) 1484 (C=N), 980 (C–S) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.19 (m, 2H), 7.53 (m, 2H), 6.70 (m, 2H), 6.66 (m, 2H), 3.90 (m, 8H), 3.66 (m, 8H). *Anal.* Calc. for $Ni_1S_4N_6C_{20}H_{24}$: C, 43.62 (44.88); H, 4.48 (4.49); N, 15.05 (15.71).

6a *(0.75 g, 55%):* IR (KBr) 1504 (C=N), 1014 (C–S) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.34 (d, *J* 7.5, 4H), 6.58 (t, *J* 7.5, 2H), 3.93 (m, 8H), 3.85 (m, 8H). *Anal.* Calc. for $Ni_1S_4N_8C_{18}H_{22}$: C, 39.99 (40.23); H, 4.19 (4.13); N, 20.72 (20.85).

7a *(0.93 g, 70%):* IR (KBr) 1508 (C=N), 1008 (C–S) cm^{-1}; *MS: m/z* 535 (M^+ 26%). *Anal.* Calc. for $Ni_1S_4N_6C_{20}H_{24}{\cdot}CH_2Cl_2$: C, 41.23 (40.66); H, 4.59 (4.22); N, 13.76 (13.55).

1b *(0.80 g, 67%):* IR (KBr) 1494 (C=N), 982 (C–S) cm^{-1}. *Anal.* Calc. for $Cu_1S_4N_2C_{20}H_{20}$: C, 49.58 (50.02); H, 5.22 (4.26); N, 5.67 (5.83).

2b *(0.74 g, 63%):* IR (KBr) 1499 (C=N), 982 (C–S) cm^{-1}. *MS: m/z* 460 (M^+ 14%). *Anal.* Calc. for $Cu_1S_4N_2C_{18}H_{24}$: C, 46.41 (46.98); H, 5.21 (5.26); N, 5.90 (6.09).

3b *(0.77 g, 75%):* IR (KBr) 1484 (C=N), 987 (C–S) cm^{-1}. *Anal.* Calc. for $Cu_1S_4N_2C_{18}H_{16}{\cdot}CHCl_3$: C, 40.68 (39.92); H, 3.04 (2.99); N, 4.96 (4.89).

4b *(0.94 g, 70%):* IR (KBr) 1508 (C=N), 1019 (C–S) cm^{-1}. *Anal.* Calc. for $Cu_1S_4N_4C_{24}H_{30}{\cdot}CHCl_3$: C, 43.84 (43.79); H, 4.72 (4.56); N, 7.99 (8.17).

5b *(0.82 g, 60%):* IR (KBr) 1478 (C=N), 980 (C–S) cm^{-1}. *Anal.* Calc. for $Cu_1S_4N_6C_{20}H_{24}{\cdot}CHCl_3$: C, 38.84 (38.24); H, 4.11 (3.79); N, 13.81 (12.71).

6b *(0.85 g, 63%):* IR (KBr) 1508 (C=N), 1016 (C–S) cm^{-1}. *Anal.* Calc. for $Cu_1S_4N_8C_{18}H_{22}{\cdot}CHCl_3$: C, 34.31 (34.49); H, 3.66 (3.48); N, 16.41 (16.94).

7b *(0.99 g, 73%):* IR (KBr) 1512 (C=N), 1013 (C–S) cm^{-1}. *Anal.* Calc. for $Cu_1S_4N_6C_{20}H_{24}{\cdot}CHCl_3$: C, 37.49 (38.23); H, 4.22 (3.79); N, 13.23 (12.75).

1c *(0.80 g, 65%):* IR (KBr) 1495 (C=N), 980 (C–S) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ7.23–7.12 (m, 8H), 5.14 (s, 4H), 4.23 (t, *J* 6.0, 4H), 3.02 (t, *J* 6.0, 4H). *Anal.* Calc. for $Zn_1S_4N_2C_{20}H_{20}$: C, 49.28 (49.83); H, 4.15 (4.18); N, 5.47 (5.81).

2c *(0.72 g, 66%):* IR (KBr) 1484 (C=N), 982 (C–S) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.66 (s, 4H), 3.81 (m, 4H), 3.59 (m, 4H), 2.51 (m, 4H), 2.28 (m, 4H), 1.93 (m, 4H). *Anal.* Calc. for $Zn_1S_4N_2C_{18}H_{24}$: C, 46.84 (46.79); H, 5.66 (5.24); N, 6.03 (6.06).

3c *(0.90 g, 77%):* IR (KBr) 1472 (C=N), 982 (C–S) cm^{-1}. *Anal.* Calc. for $Zn_1S_4N_2C_{18}H_{16}$: C, 46.80 (47.62); H, 3.69 (3.55); N, 5.63 (6.17).

4c *(1.05 g, 75%):* IR (KBr) 1515 (C=N), 1013 (C–S) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.09 (d, *J* 8.4, 4H), 6.83 (d, *J* 8.4, 4H), 4.24 (m, 8H), 3.25 (m, 8H), 2.28 (s, 6H). *Anal.* Calc. for $Zn_1S_4N_4C_{24}H_{30}$: C, 51.93 (50.73); H, 5.54 (5.32); N, 9.63 (9.86).

5c *(0.90 g, 65%):* IR (KBr) 1474 (C=N), 980 (C–S) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.20 (m, 2H), 7.50 (m, 2H), 6.70–6.63 (m, 4H), 4.24 (m, 8H), 3.70 (m, 8H). *Anal.* Calc. for $Zn_1S_4N_6C_{20}H_{24}{\cdot}CH_2Cl_2$: C, 40.84 (40.23); H, 4.56 (4.18); N, 14.00 (13.50).

6c *(0.96 g, 70%):* IR (KBr) 1500 (C=N), 1014 (C–S) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.32 (d, *J* 7.4, 4H), 6.57 (t, *J* 7.4, 2H), 4.19 (t, *J* 5.4, 8H), 3.97 (t, *J* 5.4, 8H). *Anal.* Calc. for $Zn_1S_4N_8C_{18}H_{22}$: C, 40.30 (39.74); H, 4.33 (4.08); N, 21.09 (20.60).

7c *(0.90 g, 67%):* IR (KBr) 1525 (C=N), 1006 (C–S) cm^{-1}. *Anal.* Calc. for $Ni_1S_4N_6C_{20}H_{24}{\cdot}CH_2Cl_2$: C, 40.55 (40.23); H, 4.37 (4.18); N, 13.22 (13.40).

4.6. Synthesis of ruthenium complexes

A dichloromethane (10 ml) solution of *cis*-$[RuCl_2(dppm)_2]$ (0.136 g, 0.14 mmol) was added to a methanol solution of the dithiocarbamate salt (0.14 mmol). This was stirred for 1 h resulting in a slow formation of a cloudy cream solution. Solid $NaBF_4$ (0.032 g, 0.30 mmol) was then added. The solution was filtered and the filtrate collected. Removal of volatiles afforded a cream solid which was washed consecutively with water (3 × 5 ml), methanol (3 × 5 ml) and diethyl ether (3 × 5 ml). Air drying afforded the product as a dry cream powder.

8 *(0.13 g, 75%):* IR (KBr) 1485 (C=N), 1000 (C–S) cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) −0.87 (t, *J* 35.2, 1P), −5.03 (m, 1P), −18.83 (t, *J* 34.9, 1P), −27.14 (t, *J* 35.6, 1P); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 55 °C) −0.85 (t, *J* 35.2, 1P), −5.24 (br, 1P), −18.71 (t, *J* 34.9, 1P), −6.41 (t, *J* 35.3, 1P); ^{1}H NMR ($CDCl_3$, 20 °C) δ 8.21 (q, *J* 5.24, 4H, Ph), 7.94 (q, *J* 5.32, 4H, Ph), 7.67 (br, 4H, Ph), 7.46–6.95 (m, 28H, Ph), 6.79 (t, *J* 7.20, 2H, Ph), 6.57 (m, 4H, Ph), 4.94 (brm, 2H, PCH_2P), 4.83 (d, *J* 16.7, 1H), 4.66 (brm, 2H, PCH_2P), 4.50 (d, *J* 16.7, 1H), 3.82 (t, *J* 5.6), 2.86 (m, 1H), 2.77 (m, 1H); ^{1}H NMR ($CDCl_3$, 55 °C)

δ 8.23 (q, *J* 5.24, 4H, Ph), 7.96 (q, *J* 5.32, 4H, Ph), 7.71 (br, 4H, Ph), 7.46–6.95 (m, 28 H, Ph), 6.79 (t, *J* 7.20, 2H, Ph), 6.57 (br, 4H, Ph), 5.06 (m, 1H, PCH_2P), 4.91 (m, 1H, PCH_2P), 4.82 (d, *J* 16.7, 1H), 4.68 (brm, 2H, PCH_2P), 4.50 (d, *J* 16.7, 1H), 3.82 (m, *J* 4.9), 2.88 (m, 1H), 2.80 (m, 1H). *Anal.* Calc. for $Ru_1P_4S_2N_1C_{60}H_{54}B_1F_4$: C, 61.16 (61.86); H, 4.60 (4.60); N, 1.05 (1.20).

9 *(0.15 g, 70%):* IR (KBr) 1480 (C═N), 978 (C–S) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.22 (dd, *J* 4.9, 1.3, 1H), 7.65–6.52 (m, 43H), 4.96 (m, 2H), 4.64 (m, 4H), 3.82–3.64 (m, 4H), 3.52–3.40 (m, 4H); $^{31}P\{^1H\}$ NMR ($CDCl_3$) −4.91 (t, *J* 34.4, 2P), −18.3 (t, *J* 34.4, 2P); *MS: m/z* 1108 (M^+ 5%). *Anal.* Calc. for $Ru_1P_4S_2N_3C_{60}H_{56}B_1F_4$: C, 60.16 (60.30); H, 4.72 (4.71); N, 3.27 (3.52).

10 *(0.12 g, 68%):* IR (KBr) 1514 (C═N), 1020 (C–S) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.62–6.52 (m, 44H), 5.12 (m, 2H), 4.51 (m, 2H), 3.83–3.74 (m, 4H), 3.12–2.96 (m, 4H), 2.30 (s, 3H); $^{31}P\{^1H\}$ NMR ($CDCl_3$) −4.77 (t, *J* 34.8), −18.03 (t, *J* 34.8). *Anal.* Calc. for $Ru_1P_4S_2N_2C_{60}H_{59}B_1F_4$: C, 62.80 (61.64); H, 5.28 (4.93); N, 2.01 (2.32).

11 *(0.15 g, 63%):* ^1H NMR ($CDCl_3$) δ 7.73–6.39 (m, 84H), 4.97 (m, 4H), 4.55 (m, 4H), 3.82–3.64 (m, 8H), 3.06–2.82 (m, 8H); $^{31}P\{^1H\}$ NMR ($CDCl_3$) −4.7 (t, *J* 34.3), −17.9 (t, *J* 34.3).

Appendix A. Supplementary material

Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 764857. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.05.061.

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