CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201001354

Enhanced Anion Binding from Unusual Coordination Modes of Bis(thiourea) Ligands in Platinum Group Metal Complexes

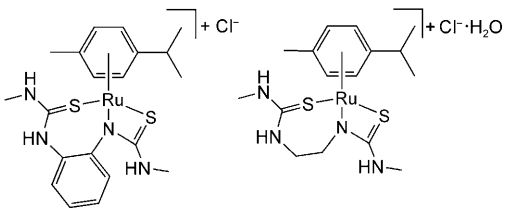
M. Laura Soriano,[a] Joseph T. Lenthall,[a] Kirsty M. Anderson,[a] Stephen J. Smith,[b] and Jonathan W. Steed*[a]

Abstract: Treatment of a range of bis(thiourea) ligands with inert organometallic transition-metal ions gives a number of novel complexes that exhibit unusual ligand binding modes and significantly enhanced anion binding ability. The ruthenium(II) complex $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa S,S',N\text{-}\mathbf{L^3}-H)]^+$ (**2b**) possesses juxtaposed four- and seven-membered chelate rings and binds anions as both 1:1 and 2:1 host guest complexes. The pyridyl bis(thiourea) complex $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa S,S',N_{py}\text{-}\mathbf{L^4})]^{2+}$ (**4**) binds anions in both 1:1 and 1:2 species, whereas the free ligand is ineffective because of intramolecular NH···N hydrogen bonding. Novel palladium(II) complexes with nine- and ten-membered chelate rings are also reported.

Keywords: anion binding · chelates · supramolecular chemistry · transition metals · thiourea

Introduction

The design of host molecules capable of selective recognition of anionic species is still an area of intense current academic and industrial interest,[1–6] particularly in the detection and extraction of environmentally relevant anionic species such as nitrate, phosphates, pertechnetate, perchlorate, arsenate and chromate.[7–11] We are particularly concerned with the understanding and use of structure, conformational aspects and supramolecular interactions to modulate the ability of the receptors to bind different anions. A particularly important class of anion receptors are those based on thiourea[2,12–21] functionalities because of their ability to form strong hydrogen-bond complexes with anions, and their synthetic accessibility. Simple bis(thioureas) have been shown to bind glutarate, dihydrogenphosphate and acetate in DMSO[22–26] and have been incorporated into monolayers to mimic ion-channel sensing of hydrophilic anions.[27]



2a R = Me
2b R = *i*Pr

3

They also act as phase-transfer agents from water to nitrobenzene for hydrophilic anions, such as Cl^-, AcO^-, $H_2PO_4^-$, HPO_4^{2-} and SO_4^{2-}.[28] A fluorescent anion sensor based on a pyrene electron acceptor linked to a thiourea donor and a colorimetric sensor based on *p*-nitrophenylthiourea have been prepared.[29,30] Gunnlaugsson and co-workers have developed similar chemosensors for anions by using anthracene-based fluorescent sensors.[20,31,32] Other examples of recently synthesised thiourea sensors include hosts with the thiourea group linked to fluorescent sensor moieties by a rigid hydrazine spacer selective for acetate,[33–36] Hosts based on coumarin sensors that act as both fluorescent and colorimetric sensors[37] and compounds that utilise cooperativity between the thiourea group and an amine group adjacent to a naphthalimide sensor are also known.[38,39] Sensors using

[a] Dr. M. L. Soriano, Dr. J. T. Lenthall, Dr. K. M. Anderson, Prof. J. W. Steed
Department of Chemistry, Durham University
South Road, Durham
DH1 3LE (UK)
Fax: (+44) 191-384-4737
E-mail: jon.steed@durham.ac.uk

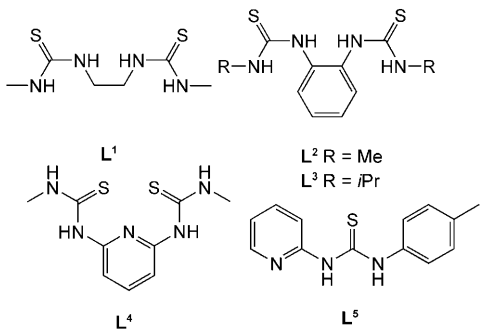
[b] Dr. S. J. Smith
BP Chemicals Ltd., Hull Research and Technology Centre
Saltend, Hull
HU12 8D (UK)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201001354.

bis(thiourea) groups have been developed based on azophenol, biaryls and anthraquinone.[40–42] A range of tripodal trisureas that bind dihydrogenphosphate and acetate anions have also been reported.[43] Thioureas in particular are relatively acidic, which leads to strong hydrogen-bonding interactions (although the stabilisation of the conjugate base can lead to deprotonation by basic anions[44–47]). The thiourea sulfur atom is more exposed than the urea carbonyl oxygen atom, however, and thus urea self-association can compete with hydrogen bonding to a target anion guest, in some cases leading to species such as gels.[48,49] A particularly attractive class of thiourea-based anion receptors are bis(thioureas), in which the urea functionalities are linked by a spacer and arranged in such a way that all four sets of NH hydrogen bond donors converge on an anion binding site. Such complexes have been reported to act as effective anion-binding receptors.[13,15,17,19,46,50,51] However, problems can arise in these neutral acyclic systems due to lack of preorganisation and solvent competition. Although cyclic bis(thiourea) macrocycles are more preorganised, their synthesis is more challenging.[52,53] Herein, we compare the anion-binding ability of a range of acyclic bis(ureas) and their complexes with a range of platinum group metals. The presence of a metal centre can exert a significant preorganising effect and also modulate the electronic properties of the ligand. As a result, metal-based anion receptors are increasingly topical.[1,6,7,54–74] We also report the extensive, varied and novel coordination chemistry of a range of platinum group metal bis(thiourea) compounds.

Results and Discussion

Ligand synthesis: The bis(thiourea) ligands 1-methyl-3-[2-(3-methylthioureido)ethyl]thiourea (**L^1**), 1-methyl-3-[2-(3-methylthioureido)phenylene]thiourea (**L^2**) and 1-methyl-3-[6-(3-methylthioureido)pyridin-2-yl]thiourea (**L^4**) were easily synthesised by treating methyl isothiocyanate with ethylenediamine, 1,2-phenylenediamine and 2,6-diaminopyridine, respectively. The ligands were isolated in pure form as a precipitate after concentration of the original reaction solutions. In all reactions, an excess ($\approx$10%) of methyl isothiocyanate was used, and this excess was washed away from the product with diethyl ether. A low yield for pyridyl ligand **L^4** may be attributed to the reduced nucleophilicity of the pyridyl diamine. The monothiourea 1-pyridin-2-yl-3-*p*-tolyl thiourea (**L^5**) was also synthesised in good yield by treating 2-aminopyridine with *p*-tolyl isothiocyanate.[75] Ligands **L^1** and **L^2** are only soluble in DMSO. To increase the solubility, treatment of 1,2-phenylenediamine with bulkier isothiocyanates, such as *i*Pr-NCS or *t*Bu-NCS, was undertaken in a variety of solvents under both thermal and microwave conditions, but several problems occurred: no reaction, monosubstitution of the precursor *o*-phenylene diamine or production of the cyclised product benzimidazoline-2-thione[76,77] (see the Supporting Information for a full discussion). To disfavour internal cyclisation and encourage reaction of the singly functionalised ligands with a further equivalent of isothiocyanate, treatment of 1,2-phenylenediamine and the isothiocyanates in high concentrations was attempted. A minimum amount of hot ethanol was added to the mixture to dissolve the phenylenediamine. The mixture was sonicated and left overnight. From this concentrated solution, the isopropyl derivative 1-isopropyl-3-[2-(3-isopropylthioureido)phenylene]-thiourea (**L^3**) can be isolated in good yield and highly crystalline form. This reaction indicates that the use of concentrated solutions to favour the intermolecular reaction of the intramolecular cyclisation is a key factor in the synthesis. However, using this technique with *t*BuNCS gave only the singly functionalised compound.



Ruthenium complexes: "Piano-stool" complexes of type [Ru(η^6-arene)L*] (L* = mono- or bidentate pyridine or biimidazole derivatives) have proved to be successful anion hosts in a number of recently reported systems.[70,78–80] To investigate the coordination chemistry of thiourea ligands **L^1**–**L^5**, particularly with a view to preorganising the ligand and tying up the sulfur atoms that can compete with anions as hydrogen-bond acceptors, the reaction of the convenient *p*-cymene complex [{Ru(η^6-$C_6H_4MeCH(Me)_2$)Cl(μ-Cl)}$_2$][81] with two equivalents of ligand **L^3** was undertaken in $CHCl_3$ at room temperature for 3 h. This reaction resulted in a material that was found to be a 1:1 complex of empirical formula Ru(η^6-$C_6H_4MeCH(Me)_2$)Cl_2(**L^3**) (**1**), which exhibits a broad ^{1}H NMR spectrum with many resonances, suggesting a number of equilibrating species (vide infra). This crude product was dissolved in distilled water and then extracted into $CHCl_3$ to give a compound of formula [Ru(η^6-$C_6H_4MeCH(Me)_2$)($\kappa S,S',N$-**L^3**$-$H)]Cl (**2b**), which is a single complex that involves a deprotonated form of **L^3**. It also proved possible to exchange the chloride counterion for BF_4^- by treating **2b** with $AgBF_4$ in CH_2Cl_2 to give [Ru(η^6-$C_6H_4MeCH(Me)_2$)($\kappa S,S',N$-**L^3**$-$H)]BF_4 (**2b′**). The ^{1}H NMR spectrum of **2b** shows that the thiourea ligand has become unsymmetrical and exhibits only three NH signals. The AA′BB′ pattern for the *p*-cymene resonances and the diastereotopic isopropyl methyl groups on both ligands are magnetically inequivalent, with a spectrum characteristic of a stereogenic metal centre.[79,82,83] For example, the isopropyl CH_3 resonances of **L^3** occur at δ = 1.03, 1.04, 1.13 and 1.14 ppm, showing that not only are both isopropyl arms

within the ligand unsymmetrical but that each CH_3 within each arm is inequivalent. COSY NMR spectroscopic data indicate that deprotonation occurs on one of the NH protons adjacent to the aryl ring. There are a total of 24 resonances in the $\{^1H\}^{13}C$ NMR spectrum, which again confirms the asymmetrical nature of the molecule, in particular the two resonances for the C=S carbon atoms at $\delta = 178.62$ and 180.20 ppm. Given that this species is obtained from the crude material in a yield of 75%, it is clear that the water is not simply extracting one complex from the initial crude mixture but inducing the deprotonation and coordination of a urea nitrogen atom and driving the mixture over to an ionic product.

Compound **2b** exhibits a single peak in the ESI-MS, with a 100% relative abundance at *m/z* 545.1 with a ruthenium isotope envelope, which may be assigned to the proposed monocationic monomeric compound, $[^{102}Ru(\eta^6\text{-}C_6H_4MeCH(Me)_2(\mathbf{L^3}-H)]^+$. The IR spectrum of the uncoordinated ligand exhibits strong bands at $\tilde{\nu} = 3315$ and 3256 cm^{-1} assigned as N–H stretching modes. In the complex, these bands are replaced by a strong band at $\tilde{\nu} =$ 3216 cm^{-1} and a weaker band at $\tilde{\nu} = 3130$ cm^{-1}, which shows a significant change in the NH environment. This is also reflected in a smaller change in absorbance bands assignable to the NH bending from ligand bands at $\tilde{\nu} = 1598$ and 1563 cm^{-1} to $\tilde{\nu} = 1591$ and 1561 cm^{-1} in the complex. A strong absorbance band in the C=S stretch region shifts from $\tilde{\nu} = 1265$ cm^{-1} in the ligand to $\tilde{\nu} = 1167$ cm^{-1} in the complex.

The formulation of **2b** was confirmed by an X-ray crystal structure determination (Figure 1a) that proved to be fully consistent with the NMR spectroscopic and analytical data. The ligand adopts a terdentate binding mode with both sulfur atoms and the deprotonated nitrogen atom binding to the stereogenic metal centre to give adjacent four- and seven-membered chelate rings. This geometry appears to be unprecedented in the CSD.[84,85] The neutral thiourea moiety adopts a *syn* conformation in which both hydrogen atoms form an $R_2^1(6)$ motif[86,87] with the uncoordinated chloride counterion. The remaining NH group of N(1) forms a hydrogen bond to the opposite face of the chloride anion and as a result the complex in the solid state forms a centrosymmetric hydrogen-bonded dimer linked by interactions to the chloride anions (Figure 1b). A bidentate, *N*,*S*-coordination mode has been seen in a number of deprotonated monothiourea derivatives of ruthenium,[88,89] platinum(II),[90,91] cadmium,[92] zinc,[93] gold(III)[94] and gold(I).[95] The *N*,*S*-thioureido chelate binding mode is also observed for complexes with rhenium(V) in a thiol-amide-thiourea ligand,[96] and it is found in both coordinating thioureas for an analogous bis-(thiourea) ligand.[97] In this latter case, a methanolic solution of acetate deprotonates three of the four NH protons and leads to coordination of one monoanionic and one dianionic species within the same molecule.

The reactions of $[\{Ru(\eta^6\text{-}C_6H_4MeCH(Me)_2)Cl(\mu\text{-}Cl)\}_2]$ with related ligands $\mathbf{L^1}$ and $\mathbf{L^2}$ gave similar products of formula $[Ru(\eta^6\text{-}C_6H_4MeCH(Me)_2)(\kappa S,S',N\text{-}\mathbf{L^2}-H)]Cl$ (**2a**) and

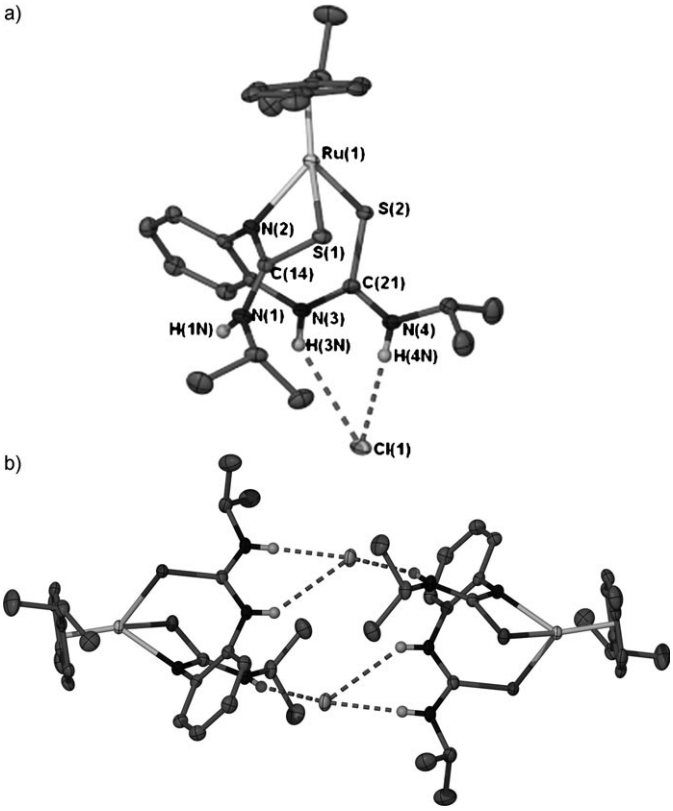


Figure 1. a) The X-ray crystal structure of **2b** showing the hydrogen bonding to the chloride anion. b) The hydrogen-bonded dimer observed in the solid state. Thermal ellipsoids are drawn at the 50% probability level.

$[Ru(\eta^6\text{-}C_6H_4MeCH(Me)_2)(\kappa S,S',N\text{-}\mathbf{L^1}-H)]Cl{\cdot}H_2O$ (**3**). Interestingly, the ^1H NMR spectrum of **3** is broad in nature, unlike the spectra obtained for the phenylene spacer compounds of **2**, and each of the NH resonances is split into two signals of different intensity (Figure 2). This data suggests that the molecule exists in two isomeric conformations in solution. This conformational isomerism may be linked to the flexibility of the ethylene spacer in $\mathbf{L^1}$ in comparison to the more rigid $\mathbf{L^2}$ and $\mathbf{L^3}$. The greatest difference in the chemical shift for the conformations is observed for the NH proton at $\delta = 7.41$ ppm for the major conformer and $\delta = 8.14$ ppm for the minor conformer. This may be attributable to two different hydrogen-bonding environments, in particular hydrogen

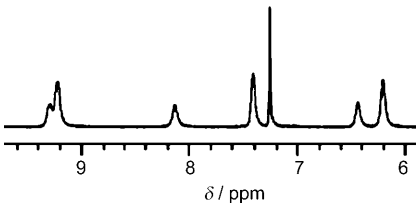


Figure 2. Partial ^1H NMR spectrum of **3** showing the two sets of three NH resonances (peak at $\delta = 7.24$ ppm is residual $CHCl_3$).

bonding to a chloride counterion that suggests a greater interaction with the chloride anion for the minor conformer.

Compounds **2a** and **3** were also characterised by X-ray crystallography and both structures give additional insight into the possible conformational isomerism observed for **3** in solution (see Figure 3). Compound **2a** crystallises as a

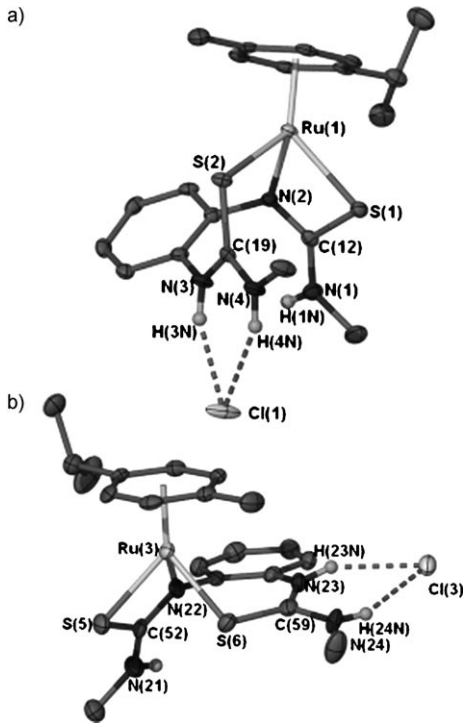


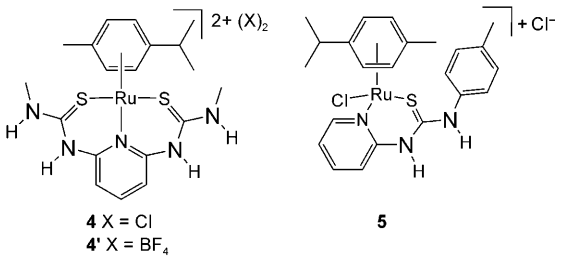
Figure 3. The X-ray crystal structures of **2a** showing the conformational isomerism at the sulfur atom. a) Molecule 1 based on Ru(1); b) molecule 3 based on Ru(3). The molecule based on Ru(2) is an enantiomer of molecule 1. Thermal ellipsoids are drawn at the 50% probability level.

conformational isomorph[98] in a remarkable structure comprised of three crystallographically independent molecules ($Z' = 3$[99]). Molecules based on Ru(1) and Ru(2) comprise an enantiomeric pair linked by hydrogen bonding to their chloride counterions. Both the conformation and mode of interaction with chloride are very similar to the structure of **2b**, and the bond lengths and angles are not significantly different from the isopropyl analogue. The molecule based on Ru(3) also forms an anion-bridged hydrogen-bonded dimer with a crystallographic inversion symmetry equivalent of itself, however the conformation of the ligand is different because of an inversion of configuration at the sulfur atom of neutral thiourea functionality S(6). This factor results in the thiourea group being approximately coplanar with the *p*-cymene ring rather than almost perpendicular to it as in the other isomer. Metal complexes of sulfur ligands can display significant conformational rigidity and the inversion barrier at sulfur is sometimes sufficiently high enough to distinguish S-inversion conformers in solution by using NMR spectroscopy.[100,101] Although this is not the case for **2a**, it is one possible explanation for the isomerism observed in **3**. The co-crystallisation of both conformers in a single crystal of **2a** might result from the fact that crystals were obtained by rapid cooling of a hot ethyl acetate solution as opposed to slow crystallisation at room temperature over a number of days in the case of **2b** and **3**.

Compound **3** was characterised by X-ray crystallography as a monohydrate. The structure is broadly similar to those of compounds **2** but interestingly reveals a second kind of isomerism that involves rotation about the C(5)–N(4) bond (the bond from the carbon atom of the neutral thiourea to the terminal NHMe group). The thiourea thus adopts an *anti* conformation, rather than *syn* as observed for the other two compounds (see Figure 4a). This change has a fundamental effect on the hydrogen bonding to the chloride counter anions. The common $R_2^1(6)$ motif observed in compounds **2** is replaced by hydrogen bonding to the water molecule, which in turn interacts with the choride counterion. The chloride anion is bound on the other side by the NH group of the deprotonated thiourea N(1)H. The remaining NH group forms a hydrogen bond to water and thus the structure comprises hydrogen-bonded dimers linked to a a Cl^-_2-$(H_2O)_2$ unit bound to each cationic complex through only a single anion (Figure 4b).

Both sulfur inversion isomerism and *syn*/*anti* isomerism of the thiourea moiety have precedent for occurring on a time scale comparable with the NMR spectroscopic time scale, however, the latter process seems to be more consistent with the significant differences in chemical shift and thus hydrogen bonding to the anion observed in the two solution conformers in **3**.

Because compounds **2** and **3** both involve thiourea deprotonation to provide three donor atoms for the ruthenium(II) centre, the treatment of [{Ru(η^6-C_6H_4MeCH(Me)$_2$)Cl(μ-Cl)}$_2$] with terdentate ligand $\mathbf{L^4}$ was undertaken. This reaction gave a single product with a symmetric set of resonances in the ^{1}H NMR spectrum that can be assigned to the terdentate *S*,*S*′,N_{py} chelate [Ru(η^6-C_6H_4MeCH(Me)$_2$)(κ*S*,*S*′,N_{py}-$\mathbf{L^4}$)]Cl$_2$ (**4**), which was fully characterised. The displacement



4 X = Cl
4' X = BF_4

5

of all of the chloride from the ruthenium(II) centre without treatment with silver(I) is unusual and may be related to the terdentate nature of the ligand and the involvement of the chloride ligands in hydrogen bonding in the product. Addition of water to the mixture, however, gives a mixture of **4** and a second species with an unsymmetrical ^{1}H NMR spec-

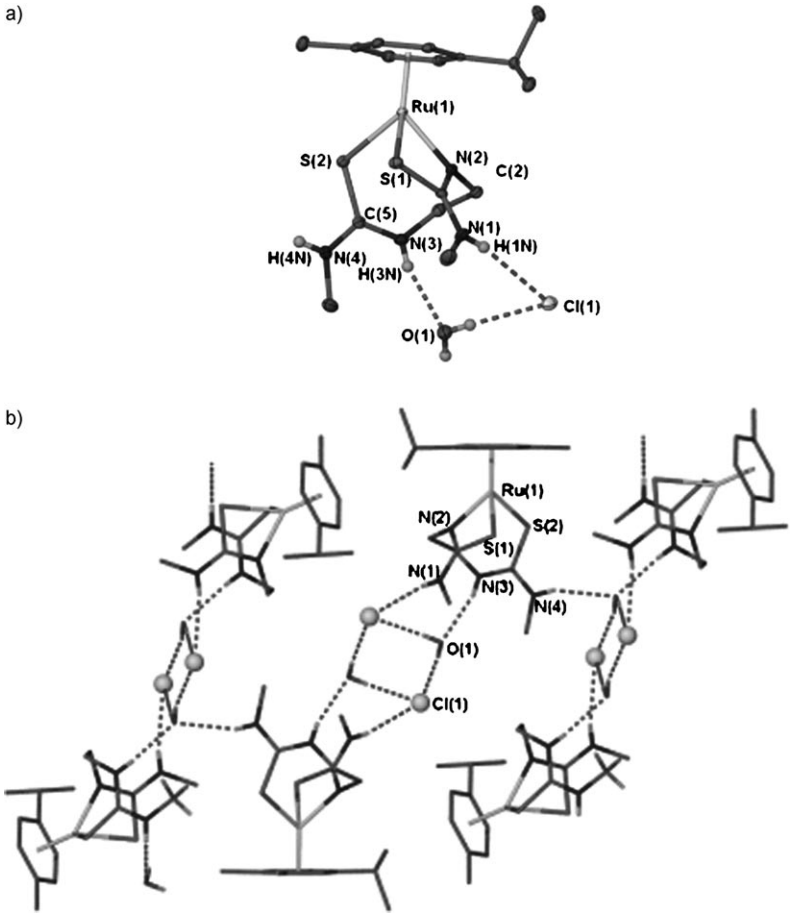


Figure 4. The X-ray crystal structure of **3**·H_2O. a) The *anti* conformation of the urea moiety based on C(5); thermal ellipsoids are drawn at the 50% probability level. b) The extended crystal packing showing counterion and water interactions.

trum that probably results from thiourea deprotonation. It is possible that in this species a bidentate deprotonated thiourea moiety replaces the pyridyl unit. This material was not isolated, but evidence for the lability of the pyridyl moiety comes from the mass spectrum of **4** in acetonitrile solution, which reveals a peak at *m/z* 265 that can be assigned to the acetonitrile adduct $[Ru(\eta^6\text{-}C_6H_4MeCH(Me)_2)(MeCN)(\kappa S,S'\text{-}\mathbf{L^4})]^{2+}$. The chloride anions in **4** could be exchanged for BF_4^- by treating **4** with $AgBF_4$ in CH_2Cl_2 followed by removal of precipitated AgCl to give the tetrafluoroborate salt $[Ru(\eta^6\text{-}C_6H_4MeCH(Me)_2)(\kappa S,S',N_{py}\text{-}\mathbf{L^4})](BF_4)_2$ (**4′**). Compound **4** was characterised by X-ray crystallography as the dichloromethane solvate and exhibits the expected symmetrical structure. The urea NH groups face away from the metal centre in a *syn* arrangement to form $R_2^1(6)$ hydrogen bonding motifs with the chloride anions (Figure 5). The Ru–N(3) bond length of 2.120(2) Å is normal and does not suggest any particular strain in the molecule.

Treatment of $[\{Ru(\eta^6\text{-}C_6H_4MeCH(Me)_2)Cl(\mu\text{-}Cl)\}_2]$ with mono-thiourea $\mathbf{L^5}$ was undertaken for comparison. The starting materials were heated at reflux under N_2 for 3 h in chloroform to give a single product that again exhibited a ^1H NMR spectrum indicative of a stereogenic metal centre, even without treatment with water. The product was identified as $[Ru(\eta^6\text{-}C_6H_4MeCH(Me)_2)Cl(\kappa S,N\text{-}\mathbf{L^5})]Cl\cdot 2H_2O$ (**5**), in which the pyridyl thiourea acts as a neutral, bidentate chelate without deprotonation. The large downfield shift in one of the NH resonances from $\delta = 8.84$ ppm in the free ligand to $\delta = 11.95$ ppm in **5** suggests significant interaction with the chloride counterion.

Reactions with platinum and palladium complexes: Reaction of bis(thioureido) ligands with $[Pd(MeCN)_2Cl_2]$ and $[Pt(MeCN)_2Cl_2]$ formed insoluble complexes of general formula ML_xCl_2 ($x = 1.5$ and 2), even if a 1:1 M/L stoichiometry was used. ESI-MS shows periodic peaks up to high molecular weights ($m/z > 2000$). It is likely that coordination oligomers or polymers are being formed. Therefore, diphenylphosphinoethane (DPPE) was used to block coordination sites and allow the formation of discrete species. The general

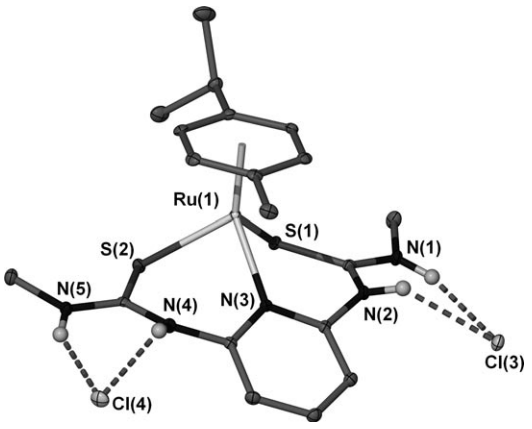
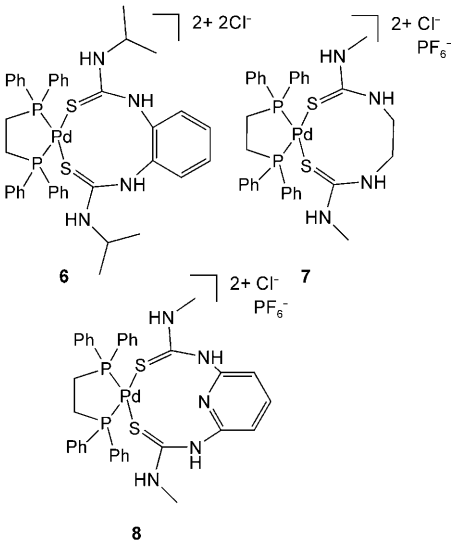


Figure 5. The X-ray crystal structure of **4**·$2CH_2Cl_2$. Thermal ellipsoids are drawn at the 30% probability level.

method for the reaction proceeds in a similar fashion to work by Burrows et al.[102] by coordinating DPPE to palladium or platinum first, followed by introduction of the chelating ligand. In this way, complexes of formulae $[M(dppe)(\kappa S,S'\text{-}\mathbf{L^3})](PF_6)_2$ (M = Pd, **6a**; M = Pt **6b**), $[Pd(dppe)(\kappa S,S'$-

L^1)]Cl(PF_6) (**7**) and [Pd(dppe)(κ*S*,*S*′-L^4)]Cl(PF_6) (**8**) were synthesised and characterised. Complexes **6**–**8** all showed ^1H, $^{13}C\{^1H\}$ (solubility allowing) and ^{31}P NMR spectra consistent with a symmetrical bidentate binding mode of the neutral bis(thiourea) ligands to give either nine-membered or, in the case of **8**, ten-membered chelate rings. No evidence for binding of the pyridyl nitrogen atom of L^4 in **8** was observed, presumably because only two sites on the palladium(II) centre are available for coordination. Nine-membered chelate rings are rare, with only one other disulfur example, nitrosyl hydrotris(3,5-dimethylpyrazolyl)borate-*N*-ethylthio(mercaptopropionamide) molybdenum, found in the CSD.[103] Ten-membered rings are also highly unusual, with the only examples involving partially coordinated sulfur macrocycles on osmium clusters.[104]



Crystals of the mixed-anion acetone solvate [Pd(dppe)(κ*S*,*S*′-L^3)]Cl(PF_6)·$(CH_3)_2CO$ were obtained by slow evaporation of a solution of **6** in acetone/diethyl ether. The molecular structure confirms the *S*,*S*′ binding mode and formation of the nine-membered chelate ring (Figure 6a). The structure adopts a conformation in which the axial region on the square-planar palladium(II) centre is occupied by the aromatic ring of the benzo-spacer bis(thiourea) ligand ($C_{centroid}$–Pd = 3.42 Å; closest C–Pd contact 3.14 Å; lower aryl C=C–Pd distance 3.07 Å). The thioureido group of one ligand arm is disordered over two sites; one site forms a hydrogen bond to the acetone solvent of crystallisation molecule (N(4) and N(3)), whereas in the other conformation both N(4′) and N(3′) form hydrogen bonds to the chloride counterion to give a chloride-bridged, hydrogen-bonded dimer (Figure 6b). The bond lengths to the metal are within expected ranges and the angles around the square-planar palladium centre deviate only slightly from 90°. The crystals obtained arise from incomplete metathesis of chloride counterions with hexafluorophosphate anions and thus the crystals contain one anion of each type. For analytical purposes, the

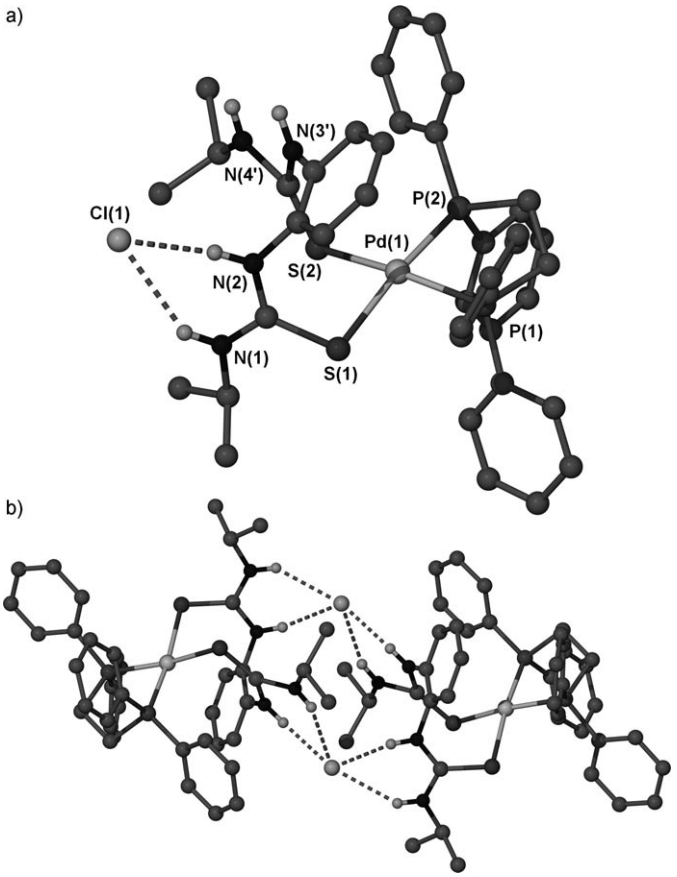


Figure 6. a) The molecular structure of [Pd(dppe)(L^3)]Cl(PF_6)·$(CH_3)_2CO$, displaying the ligand aryl···Pd interaction and hydrogen bonding to the chloride counterion and acetone solvent molecule. b) Hydrogen bonding to the chloride counterion to give a dimeric structure.

product was stirred with an excess of NH_4PF_6 to force complete metathesis. However, this tendency to retain at least one chloride anion proved to be a general feature of these types of compound and **7** and **8** were characterised as mixed salts.

Reactions with iridium complexes: Although a complex mixture of products was obtained from the direct treatment of L^3 with [{Ru(η^6-$C_6H_4MeCH(Me)_2$)Cl(μ-Cl)}$_2$] in dichloromethane, an analogous reaction with the pentamethylcyclopentadienyl iridium(III) chloride-bridged dimer [{Ir(η^5-C_5Me_5)Cl(μ-Cl)}$_2$][105] proceeded cleanly to give a single product [{Cp*IrCl(μ-*S*,*S*′-L^3)}$_2$](Cl)$_2$ (**9**), which was isolated as the acetone solvate and characterised by single crystal X-ray diffraction. The structure contrasts significantly to compounds **2**–**8** in that it is a 2+2 metallomacrocycle in which two neutral L^3 ligands are bridged by their sulfur atoms between two iridium(III) centres. The structure has the same 1:1 metal/ligand ratio as adduct **1**, however, and it is possible that a similar macrocyclic species is part of the equilibrating mixture observed in the ruthenium complex. The coordination geometry about the iridium ions is of the usual pianostool variety with the "legs" comprised of two thiourea

sulfur atoms from two different $\mathbf{L^3}$ ligands and a terminal chloride ligand as shown in Figure 7. The thiourea groups adopt an *anti* conformation with one NH group from each

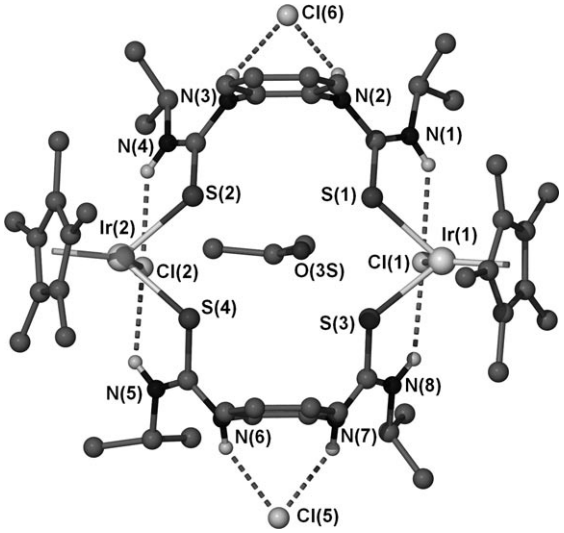


Figure 7. The X-ray crystal structure of $[\{Cp^*IrCl(\mu\text{-}S,S'\text{-}\mathbf{L^3})\}_2](Cl)_2$ (**9**), showing the included acetone molecule and hydrogen bonding to both coordinated and uncoordinated chloride. The intramolecular hydrogen bonding appears to be responsible for the *cisoid* conformation of the chloride ligands on the two metal centres.

thiourea forming a hydrogen bond to a chloride counterion whereas the other forms an unusual intramolecular hydrogen bond to the coordinated chloride ligand. The geometry of $\mathbf{L^3}$ means that these hydrogen bonds necessarily occur on one face of the ligand and thus the two chloride ligands on the two Ir^{III} ions are mutually eclipsed in a *cisoid* geometry rather than adopting a *transoid* disposition of the type seen in the halide-bridged starting materials, for example.[106] The two phenylene linkers of the two $\mathbf{L^3}$ ligands define the walls of a molecular cavity that is occupied by either an acetone molecule or a disordered acetone/THF mixture (two independent molecules). Metathesis of **9** with $AgBF_4$ gave the analogous tetrafluoroborate salt, $[\{Cp^*IrCl(\mu\text{-}S,S'\text{-}\mathbf{L^3})\}_2](BF_4)_2$ (**9′**), which still retains coordinated chloride ligands.

Anion binding by ruthenium complexes: Due to solubility constraints, we chose to study the anion-binding behaviour of ligands $\mathbf{L^3}$ and $\mathbf{L^4}$ in comparison with their ruthenium derivates as BF_4 salts (i.e., **2b′** and **4′**). A variety of anions were introduced as NBu_4^+ salts. Binding constants were measured by using ^1H NMR spectroscopic titration and, in the case of the metal BF_4^- complexes, ^{19}F NMR spectroscopy at room temperature. Binding constants were calculated by using non-linear least-squares regression with the HypNMR2006 software[107,108] and are summarised in Table 1.

In all cases, the resonances assigned to the NH groups shifted downfield upon titration with anions due to the formation of hydrogen-bonded host–anion complexes

Table 1. Anion binding constants for ligand $\mathbf{L^3}$ and complexes **2b′** and **4′**.[a]

Anion	$\mathbf{L^3}$	**2b′**		**4′**	
	$\log\beta_{11}$	$\log\beta_{11}$	$\log\beta_{21}$	$\log\beta_{11}$	$\log\beta_{12}/_{21}$
Cl^-	3.52(8)[b]	>5[b]	>5[b]	4.10(3)[d]	7.05(6)[d,e]
	1.29(2)[c]	1.50(6)[c]	2.82(5)[c]	3.02(3)[c]	5.20(9)[c,f]
AcO^-	3.52(9)[b]	dep	dep	dep[d]	dep[d]
Br^-	3.01(3)[b]	>5[b]	>5[b]	3.92(2)[d]	6.10(6)[d,e]
NO_3^-	2.30(2)[b]	4.34(7)	5.66(7)	3.96(2)[d]	6.22(5)[d,e]
HSO_4^-	2.28(3)[b]	>5[b]	>5[b]	ppt[d]	ppt[d]
I^-	1.81(1)[b]	3.59(1)[b]	5.91(4)[b]	3.29(5)[d]	5.79(12)[d,e]
ReO_4^-	0.78(1)[b]	<1[b]	–	–	–

[a] Abbreviations: dep = deprotonation, ppt = precipitation. [b] Acetone. [c] DMSO. [d] Chloroform. [e] $\text{Log}\beta_{12}$ (two anions per host) also includes host dimerisation constant $\log\beta_{20} = 2.07$. [f] $\text{Log}\beta_{21}$ (anion binding by host dimer).

(Figure 8). For the metal complexes, these changes were mirrored by a corresponding upfield shift in the chemical shift of the BF_4^- ions in the ^{19}F NMR spectra due to the displacement of the weakly bound BF_4^- ion by the more strongly bound guest anions (Figure 9).

For free $\mathbf{L^3}$, titration experiments were undertaken in $[D_6]$acetone. The free ligand shows the highest binding constants for chloride and acetate, with affinity decreasing according to the negative charge density of the anion in an anti-Hofmeister fashion (Table 1). The small variation in the chemical shift observed for perrhenate indicates very weak binding. A Job plot with Cl^- confirmed that binding occurs through a 1:1 complex and the binding mode was confirmed by means of a single-crystal X-ray structure of the bromide complex of $\mathbf{L^3}$ (Figure 10). The structure shows the anion bound within a receptor cleft formed by the two *syn* thiourea units to form four NH···Br^- hydrogen bonds in a similar fashion to carboxylate binding by the related bis(urea) analogue.[109,110] Anion binding by the diphenyl analogue of $\mathbf{L^3}$ has been previously reported to be weak in the highly competitive solvent DMSO/water because of steric interactions between the sulfur atoms and the phenylene hydrogen atoms. The structure of $\mathbf{L^3}\cdot Br^-$ shows that the sulfur atoms do indeed adopt an out-of-plane conformation but this does not entirely prevent effective anion binding in the present case, albeit in less competitive media.[109]

The anion binding of $\mathbf{L^4}$ was examined in acetone and DMSO. Anion binding was extremely weak in both solvents, with only small chemical shift changes observed. This ineffective complexation is attributed to the formation of intramolecular hydrogen bonding from the thiourea NH groups to the pyridyl nitrogen atom. This hypothesis was confirmed by the X-ray crystal structure of the $NBu_4^+Cl^-$ complex of $\mathbf{L^4}$, which shows chloride binding to only one thiourea group, with the other forming an intramolecular NH···N_{py} interaction with a bifurcated component (Figure 10b).

In comparison with the free ligand, anion binding by both **2b′** and **4′** proved to be extremely strong, with the Cl^- affinity of **2b** in acetone being too high to measure accurately by NMR spectroscopic methods (acetone was used for comparison with the free ligand). This added affinity is interpreted

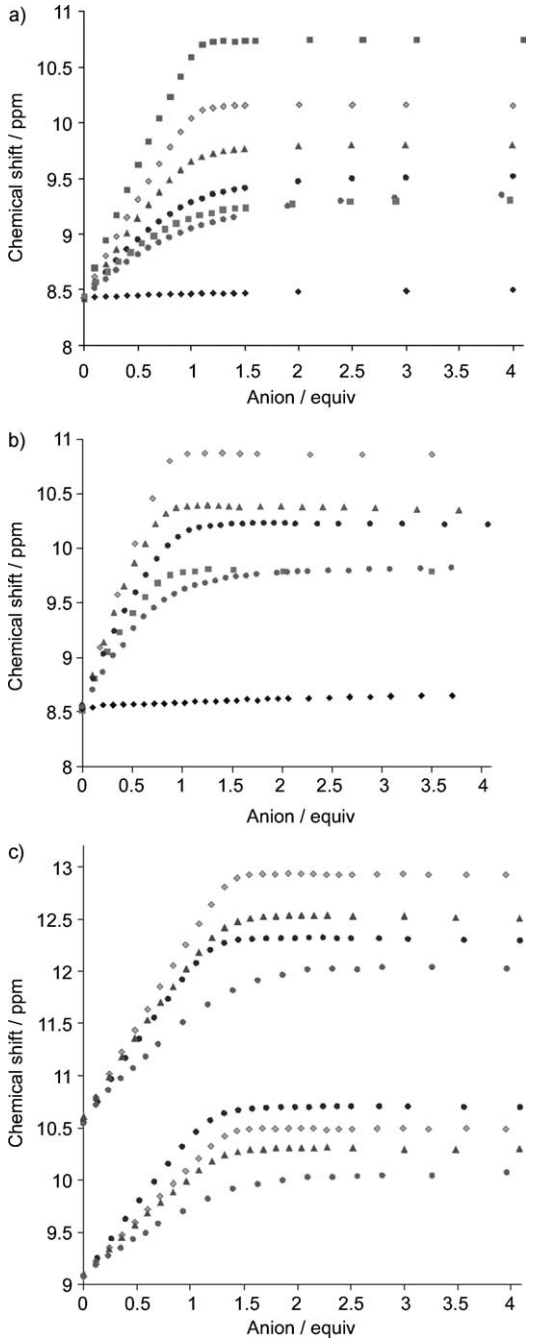


Figure 8. The change in chemical shift of the NH resonance adjacent to the phenylene ring for a) $\mathbf{L^3}$, b) ruthenium complex $\mathbf{2b'}$ in [D_6]acetone and c) both NH resonances in complex $\mathbf{4'}$ in chloroform upon addition of different anions (■: AcO^-, ◆: Cl^-, ▲: Br^-, ●: I^-, ●: NO_3^-, ■: HSO_4^-, ◆: ReO_4^-).

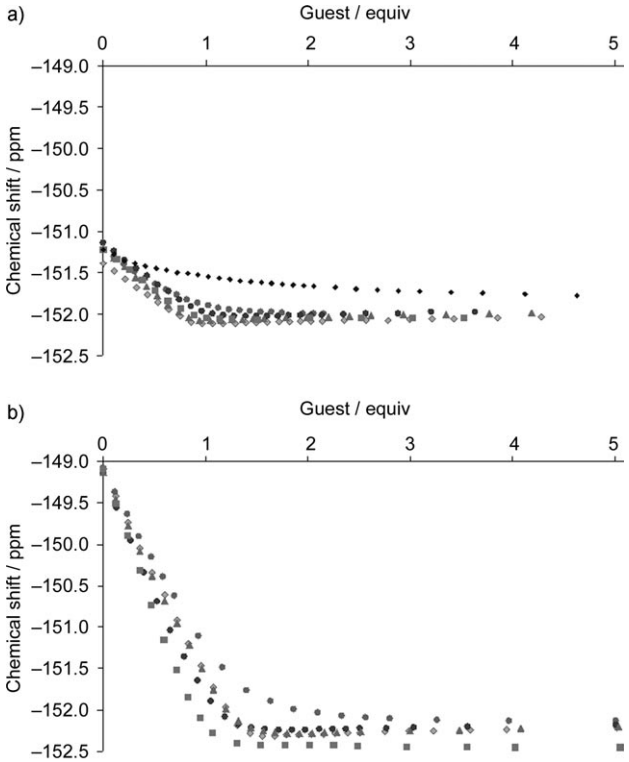


Figure 9. The change in chemical shift for BF_4^- anion by ^{19}F NMR spectroscopy (a) of **2b'** in [D_6]acetone and (b) **4'** in chloroform upon addition of different anions (■: AcO^-, ◆: Cl^-, ▲: Br^-, ●: I^-, ●: NO_3^-, ■: HSO_4^-, ◆: ReO_4^-).

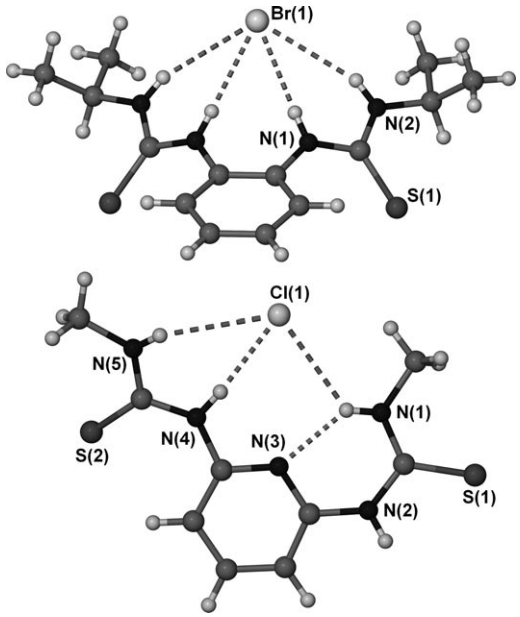


Figure 10. The X-ray crystal structures of the NBu_4^+ bromide complex of $\mathbf{L^3}$ (top) and the NBu_4^+ chloride complex of $\mathbf{L^4}$ (bottom).

as arising from the high degree of preorganisation afforded by the metal centre, the polarising effect on the NH bonds from coordination to the dicationic metal ion and the positive charge itself. This enhancement occurs despite the fact that only three NH groups are available in **2b** as opposed to four in $\mathbf{L^3}$. A Job plot of Cl^- complexation by $\mathbf{2b'}$ in acetone shows a peak at around 0.6 host/guest ratio, suggesting the coexistence of both 1:1 and 2:1 host guest complexes (Figure 11a). This stoichiometry fits the titration data well in cases where binding constants were low enough to be refined. It is likely that at low chloride concentration two monocationic hosts fit around the guest anion because a

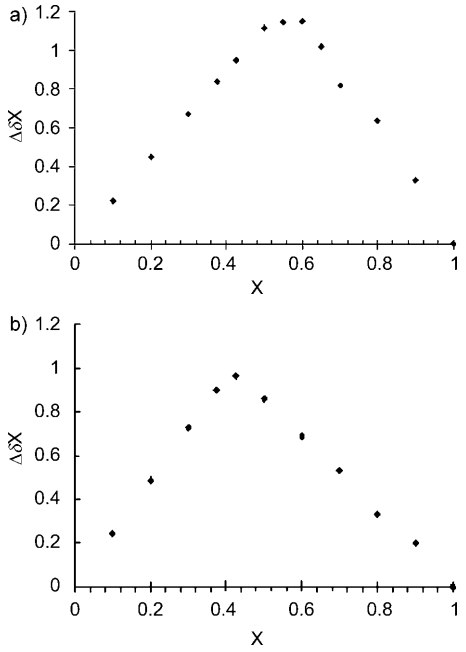


Figure 11. Job plots for Cl^- binding by a) **2b′** in [D_6]acetone and b) **4′** in chloroform. X is the mole fraction of the host.

single host does not cover more than half of the anion surface. Similar 2:1 complexes have been observed in other organometallic anion hosts.[70] In the more competitive DMSO, both 1:1 and 2:1 binding constants for **2b′** chloride complexes were obtained and the complex again proved to be a stronger anion-binding receptor than the free ligand (Table 1). In acetone, **2b′** bound strongly in a similar 1:1 and 2:1 stoichiometry with all other anions studied except ReO_4^-, which did not displace the BF_4^- counterion, and acetate, which resulted in loss of the NH resonance due to host deprotonation.

Complex **4** also proved to be an effective anion receptor in both chloroform and DMSO. The coordination of the pyridyl nitrogen atom makes the thiourea NH groups available for anion complexation and thus the coordination-induced enhancement is very significant compared to the negligible binding observed for the free ligand. Interestingly, a Job plot for this receptor (Figure 11b) suggested a mixture of 1:1 and 1:2 host–guest complexes with each of the two diverging coordinated thiourea groups binding to a single anion in this non-competitive medium, albeit in a non-cooperative fashion. The data proved difficult to fit without the introduction of a host dimerisation equilibrium for all anions, $\log\beta_{20} = 2.07$. Thiourea self-association in non-competitive solvents is known[111] and appears to be in competition with anion binding. However, the speciation behaviour was reversed in the more competitive DMSO, with the formation of 1:1 and 2:1 host–guest complexes similarly to **2b′**. Complexation of two anions in DMSO may be inhibited by solvent competition.

The ^{19}F NMR spectroscopic data for the displacement of BF_4^- by the more strongly bound anion guests is shown in Figure 9. This data bears out the 1:2 limiting stoichiometry of the complexes of **4′** in chloroform (Figure 9b). The chloroform data for **4′** shows a much larger change in chemical shift on going from bound to free BF_4^- as compared with the data obtained in acetone for **2b′**, probably as a result of more significat ion pairing of even the labile BF_4^- in chloroform. No chemical shift change for the BF_4^- anion was observed in DMSO, which confirms that tetrafluoroborate is not bound by these compounds in such a competitive solvent.

Conclusion

This work has revealed a number of unusual chelating coordination modes of bis(thiourea) ligands, including the formation of complexes with seven-, nine- and ten-membered chelate rings. Compounds of type **2** exhibit interesting *syn*/*anti* isomerism that is slow on the NMR spectroscopic timescale in some complexes and impacts on their anion-binding behaviour. Generally, however, metal coordination enhances the preorganisation and hydrogen-bond acidity of bis(thiourea) receptors as well as imparting a positive charge that makes them more effective as anion hosts as compared with the free ligands. Metal coordination can also remove the possibility of competing ligand–ligand hydrogen-bonding interactions. The strong coordination of sulfur donor ligands and second- and third-row transition-metal complexes, along with the terdentate chelate nature of the complexes in compounds of type **2** and **4** means that these species are stable even in highly competitive solvents, such as DMSO, and function as effective anion-binding hosts. In addition to the usual ^1H NMR spectroscopic titration, ^{19}F NMR spectroscopy has been shown to be an effective complementary tool for the study of anion-binding processes.

Experimental Section

General procedures: All procedures were carried out under an atmosphere of dry oxygen-free nitrogen by using standard Schlenk techniques. Elemental analyses were performed by using a Carlo Erba Instruments EA 1108 CHNS/O microanalyser. IR spectra were recorded by using a Shimadzu IRPRESTIGE-21 spectrophotometer using a pure solid sample over an ATR device (4000–700 cm^{-1} range). FAB mass spectra were recorded by using a VG Biotech Quattro Spectrometer. NMR spectra were recorded at RT (25 °C) by using Varian Unity Inova-400 (400 MHz for ^1H; 100.6 MHz for ^{13}C) and Varian Inova FT-500 (500 MHz for ^1H; 125 MHz for ^{13}C) spectrometers. ^1H shifts (ppm) were recorded by using the residual proton of the solvent as the internal standard. Solvents were supplied by SDS (reactive degree), and distilled from the appropriate drying agents and degassed before use. Starting materials $[\{Ru(\eta^6\text{-}C_6H_4MeCH(Me)_2)Cl(\mu\text{-}Cl)\}_2]$,[81] $[\{Ir(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$,[105] $[Pt(MeCN)_2Cl_2]$,[112] $[Pt(MeCN)_2Cl_2]$[112] and ligand **L**[5][75] were prepared according to literature procedures. $AgBF_4$ and isothiocyanate derivatives were purchased from Aldrich and used without further purification.

Anion titration

Job plot: Equimolar solutions of the host (2.9 mM) and guest in [D_6]acetone and [D_6]DMSO were prepared and mixed in various ratios. ^1H and ^{19}F NMR spectra of the solutions were recorded, and the change

in the chemical shifts of the protons of the amine groups and the fluorine atoms of the BF_4 counterion were analysed.

Titration: ^{1}H NMR spectroscopic titration experiments were carried out by using a Varian Inova 500 MHz NMR spectrometer. All chemical shifts are reported in ppm relative to tetramethylsilane as an internal reference. A known concentration of the host species (typically 0.06 M) in deuterated solvent (0.5 mL) was made up in a NMR tube. Solutions of the anions (as NBu_4^+ salts) were made up in the same deuterated solvent in volumetric flasks (2 mL) at a concentration five times greater than the host. The solution of the guest was titrated into the host solution at initial volumes of 10 μL (0.1 equiv with respect to the host) and homogenised by rigorous shaking, then spectra were recorded after each addition. Larger aliquots were added when little change was observed in the spectra. Results were analysed by using the curve-fitting program HypNMR 2006, simultaneously fitting as many resonances as could be accurately monitored during the experiment.

Synthesis of ligands

*Methyl-3-[2-(3-methylthioureido)ethyl]thiourea (**L^1**)*: Ethylenediamine (0.60 g, 10.3 mmol) and methylisothiocyanate (1.6 g, 21.9 mmol) were dissolved in dichloromethane (30 mL), and the solution was heated at reflux for 1.5 h. After this time, the white precipitate was removed by filtration (yield = 1.9 g, 9.2 mmol, 89%). ^{1}H NMR (CD_3CN/[D_6]DMSO, 400 MHz) δ = 2.88 (br, s, 6H; CH_3), 3.58 (br, s, 4H; CH_2), 7.10 (br, s, 2H; NH-(CH_2)), 7.23 ppm (br, s, 2H; NH(CH_3)); {^{1}H}^{13}C NMR ([D_6]DMSO, 101 MHz) δ = 31.15, 43.49, 182.68 ppm; IR: $\tilde{\nu}$ = 3267 (br, N–H), 3209 (br, N–H), 1557 (s, NH), 1224 (m, C=S), 1063 cm^{-1} (m, C=S); EI-MS: *m*/*z*: 206 [*M*]$^+$; elemental analysis calcd (%) for $C_6H_{14}N_4S_2$: C 34.93, H 6.84, N 27.15; found: C 34.74, H 6.96, N 27.18.

*Methyl-3-[2-(3-methylthioureido)phenylene]thiourea (**L^2**)*: 1,2-Phenylenediamine (0.88 g, 8.2 mmol) was dissolved in methanol (50 mL) and slowly added (ca. 1 h) to a stirred solution of methylisothiocyanate (1.28 g, 17.6 mmol) in methanol (30 mL). The mixture was heated at reflux for 2 h. The solvent was removed in vacuo and the resulting solid was washed with anhydrous diethyl ether (2×10 mL) and methanol (4×5 mL) to give a white solid (yield = 1.35 g, 5.3 mmol, 65%). ^{1}H NMR ([D_6]DMSO, 300 MHz): δ = 2.89 (br, s, 6H; CH_3), 7.20 (br, s, 2H; CH_{Ar}), 7.41 (br, s, 2H; CH_{Ar}), 7.73 (br, s, 2H; NH), 9.03 ppm (br, s, 2H; NH); {^{1}H}^{13}C NMR ([D_6]DMSO, 101 MHz): δ = 31.81, 126.62, 128.18, 134.23, 182.21 ppm; IR: $\tilde{\nu}$ = 3275 (br, N–H), 3224 (br, N–H), 1613 (s, NH), 1262 (s, C=S), 1055 cm^{-1} (s, C=S); ESI-MS: *m*/*z*: 255.1 [*M*+H]$^+$ (100); elemental analysis calcd (%) for $C_{10}H_{14}N_4S_2$: C 47.22, H 5.55, N 22.03; found: C 47.04, H 5.64, N 21.66.

*Isopropyl-3-[2-(3-isopropylthioureido)phenylene]thiourea (**L^3**)*: 1,2-Phenylenediamine (0.7 g, 6.5 mmol) and isopropyl isothiocyanate (1.5 g, 14.8 mmol) were sonicated together for 5 min in hot EtOH (2 mL). Crystals suitable for X-ray crystallography crystallised from solution over the course of 2 d, and more product could be isolated from the mother liquor over a period of a few days (yield = 1.9 g, 6.1 mmol, 95%). ^{1}H NMR ([D_6]acetone, 400 MHz): δ = 1.21 (d, ^3J = 6.4 Hz, 12H; C-(CH_3)$_2$), 4.50 (br, s, 2H; CH-(Me)$_2$), 7.05 (br, s, 2H; NH), 7.24 (m, 2H; CH_{Ar}), 7.45 (br, s, 2H; CH_{Ar}), 8.43 ppm (br, s, 2H; NH); {^{1}H}^{13}C NMR ([D_6]DMSO, 101 MHz): δ = 22.31, 46.41, 126.52, 128.24, 134.36, 180.06 ppm; IR: $\tilde{\nu}$ = 3315 (br, N–H), 3256 (br, N–H), 1598 (s, NH), 1264 (s, C=S), 1126 cm^{-1} (s, C=S); ESI-MS: 311.1 [*M*+H]$^+$ (100); elemental analysis calcd (%) for $C_{14}H_{22}N_4S_2$: C 54.16, H 7.14, N 18.04; found: C 54.15, H 7.23, N 18.02.

*1-Methyl-3-[6-(3-methylthioureido)pyridin-2-yl]thiourea (**L^4**)*: 2,6-Diaminopyridine (1.0 g, 9.2 mmol) and methylisothiocyanate (1.5 g, 20.5 mmol) were dissolved in methanol (20 mL) and heated at reflux for 4 H; then cooled and the grey precipitate was filtered off (yield = 0.97 g, 3.8 mmol, 42%). ^{1}H NMR ([D_6]DMSO, 400 MHz): δ = 3.03 (d, ^3J = 4.4 Hz, 6H; CH_3), 6.90 (d, ^3J = 8.4 Hz, 2H; H_{Ar}), 7.66 (t, ^3J = 8.4 Hz, 1H; H_{Ar}), 9.75 (br, s, 2H; NH_{Me}), 10.36 ppm (br, s, 2H; $NH_{(Ar)}$); {^{1}H}^{13}C NMR ([D_6]DMSO, 101 MHz): δ = 32.04, 106.60, 140.72, 150.92, 180.33 ppm; IR: $\tilde{\nu}$ = 3238 (s, N–H), 1633 (m, N–H), 1618 (s), 1225 (s, C=S), 1156 (s, C=S), 1066 cm^{-1} (s, C=S); ESI-MS (MeCN): *m*/*z*: 256.0 [*M*+H]$^+$ (100); elemental analysis calcd (%) for $C_9H_{13}N_5S_2$: C 42.33, H 5.13, N 27.42; found: C 42.29, H 5.13, N 27.43.

Synthesis of metal complexes

*[Ru(η^6-$C_6H_4MeCH(Me)_2$)(κS,S′,N-**L^2**−H)]Cl (**2a**)*: [{Ru(η^6-$C_6H_4MeCH(Me)_2$)Cl(μ-Cl)}$_2$] (0.31 g, 0.5 mmol) was dissolved in chloroform (50 mL) that had been degassed for 30 min with N_2. Under a nitrogen atmosphere, **L^2** (0.25 g, 1.0 mmol) was added and dissolved in the reaction mixture, which was then heated at reflux for 4 h. All solvent was then removed in vacuo to provide a crude product that displayed many broad resonances in the ^{1}H NMR spectrum. The crude product was dissolved in distilled water (50 mL) and filtered to remove a dark residue. The aqueous solution was washed with chloroform (5×20 mL) to extract the desired product. The combined organic fractions were dried ($MgSO_4$), filtered and all solvent was removed in vacuo to give an orange solid (yield = 0.4 g, 0.76 mmol, 76%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.07 (d, ^3J = 7.2 Hz, 3H; N-CH_3), 1.16 (d, ^3J = 7.2 Hz, 3H; N-CH_3), 2.05 (s, 3H; Ar-CH_3), 2.62 (m, 1H; CH cym) 2.77 (d, ^3J = 4.8 Hz, 3H; C-CH_3 *i*Pr), 2.99 (d, ^3J = 4.8 Hz, 3H; C-CH_3 *i*Pr), 5.03 (d, ^3J = 5.6 Hz, 1H; CH_{Ar}) 5.07 (d, ^3J = 5.6 Hz, 1H; CH_{Ar}), 5.16 (d, ^3J = 5.6 Hz, 1H; CH_{Ar}), 5.21 (d, ^3J = 5.6 Hz, 1H; CH_{Ar}), 5.44, (q, ^3J = 7.2 Hz, 1H; NH(Me)), 7.12 (br, s, 1H; CH_{Ar}), 7.13 (br, s, 1H; CH_{Ar}), 7.21 (br, s, 1H; CH_{Ar}), 7.23 (br, s, 1H; CH_{Ar}), 8.82 (q, ^3J = 7.2 Hz, 1H; NH(Me)), 10.94 ppm (s, 1H; NH(Ar)); {^{1}H}^{13}C NMR ($CDCl_3$, 400 MHz): δ = 18.75, 22.09, 22.77, 28.67, 31.46, 32.49, 82.22, 82.74, 82.85, 82.89, 97.55, 104.20, 126.09, 126.21, 127.10, 127.17, 132.91, 140.83, 181.43, 182.47 ppm; IR: $\tilde{\nu}$ = 3192 (br, N–H), 3044 (br, N–H), 1595 (s, NH), 1567 (s, NH), 1263 (m, C=S), 1040 cm^{-1} (m, C=S); ESI-MS: *m*/*z*: 489.1 [^{102}Ru(η^6-$C_6H_4MeCH(Me)_2$)(**L^2**−H)]$^+$ (100; Ru isotope envelope); elemental analysis calcd (%) for $RuC_{20}H_{27}N_4S_2Cl$: C 45.83, H 5.19, N 10.69; found: C 45.84, H 5.60, N 10.50.

*[Ru(η^6-$C_6H_4MeCHMe_2$)(κS,S′,N-**L^3**−H)]Cl (**2b**)*: [{Ru(η^6-$C_6H_4MeCH(Me)_2$)Cl(μ-Cl)}$_2$] (79 mg, 0.13 mmol) and **L^3** (81 mg, 0.26 mmol) were dissolved in $CHCl_3$ (25 mL) and stirred at RT for 3 h. The crude product was obtained by removing all solvent in vacuo (150 mg), and was then sonicated for 10 min in distilled water to dissolve the product. The aqueous solution was filtered to remove any undissolved material and extracted with $CHCl_3$ (3×8 mL). The orange organic fraction was dried ($MgSO_4$) and filtered, then all solvent was removed in vacuo to give an orange solid (yield = 55 mg, 0.095 mmol, 65%). ^{1}H NMR (acetone, 400 MHz): δ = 1.08 (d, ^3J = 6.90 Hz, 3H; $Me_{a'}$), 1.10 (d, ^3J = 6.6 Hz, 3H; Me_a), 1.20 (d, ^3J = 6.6 Hz, 3H; $Me_{b'}$), 1.23 (d, ^3J = 6.0 Hz, 3H; Me_b), 1.24 (d, ^3J = 6.0 Hz, 6H; $Me_{c,d}$), 2.12 (s, 3H; Me′), 2.70 (sept., ^3J = 6.9 Hz, 1H; CH ($H_{7'}$)), 3.88 (m, 1H; CH (H_8)), 4.38 (m, 1H; CH (H_{10})), 5.30 (d, ^3J = 5.5 Hz, 2H; $H_{3',5'}$), 5.39 (d, ^3J = 5.8 Hz, 1H; $H_{2'}$), 5.47 (d, ^3J = 5.5 Hz, 1H; $H_{6'}$), 6.78 (d, ^3J = 8.35 Hz, 1H; NH_b), 7.06 (d, ^3J = 7.6 Hz, 1H; H_6), 7.13 (dd, ^3J = 7.3, 7.6 Hz, 1H; H_5), 7.19 (dd, ^3J = 7.3, 7.6 Hz, 1H; H_4), 7.37 (d, ^3J = 7.6 Hz, 1H; H_3), 10.85 (d, ^3J = 6.9 Hz, 1H; NH_c), 11.69 ppm (s, 1H; NH_a); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.03 (d, ^3J = 6.0 Hz, 3H; CH_3 (L, *i*Pr)), 1.04 (d, ^3J = 6.0 Hz, 3H; CH_3 (L, *i*Pr)), 1.13 (d, ^3J = 6.0 Hz, 3H; CH_3 (L, *i*Pr)), 1.15 (d, ^3J = 6.0 Hz, 3H; CH_3 (L, *i*Pr)), 1.23 (d, ^3J = 6.0 Hz, 3H; CH_3 (cym, *i*Pr)), 1.28 (d, ^3J = 6.0 Hz, 3H; CH_3 (cym, *i*Pr)), 2.03 (s, 3H; CH_3 (cym)), 2.60 (sept., ^3J = 6.0 Hz, 1H; CH (cym)), 3.78 (m, 1H; CH (L)), 4.35 (m, 1H; CH (L)), 4.89 (d, ^3J = 8.0 Hz, 1H; NH), 5.03, 5.04 (d, ^3J = 6.0 Hz, 2H; H_{Ar} (cym)), 5.14 (d, ^3J = 6.0 Hz, 1H; H_{Ar} (cym)), 5.21 (d, ^3J = 6.0 Hz, 1H; H_{Ar} (cym)), 7.09, 7.11, 7.12 (m, 3H; H_{Ar} (L)), 7.33 (m, 1H; H_{Ar} (L)), 9.91 (d, ^3J = 8.0 Hz, 1H; NH), 11.08 ppm (s, 1H; NH); {^{1}H}^{13}C NMR ($CDCl_3$, 500 MHz): δ = 19.05, 22.03, 22.63, 22.69, 22.93, 23.11, 23.61, 31.67, 44.78, 48.38, 82.50, 83.13, 83.38, 83.64, 98.07, 104.44, 126.35, 126.88, 126.95, 127.00, 133.03, 140.77, 178.62, 180.20 ppm; IR: $\tilde{\nu}$ = 3216 (br, N–H), 3132 (br, N–H), 1591 (s, N–H), 1561 (s, N–H), 1168 (m, C=S), 1129 cm^{-1} (m, C=S); ESI-MS: *m*/*z*: 545.1 [^{102}Ru(η^6-$C_6H_4MeCHMe_2$)(κ*S*,*S*′,*N*-**L^3**−H)]$^+$ (100; Ru isotope envelope); elemental analysis calcd (%) for $RuC_{24}H_{35}N_4S_2Cl$: C 49.68, H 6.08, N 9.66; found: C 48.70, H 6.08, N 9.33.

*[Ru(η^6-$C_6H_4MeCH(Me)_2$)(κS,S′,N-**L^1**−H)]Cl·H_2O (**3**)*: Compound **3** was prepared by using [{Ru(η^6-$C_6H_4MeCH(Me)_2$)Cl(μ-Cl)}$_2$] (80 mg, 0.13 mmol) and **L^1** (54 mg, 0.26 mmol) in a similar procedure to **2a** (yield = 88 mg, 0.18 mmol, 68%). ^{1}H NMR ($CDCl_3$, 400 MHz, two conformers were in ≈2:1 ratio): major conformer: δ = 1.26, 1.27 (d, ^3J = 6.0 Hz, 6H; CH_3 cym), 2.22 (s, 3H; CH_3 L), 2.67 (s, 3H; CH_3 L), 2.76 (sp, ^3J = 6.0 Hz, 1H; CH cym), 2.97 (br, s, 3H; CH_3 cym), 3.07 (m, 1H;

CH_2 L), 3.57 (m, 1H; CH_2 L), 3.79 (m, 1H; CH_2 L), 3.97 (m, 1H; CH_2 L), 5.12 (br, s, 1H; CH_{Ar}), 5.24 (br, s, 1H; CH_{Ar}), 5.32 (br, s, 1H; CH_{Ar}), 5.38 (br, s, 1H; CH_{Ar}), 6.21 (br, s, 1H; NH), 7.41 (br, s, 1H; NH), 9.22 ppm (br, s, 1H; NH); minor conformer: $\delta = 1.26$, 1.27 (d, $^3J = 6.0$ Hz, 6H; CH_3 cym), 2.22 (s, 3H; CH_3 L), 2.67 (s, 3H; CH_3 L), 2.76 (sp, $^3J = 6.0$ Hz, 1H; CH cym), 3.00 (br, s, 3H; CH_3 cym) 3.07 (m, 1H; CH_2 L), 3.31 (m, 1H; CH_2 L), 3.57 (m, 1H; CH_2 L), 3.97 (m, 1H; CH_2 L), 5.12 (br, s, 1H; CH_{Ar}), 5.24 (br, s, 1H; CH_{Ar}), 5.32 (br, s, 1H; CH_{Ar}), 5.42 (br, s, 1H; CH_{Ar}), 6.44 (br, s, 1H; NH), 8.14 (br, s, 1H; NH), 9.29 ppm (br, s, 1H; NH); $\{^1H\}^{13}C$ NMR ($CDCl_3$, 400 MHz): $\delta = 18.99$, 22.60, 23.21, 27.99, 31.83, 45.48, 46.92, 81.11, 82.47, 97.54, 104.47, 177.16, 180.79 ppm; ESI-MS: 441.2 $[^{102}Ru(\eta^6\text{-}C_6H_4MeCH(Me)_2)(\mathbf{L^1}-H)]^+$ (100; Ru isotope envelope); elemental analysis calcd (%) for $RuC_{16}H_{27}N_4S_2Cl.H_2O$: C 38.89, H 5.92, N 11.34; found C 38.77, H 5.96, N 10.91.

$[Ru(\eta^6\text{-}C_6H_4MeCH(Me)_2)(\kappa S,S',N\text{-}\mathbf{L^4})]Cl_2$ ***(4)***: $[\{Ru(\eta^6\text{-}C_6H_4MeCH(Me)_2)Cl(\mu\text{-}Cl)\}_2]$ (470.9 mg, 0.77 mmol) and $\mathbf{L^4}$ (393.0 mg, 1.54 mmol) were dissolved in degassed CH_2Cl_2 (40 mL) and heated at reflux under N_2 for 6 h. Orange crystals were obtained after concentrating the resultant red solution and crystallised by adding a layer of diethyl ether at 5 °C. Filtering and drying the crystals gave the pure product. Addition of water causes the formation of two isomers, the main one corresponds to a symmetric species while the minor one is asymmetric and is likely to arise from deprotonation (yield = 178 mg, 0.33 mmol, 95%). ^1H NMR ($CDCl_3$, 700 MHz): $\delta = 1.23$ (d, $^3J = 6.9$ Hz, 6H; Me cym), 1.89 (s, 3H; Me cym), 2.74 (sp, $^3J = 6.9$ Hz, 1H; CH cym), 3.31 (d, $^3J = 4.9$ Hz, 6H; Me), 5.53 (d, $^3J = 6.1$ Hz, 2H; H_{Ar} cym), 5.66 (d, $^3J = 6.1$ Hz, 2H; H_{Ar} cym), 7.37 (d, $^3J = 8.0$ Hz, 2H; Hpy), 7.67 (t, $^3J = 8.0$ Hz, 1H; Hpy), 10.55 (q, $^3J = 4.6$ Hz, 2H; NH), 13.01 ppm (s, 2H; NH); $\{^1H\}^{13}C$ NMR ($CDCl_3$, 700 MHz): $\delta = 18.62$ (Me′), 22.79 (Me″), 30.91 (CH_{cym}), 32.35 (Me), 88.32 (C^3_{cym}), 89.83 (C^2_{cym}), 105.88 (C^4_{cym}), 107.38 (C^1_{cym}), 112.79 (C^3_{py}), 142.38-(C^4_{py}), 153.62 (C^2_{py}), 179.74 ppm (C=S); IR: $\tilde{\nu} = 3167$ (br, N–H), 1621 (s, N–H), 1563 and 1545 (m, C=N), 1273 (m, C=S), 1180 (m, C=S), 1052 cm^{-1} (m, C=S); ESI-MS: *m/z*: 245.5 $[^{102}Ru(\eta^6\text{-}C_6H_4MeCH(Me)_2)L]^{2+}$, 265.5 $[^{102}Ru(\eta^6\text{-}C_6H_4MeCH(Me)_2)L(MeCN)]^{2+}$; elemental analysis calcd (%) for $RuC_{19}H_{27}N_5S_2Cl_2$: C 40.64, H 4.85, N 12.47; found: C 40.43, H 4.76, N 12.28.

$[Ru(\eta^6\text{-}C_6H_4MeCH(Me)_2)(\kappa S,S',N_{py}\text{-}L^4)](BF_4)_2$ ***(4′)***: Complex **4** (60 mg, 0.11 mmol) was dissolved in degassed CH_2Cl_2 (10 mL) and $AgBF_4$ (41.6 mg, 0.21 mmol) was added to produce a precipitation of AgCl. An orange powder was obtained by filtration of the solution and removal of the solvent by vacuum (yield = 178 mg, 0.33 mmol, 97%). ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 1.26$ (d, $^3J = 6.9$ Hz, 6H; Me cym), 1.89 (s, 3H; Me cym), 2.79 (sp, $^3J = 6.9$ Hz, 1H; CH cym), 3.38 (br, s, 6H; Me), 5.74 (d, $^3J = 6.1$ Hz, 2H; H_{Ar} cym), 5.82 (d, $^3J = 6.1$ Hz, 2H; H_{Ar} cym), 7.25 (d, $^3J = 8.0$ Hz, 2H; Hpy), 7.77 (t, $^3J = 8.0$ Hz, 1H; Hpy), 9.08 (br, s, 2H; NH), 10.51 ppm (s, 2H; NH); ^{19}F NMR ($CDCl_3$, 400 MHz): $\delta = -149.06$ ppm; IR: $\tilde{\nu} = 3318$ (br, N–H), 1613 (s, N–H), 1558 (m, C=N), 1282 (m, C=S), 1185 (m, C=S), 1024 cm^{-1} (br, B–F); elemental analysis calcd (%) for $RuC_{19}H_{27}N_5S_2B_2F_8$: C 34.36, H 4.10, N 10.54; found: C 34.29, H 4.25, N 9.99.

$[Ru(\eta^6\text{-}C_6H_4MeCH(Me)_2)Cl(\kappa S,N_{py}\text{-}L^5)]Cl{\cdot}2H_2O$ ***(5)***: $[\{Ru(\eta^6\text{-}C_6H_4MeCH(Me)_2)Cl(\mu\text{-}Cl)\}_2]$ (76 mg, 0.125 mmol) and $\mathbf{L^5}$ (60 mg, 0.25 mmol) were heated at reflux under N_2 in degassed $CHCl_3$ for 3 h. All solvent was then removed in vacuo to give a dark orange solid (yield = 124 mg, 0.21 mmol, 84%). ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 1.13$ (d, $^3J = 4.4$ Hz, 3H; CH_3 cym), 1.15 (d, $^3J = 4.4$ Hz, 3H; CH_3 cym), 1.87 (s, 3H; CH_3), 2.32 (s, 3H; CH_3), 2.71 (m, 1H; CH, cym), 5.22 (d, $^3J = 6.0$ Hz, 1H; CH_{Ar}, cym), 5.24 (d, $^3J = 6.0$ Hz, 1H; CH_{Ar}, cym), 5.38 (d, $^3J = 6.0$ Hz, 1H; CH_{Ar}, cym), 5.46 (d, $^3J = 6.0$ Hz, 1H; CH_{Ar}, cym), 7.13, (d, $^3J = 6.8$ Hz, 1H; CH_{Ar}, pyridyl), 7.17 (d, $^3J = 8.4$ Hz, 2H; CH_{Ar}, tolyl), 7.41 (d, $^3J = 8.4$ Hz, 2H; CH_{Ar}, tolyl), 7.56 (d, $^3J = 6.8$ Hz, 1H; CH_{Ar}, pyridyl), 7.73 (t, $^3J = 6.8$ Hz, 1H; CH_{Ar}, pyridyl), 8.83 (d, $^3J = 6.8$ Hz, 1H; CH_{Ar}, pyridyl), 11.95 (br, s, 1H; NH), 13.11 ppm (br, s, 1H; NH); $\{^1H\}^{13}C$ NMR ($CDCl_3$, 101 MHz): $\delta = 17.19$, 20.21, 21.29, 21.39, 29.69, 83.40, 84.05, 84.24, 85.76, 99.16, 105.96, 116.13, 120.32, 124.14, 128.70, 132.91, 136.87, 139.241, 152.00, 153.76, 176.79 ppm; IR (NH peaks obscured by H_2O peak): $\tilde{\nu} = 1628$ (s, N–H), 1219 (m, C=S), 1160 (m, C=S), 1057 cm^{-1} (m, C=S); ESI-MS: *m/z*: 478.0 $[^{102}Ru(\eta^6\text{-}C_6H_4MeCH(Me)_2)(\mathbf{L^5}-H)]^+$ (100; Ru isotope envelope); 519.0 $[^{102}Ru(\eta^6\text{-}C_6H_4MeCH(Me)_2)(\mathbf{L^5}-H)(MeCN)]^+$ (Ru isotope envelope); elemental analysis calcd (%) for $RuC_{23}H_{23}N_3SCl_2.2(H_2O)$: C 47.50, H 4.68, 7.23; found C 47.43, H 4.74, 7.14.

$[Pd(dppe)(\kappa S,S'\text{-}\mathbf{L^3})](PF_6)_2$ ***(6a)***: $Pd(MeCN)_2Cl_2$ (60 mg, 0.23 mmol) and DPPE (92 mg, 0.23 mmol) were dissolved in dichloromethane (20 mL) and stirred for 30 min to generate $Pd(dppe)Cl_2$ in situ, then a solution of $\mathbf{L^3}$ (72 mg, 0.23 mmol) in acetone (20 mL) was added. The solution was stirred for 5 H; then all solvent was removed in vacuo and the yellow solid was washed with hexane to give the crude product (180 mg). This crude product (90 mg) was dissolved in acetone/ethanol (50 mL; 1:1) before NH_4PF_6 (200 mg, excess) was added and the mixture stirred overnight. All solvent was then removed and the compound was extracted into $CDCl_3$ (2 mL) for NMR spectroscopy studies. After spectra had been obtained, all solvent was removed from this solution to give a yellow solid that was washed with diethyl ether (yield = 101 mg, 0.09 mmol, 89% based on 90 mg crude solid used in metathesis). ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 1.25$ (br, s, 6H; CH_3 L), 2.37 (br, s, 2H; CH_2 DPPE), 2.82 (br, s, 2H; CH_2 dppe), 4.28 (br, s, 2H; CH L), 5.91 (br, s, 2H; CH_{Ar}), 6.39 (br, s, 2H; CH_{Ar}), 7.38, 7.47, 7.60 (br, s, 20H; CH_{Ar} dppe), 7.82 (br, s, 2H; NH), 8.7 ppm (br, s, 2H; NH); $\{^1H\}^{13}C$ NMR ($CDCl_3$, 101 MHz): $\delta = 21.13$, 21.33, 29.88, 47.35, 127.63, 128.53, 128.64, 130.47, 131.67, 131.76, 131.86, 132.10, 132.81, 132.92, 175.07 ppm; $\{^1H\}^{31}P$ NMR ($CDCl_3$, 162 MHz): $\delta = 61.64$ (s, PPh_2), −144.02 ppm (sp, ^1J-(P,F) = 715 Hz, PF_6); IR: $\tilde{\nu} = 3353$ (br, N–H), 3220 (br, N–H), 1578 (s, N–H), 1243 (m, C=S), 1167 (m, C=S), 1104 (m, C=S), 840 cm^{-1} (vs, P–F); ESI-MS: *m/z*: 812.9 $[^{106}Pd(dppe)(\mathbf{L^3}-H)]^+$ (100; Pd isotope envelope); elemental analysis calcd (%) for $PdC_{40}H_{46}N_4S_2P_4F_{12}$: C 43.47, H 4.19, N 5.04; found: C 44.54, H 4.19, N 5.16.

$[Pt(dppe)(\kappa S,S'\text{-}\mathbf{L^3})](PF_6)_2$ ***(6b)***: $Pt(MeCN)_2Cl_2$ (100 mg, 0.29 mmol) and DPPE (114 mg, 0.29 mmol) were dissolved in CH_2Cl_2 (20 mL) to form Pt-(dppe)Cl_2 in situ, then $\mathbf{L^3}$ (78 mg, 0.29 mmol) in ethanol (20 mL) was added and the mixture was stirred for 2 h at RT. Then NH_4PF_6 (200 mg, excess) in acetone (10 mL) was added and the mixture was stirred for a further 1 h. All solvent was then removed in vacuo and the yellow solid was washed with CH_2Cl_2. The organic fraction was dried in vacuo to give a yellow solid (yield = 140 mg, 0.12 mmol, 40%). ^1H NMR ($CDCl_3$, 200 MHz): $\delta = 1.20$ (d, $^3J = 6.4$ Hz, 6H; CH_3), 1.28 (d, $^3J = 6.4$ Hz, 6H; CH_3), 2.0 (br, s, 2H; CH_2), 2.7 (br, s, 2H; CH_2), 4.26 (q, $^3J = 6.4$ Hz, 2H; CH), 6.00 (d, $^3J = 4.6$ Hz, 2H; CH_{Ar}), 6.41 (d, $^3J = 4.6$ Hz, 2H; CH_{Ar}), 7.06 (br, s, 2H; NH), 7.4–7.6 (m, 20H; CH_{Ar}), 8.68 ppm (br, s, 2H; NH); $\{^1H\}^{13}C$ NMR ($CDCl_3$, 101 MHz): $\delta = 21.22$, 29.92, 47.68, 124.60, 125.20, 126.13, 126.74, 127.03, 127.34, 127.64, 128.51, 130.14, 131.44, 132.07, 132.89, 173.44 ppm; $\{^1H\}^{31}P$ NMR ($CDCl_3$, 121 Hz): $\delta = 45.87$ (s with Pt satellites, ^1J(P,Pt) = 3128 Hz, $P(Ph_2)$), −141.16 ppm (sp, ^1J(P,F) = 715 Hz, PF_6); IR: $\tilde{\nu} = 3345$ (br, N–H stretch), 3246 (br, N–H stretch), 1574 (s, NH bend), 1166 (m, C=S stretch), 1105 (m, C=S stretch), 840 cm^{-1} (vs, P–F); ESI-MS: *m/z*: 905.3 $[^{195}Pt(dppe)(\kappa S,S'\text{-}\mathbf{L^3})]^+$ (^{195}Pt isotope envelope); elemental analysis calcd (%) for $PtC_{40}H_{46}N_4S_2P_4F_{12}$: C 40.24, H 3.88, N 4.69; found: C 40.14, H 3.98, N 5.03.

$[Pd(dppe)(\kappa S,S'\text{-}\mathbf{L^1})]Cl{\cdot}PF_6$ ***(7)***: A solution of $Pd(MeCN)_2Cl_2$ (50 mg, 0.19 mmol) and DPPE (77 mg, 0.19 mmol) in CH_2Cl_2 (20 mL) was stirred for 30 min to generate $Pd(dppe)Cl_2$ in situ, then $\mathbf{L^1}$ (39 mg, 0.19 mmol) in ethanol (20 mL) was added. This mixture was stirred for 1 h before an excess of NH_4PF_6 (120 mg) in ethanol (20 mL) was added and the mixture was stirred for a further 30 min. All solvent was then removed and the compound was extracted into chloroform (20 mL). The solvent was removed from this solution to give a yellow solid that was washed with diethyl ether (yield = 142 mg, 0.16 mmol, 84%). ^1H NMR (CD_3CN, 400 MHz): $\delta = 2.65$ (br, s, 6H; CH_3), 2.72 (br, s, 4H; CH_2), 3.32 (br, s, 2H; CH_2), 3.43 (br, s, 2H; CH_2), 6.83 (br, s, 2H; NH), 7.58 (br, s, 8H; CH_{Ar}), 7.67 (br, s, 4H; CH_{Ar}), 7.80 (br, s, 8H; CH_{Ar}), 8.26 ppm (br, s, 2H; NH); $\{^1H\}^{31}P$ NMR ($CDCl_3$, 162 MHz): $\delta = -136.2$ (sept., ^1J(P,F) = 715 Hz, PF_6), 67.9 ppm (s, PPh_2); IR: 3385 (br), 3241 (br), 1588 (s), 1229 (m, C=S), 1188 (m, C=S), 1104 (m, C=S), 840 cm^{-1} (vs, P–F); ESI-MS (MeCN): *m/z*: 709.1 $[^{106}Pd(dppe)(\mathbf{L^1}-H)]^+$ (100; Pd isotopic envelope); elemental analysis calcd (%) for $PdC_{32}H_{38}N_4S_2P_3F_6Cl$: C 43.11, H 4.30, N 6.28; found: C 43.39, H 4.00, N 3.82.

*[Pd(dppe)(κS,S′-**L**^{4})]Cl·PF$_6$ (**8**)*: $Pd(MeCN)_2Cl_2$ (50 mg, 0.19 mmol) and DPPE (77 mg, 0.19 mmol) were dissolved in CH_2Cl_2 (20 mL) and stirred for 30 min to generate [Pd(dppe)Cl_2] in situ, then **L**^{4} (48 mg, 0.19 mmol) in ethanol (20 mL) was added. This mixture was stirred for 1 h before an excess of NH_4PF_6 (120 mg) in ethanol (20 mL) was added. The mixture was stirred for a further 30 min, then all solvent was removed and the compound was extracted into $CHCl_3$ (20 mL). The solvent was then removed to give a yellow solid that was washed with diethyl ether (yield = 157 mg, 0.17 mmol, 88%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.66 (m, 2H; CH_2-P), 2.72 (m, 2H; CH_2-P), 2.98 (d, ^3J = 4.4 Hz, 6H; CH_3-N), 6.98 (br, s, 2H; CH_{Ar} (L)), 7.38 (br, s, 1H; CH_{Ar} (L), 7.45 (d, ^3J = 6.0 Hz, 8H; Ph-P), 7.54 (d, ^3J = 6.4 Hz, 4H; Ph-P), 7.70 (dd, ^3J = 6.4, 6.0 Hz, 8H; Ph-P), 9.26 (br, s, 2H; NH-Me), 10.26 ppm (br, s, 2H; NH-Ar); {^{1}H}^{31}P NMR ($CDCl_3$, 162 MHz): δ = −135.7 (sept., ^1J(P,F) = 715 Hz, PF_6), 66.5 ppm (s, PPh_2); IR: $\tilde{\nu}$ = 3393 (br, N−H), 3170 (br, N−H), 1612 (s, NH), 1259 (m, C=S), 1163 (m, C=S), 1103 (m, C=S), 1052 (m, C=S), 840 cm^{-1} (vs, P−F); ESI-MS (MeCN): *m/z*: 758.1 [^{106}Pd(dppe)(**L**^{4}−H)]$^+$ (100; Pd isotope envelope); elemental analysis calcd (%) for $PdC_{35}H_{37}N_5S_2P_3F_6Cl$: C 44.69, H 3.96, N, 7.45; found: C 44.40, H 4.00, N, 6.80.

*[{Cp*IrCl(μ-**L**^{3})}$_2$](Cl)$_2$ (**9**)*: A solution of **L**^{3} (101.5 mg, 0.33 mmol) in CH_2Cl_2 (2 mL) was added to a suspension of [{Cp*IrCl(μ-Cl)}$_2$] (123.4 mg, 0.16 mmol) in CH_2Cl_2 (2 mL) to give an orange solution. The mixture was stirred for 2 h and a yellow powder was obtained by precipitation with Et_2O. Orange single crystals were obtained by diffusion of a solution of the complex in acetone and Et_2O (yield 234 mg, 0.15 mmol, 50%). IR: $\tilde{\nu}$ = 3209 (br, N−H), 1260 (s, C=S), 1027 cm^{-1} (s, C=S); MALDI MS: 637.4 [Cp*Ir(**L**^{3})]$^+$ (100), 673.3 [Cp*Ir(L)Cl]$^+$ (25), 997.5 [(Cp*Ir)$_2$(**L**^{3}−4H)Cl]$^+$ (10); elemental analysis calcd (%) for $H_{74}C_{48}N_8S_4Cl_4Ir_2$·2($Me_2CO$): C 42.29, H 5.65, N 7.31; found C 42.12, H 5.59, N 7.30.

*[{Cp*IrCl(μ-**L**^{3})}$_2$](BF$_4$)$_2$ (**9′**)*: $AgBF_4$ was added to a solution of **9** in dry CH_2Cl_2 (2 mL) and filtered to give a yellow solution that was concentrated in vacuo to give a yellow solid that was washed with Et_2O (95% yield). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 12.40 (s, 1H; NH), 10.51 (s, 1H; NH), 10.09 (s, 1H; NH), 9.84 (s, 1H; NH), 7.97 (t, J = 8.1 Hz, 1H; CH_{Ar}), 7.63 (t, J = 8.1 Hz, 1H; CH_{Ar}), 7.09 (d, J = 8.1 Hz, 1H; CH_{Ar}), 6.99 (d, J = 8.0 Hz, 1H; CH_{Ar}), 1.53 ppm (s, 15H; Me); IR: $\tilde{\nu}$ = 3223 (br, N−H), 1232 (s, C=S), 1096 (s, C=S), 1052 cm^{-1} (s, B−F); MALDI MS: *m/z*: 637.3 [Cp*Ir(L)]$^+$ (100), 673.3 [Cp*Ir(L)Cl]$^+$ (25), 997.5 [(Cp*Ir)$_2$(L−4H)Cl]$^+$ (10); elemental analysis calcd (%) for $H_{74}B_2C_{48}N_8F_8S_4Cl_2Ir_2$: C 42.29, H 5.65, N 7.31; found C 41.92, H 5.91, N 7.37.

Crystal structure refinement and analysis: The diffraction experiments, performed by using graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å), were carried out by using SMART 1000, SMART 6000 or APEX ProteumM instruments (X-rays from a 60 W microfocus Bede Microsource with glass polycapillary optics), covering a full sphere of the reciprocal space by using three or four runs of narrow-frame (0.3°) ω scans. The crystals were cooled by using Cryostream (Oxford Cryosystems) open-flow N_2 cryostats. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 for all data by using SHELXTL software.[113,114] Structure visualisation and figure preparations was carried out by using X-Seed.[115, 116] Details of individual structures are given below.

*[Ru((η^6-C$_6$H$_4$MeCH(Me)$_2$)(κS,S′,N-**L**^{2}−H)]Cl (**2a**)*: Diffraction-quality single crystals were obtained by cooling and slow evaporation of a hot solution of [Ru(η^6-C_6H_4MeCH(Me_2)(κS,S,N-**L**^{2}−H)]Cl in ethyl acetate. Crystal data for $C_{20}H_{27}ClN_4RuS_2$: M_r = 524.10; red small plate; 0.09 × 0.04 × 0.03 mm^3; triclinic; space group $P\bar{1}$ (No. 2); a = 9.9266(9), b = 14.8915(13), c = 24.231(2) Å; α = 74.849(2), β = 80.322(2), γ = 79.488(2)°; V = 3371.9(5) Å^3; Z = 6; ρ_{calcd} = 1.549 g cm^{-3}; F_{000} = 1608; APEX; T = 120(2) K; $2\theta_{max}$ = 50.0°; 54743 reflections collected, 11857 unique (R_{int} = 0.0676); final GOF = 1.020, R_1 = 0.0390, wR_2 = 0.0794, R indices based on 8771 reflections with $I > 2\sigma(I)$ (refinement on F^2); 772 parameters, 0 restraints; LP and absorption corrections applied; μ = 1.016 mm^{-1}.

*[Ru(η^6-C$_6$H$_4$MeCH(Me)$_2$)(κS,S′,N-**L**^{3}−H)]Cl (**2b**)*: Diffraction-quality single crystals were obtained by slow evaporation of a solution of the complex in acetone/diethyl ether. Crystal data for $C_{24}H_{35}ClN_4RuS_2$: M_r = 580.20; red block; 0.30 × 0.20 × 0.20 mm^3; triclinic; space group $P\bar{1}$ (No. 2); a = 10.0505(6), b = 11.2786(7), c = 13.1434(8) Å; α = 71.008(2), β = 73.421(2), γ = 83.534(2)°; V = 1349.89(14) Å^3; Z = 2; ρ_{calcd} = 1.427 g cm^{-3}; F_{000} = 600; SMART 6000; T = 120(2) K; $2\theta_{max}$ = 58.3°; 23947 reflections collected, 7277 unique (R_{int} = 0.0227); final GOF = 1.040; R_1 = 0.0244, wR_2 = 0.0601, R indices based on 6538 reflections with $I > 2\sigma(I)$ (refinement on F^2), 308 parameters, 0 restraints; LP and absorption corrections applied; μ = 0.853 mm^{-1}.

*[Ru(η^6-C$_6$H$_4$MeCH(Me)$_2$)(κS,S′,N-**L**^{1}−H)]Cl·H$_2$O (**3**)*: Diffraction-quality single crystals were obtained by slow evaporation of a solution of the complex in acetone/diethyl ether. Crystal data for $C_{16}H_{29}ClN_4ORuS_2$: M_r = 494.07; red block; 0.30 × 0.20 × 0.20 mm^3; monoclinic; space group $P2_1/c$ (No. 14); a = 15.238(3), b = 11.869(2), c = 11.441(2) Å; β = 94.029(5)°; V = 2064.1(7) Å^3; Z = 4; ρ_{calcd} = 1.590 g cm^{-3}; F_{000} = 1016; SMART 1000; T = 120(2) K; $2\theta_{max}$ = 58.3°; 29337 reflections collected, 5553 unique (R_{int} = 0.0684); final GOF = 1.024; R_1 = 0.0349, wR_2 = 0.0631, R indices based on 4347 reflections with $I > 2\sigma(I)$ (refinement on F^2), 251 parameters; 0 restraints; LP and absorption corrections applied; μ = 1.104 mm^{-1}.

*[Ru(η^6-C$_6$H$_4$MeCH(Me)$_2$)(κS,S′,N$_{py}$-**L**^{4})]Cl$_2$·2CH$_2$Cl$_2$ (**4**)*: Diffraction-quality single crystals were obtained by slow evaporation of a solution of the complex in dichloromethane. Crystal data for $C_{21}H_{31}Cl_6N_4RuS_2$: M_r = 547.54; red fragment of block; 0.18 × 0.14 × 0.12 mm^3; monoclinic; space group $P2_1/n$ (No. 14); a = 13.6090(8), b = 17.8909(10), c = 13.7951(8) Å; β = 117.888(2)°; V = 2968.7(3) Å^3; Z = 5; ρ_{calcd} = 1.531 g cm^{-3}; F_{000} = 1395; CCD area detector; T = 120(2) K; $2\theta_{max}$ = 46.5°; 14863 reflections collected, 4261 unique (R_{int} = 0.0245); final GOF = 1.073; R_1 = 0.0268, wR_2 = 0.0647, R indices based on 3751 reflections with $I > 2\sigma(I)$ (refinement on F^2), 321 parameters, 0 restraints; LP and absorption corrections applied; μ = 1.073 mm^{-1}.

*NBu$_4$(**L**^{3}·Br)*: Diffraction-quality single crystals of the bromide complex of **L**^{3} were obtained by slow evaporation of a solution of **L**^{3} in methanol in the presence of one molar equivalent of NBu_4Br. Crystal data for $C_{30}H_{58}BrN_5S_2$: M_r = 632.84; colourless block; 0.40 × 0.20 × 0.10 mm^3; monoclinic; space group $P2_1/m$ (No. 11); a = 8.922(2), b = 14.512(3), c = 13.570(3) Å; β = 99.736(5)°; V = 1731.7(7) Å^3; Z = 2; ρ_{calcd} = 1.214 g cm^{-3}; F_{000} = 680; SMART 1000; T = 273(2) K; $2\theta_{max}$ = 59.2°; 17021 reflections collected, 4955 unique (R_{int} = 0.1156); final GOF = 1.024; R_1 = 0.0703, wR_2 = 0.1134, R indices based on 2748 reflections with $I > 2\sigma(I)$ (refinement on F^2), 219 parameters, 0 restraints; LP and absorption corrections applied; μ = 1.333 mm^{-1}.

*NBu$_4$(**L**^{4}·Cl)*: Diffraction-quality single crystals of the chloride complex of **L**^{4} were obtained by slow evaporation of a solution of **L**^{4} in methanol in the presence of one molar equivalent of NBu_4Cl. Crystal data for $C_{21}H_{41}ClN_6S_2$: M_r = 477.17; colourless block; 0.40 × 0.30 × 0.20 mm^3; monoclinic; space group $P2_1/n$ (No. 14); a = 13.7716(8), b = 13.8071(8), c = 14.1391(8) Å; β = 100.408(2)°; V = 2644.3(3) Å^3; Z = 4; ρ_{calcd} = 1.199 g cm^{-3}; F_{000} = 1032; SMART 6000; T = 120(2) K; $2\theta_{max}$ = 58.5°; 37623 reflections collected, 7145 unique (R_{int} = 0.0542); final GOF = 1.008; R_1 = 0.0366, wR_2 = 0.0830, R indices based on 5059 reflections with $I > 2\sigma(I)$ (refinement on F^2), 293 parameters, 0 restraints; LP and absorption corrections applied; μ = 0.322 mm^{-1}.

[Pd(dppe)(κS,S′-**L**^{3})]Cl(PF_6)·(CH_3)$_2$CO (mixed salt of **6a**): Diffraction-quality single crystals were obtained by slow evaporation of a solution of the complex in acetone/diethyl ether. Crystal data for $C_{43}H_{52}ClF_6N_4OP_3PdS_2$: M_r = 1053.77; colourless block; 0.20 × 0.20 × 0.10 mm^3; orthorhombic; space group *Pbca* (No. 61); a = 16.7485(17), b = 22.810(2), c = 25.016(3) Å; V = 9556.7(17) Å^3; Z = 8; ρ_{calcd} = 1.465 g cm^{-3}; F_{000} = 4320; SMART 1000; T = 120(2) K; $2\theta_{max}$ = 46.6°; 81339 reflections collected, 6897 unique (R_{int} = 0.3378); final GOF = 1.042; R_1 = 0.0848, wR_2 = 0.1418, R indices based on 4070 reflections with $I > 2\sigma(I)$ (refinement on F^2), 563 parameters, 2 restraints; LP and absorption corrections applied; μ = 0.693 mm^{-1}.

*[{Cp*IrCl(μ-S,S′-**L**^{3})}$_2$](Cl)$_2$·(1.5−n)acetone·n THF (**9**)*: Diffraction-quality single crystals were obtained by slow evaporation of a solution of the complex in acetone/THF. Crystal data for $C_{105.37}H_{166.74}Cl_8Ir_4N_{16}O_3S_8$: M_r = 3014.61; yellow block; 0.30 × 0.30 × 0.20 mm^3; triclinic; space group $P\bar{1}$ (No. 2); a = 12.1392(2), b = 20.3398(3), c = 26.2094(4) Å; α = 89.7760(10), β = 83.1650(10), γ = 82.6200(10)°; V = 6371.69(17) Å^3; Z = 2; ρ_{calcd} =

1.571 g cm^{-3}; F_{000}=3014; SMART 6000; T=120(2) K; $2\theta_{max}$=58.4°; 108668 reflections collected, 34444 unique (R_{int}=0.0482); final GOF=1.010; R_1=0.0372, wR_2=0.0791, R indices based on 25594 reflections with $I>2\sigma(I)$ (refinement on F^2), 1386 parameters, 0 restraints; LP and absorption corrections applied; μ=4.514 mm^{-1}.

CCDC-777505 (**2a**), -777506 (**2b**) -777507 (**3**) -777508 (**4**) -777509 (mixed salt of **6a**) -777510 (**9**) -777511 (NBu_4(**L**^{3}·Br)) and -777512 (NBu_4(**L**^{4}·Cl)) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We thank Junta Castilla-La Mancha for a postdoctoral Fellowship to M.L.S., and the EPSRC and BP Chemicals Ltd. for a CASE studentship to J.T.L.

[1] P. D. Beer, P. A. Gale, *Angew. Chem.* **2001**, *113*, 502–532; *Angew. Chem. Int. Ed.* **2001**, *40*, 486–516.
[2] T. Gunnlaugsson, M. Glynn, G. M. Tocci, P. E. Kruger, F. M. Pfeffer, *Coord. Chem. Rev.* **2006**, *250*, 3094–3117.
[3] C. Caltagirone, P. A. Gale, *Chem. Soc. Rev.* **2009**, *38*, 520–563.
[4] J. L. Sessler, P. A. Gale, W.-S. Cho, *Anion Receptor Chemistry*, RSC, Cambridge, **2006**.
[5] Special issue: Anion Coordination Chemistry II, *Coord. Chem. Rev.* **2006**, *250*, 2917–3244.
[6] J. W. Steed, *Chem. Soc. Rev.* **2009**, *38*, 506–519.
[7] R. Custelcean, B. A. Moyer, *Eur. J. Inorg. Chem.* **2007**, 1321–1340.
[8] B. M. Maubert, J. Nelson, V. McKee, R. M. Town, I. Pàl, *J. Chem. Soc. Dalton Trans.* **2001**, 1395–1397.
[9] J. A. Gawenis, K. T. Holman, J. L. Atwood, S. S. Jurisson, *Inorg. Chem.* **2002**, *41*, 6028–6031.
[10] P. D. Beer, P. K. Hopkins, J. D. McKinney, *Chem. Commun.* **1999**, 1253–1254.
[11] C. Hogue, *Chem. Eng. News* **2003**, *81*, 37–46.
[12] V. Amendola, M. Boiocchi, L. Fabbrizzi, L. Mosca, *Chem. Eur. J.* **2008**, *14*, 9683–9696.
[13] I. Hisaki, S. I. Sasaki, K. Hirose, Y. Tobe, *Eur. J. Org. Chem.* **2007**, 607–615.
[14] L. S. Evans, P. A. Gale, M. E. Light, R. Quesada, *New J. Chem.* **2006**, *30*, 1019–1025.
[15] V. Amendola, D. Esteban-Gomez, L. Fabbrizzi, M. Licchelli, *Acc. Chem. Res.* **2006**, *39*, 343–353.
[16] F. M. Pfeffer, T. Gunnlaugsson, P. Jensen, P. E. Kruger, *Org. Lett.* **2005**, *7*, 5357–5360.
[17] S.-Y. Liu, Y.-B. He, J.-L. Wu, L.-H. Wei, H.-J. Qin, L.-Z. Meng, L. Hu, *Org. Biomol. Chem.* **2004**, *2*, 1582–1586.
[18] R. Martínez-Máñez, F. Sancenon, *Chem. Rev.* **2003**, *103*, 4419–4476.
[19] S. Nishizawa, P. Bühlmann, M. Iwao, Y. Umezawa, *Tetrahedron Lett.* **1995**, *36*, 6483–6486.
[20] T. Gunnlaugsson, A. P. Davis, J. E. O'Brien, M. Glynn, *Org. Biomol. Chem.* **2005**, *3*, 48–56.
[21] T. Gunnlaugsson, P. E. Kruger, T. C. Lee, R. Parkesh, F. M. Pfeffer, G. M. Hussey, *Tetrahedron Lett.* **2003**, *44*, 6575–6578.
[22] E. Fan, S. A. Van Arman, S. Kincaid, A. D. Hamilton, *J. Am. Chem. Soc.* **1993**, *115*, 369–370.
[23] S. Nishizawa, P. Buhlmann, M. Iwao, Y. Umezawa, *Tetrahedron Lett.* **1995**, *36*, 6483–6486.
[24] P. Bühlmann, S. Nishizawa, K. P. Xiao, Y. Umezawa, *Tetrahedron* **1997**, *53*, 1647–1654.
[25] D. A. Jose, D. K. Kumar, B. Ganguly, A. Das, *Tetrahedron Lett.* **2005**, *46*, 5343–5346.
[26] Y.-J. Kim, H. Kwak, S. J. Lee, J. S. Lee, H. J. Kwon, S. H. Nam, K. Lee, C. Kim, *Tetrahedron* **2006**, *62*, 9635–9640.
[27] K. P. Xiao, P. Buhlmann, Y. Umezawa, *Anal. Chem.* **1999**, *71*, 1183–1187.
[28] S. Nishizawa, T. Yokobori, T. Shioya, N. Teramae, *Chem. Lett.* **2001**, 1058–1059.
[29] S. Nishizawa, H. Kaneda, T. Uchida, N. Teramae, *J. Chem. Soc. Perkin Trans. 2* **1998**, 2325–2327.
[30] S. Nishizawa, R. Kato, T. Hayashita, N. Teramae, *Anal. Sci.* **1998**, *14*, 595–597.
[31] T. Gunnlaugsson, A. P. Davis, M. Glynn, *Chem. Commun.* **2001**, 2556–2557.
[32] T. Gunnlaugsson, A. P. Davis, G. M. Hussey, J. Tierney, M. Glynn, *Org. Biomol. Chem.* **2004**, *2*, 1856–1863.
[33] F.-Y. Wu, Z. Li, Z.-C. Wen, N. Zhou, Y.-F. Zhao, Y.-B. Jiang, *Org. Lett.* **2002**, *4*, 3203–3205.
[34] L. Nie, Z. Li, J. Han, X. Zhang, R. Yang, W. X. Liu, F. Y. Wu, J. W. Xie, Y. F. Zhao, Y. B. Jiang, *J. Org. Chem.* **2004**, *69*, 6449–6454.
[35] Z.-C. Wen, Y.-B. Jiang, *Tetrahedron* **2004**, *60*, 11109–11115.
[36] B. Liu, H. Tian, *Chem. Lett.* **2005**, *34*, 686–687.
[37] K. Ghosh, S. Adhikari, *Tetrahedron Lett.* **2006**, *47*, 8165–8169.
[38] F. M. Pfeffer, A. M. Buschgens, N. W. Barnett, T. Gunnlaugsson, P. E. Kruger, *Tetrahedron Lett.* **2005**, *46*, 6579–6584.
[39] F. M. Pfeffer, M. Seter, N. Lewcenko, N. W. Barnett, *Tetrahedron Lett.* **2006**, *47*, 5241–5245.
[40] D. H. Lee, K. H. Lee, J. I. Hong, *Org. Lett.* **2001**, *3*, 5–8.
[41] D. H. Lee, J. H. Im, J. H. Lee, J. I. Hong, *Tetrahedron Lett.* **2002**, *43*, 9637–9640.
[42] Y. P. Yen, K. W. Ho, *Tetrahedron Lett.* **2006**, *47*, 7357–7361.
[43] S. Sasaki, D. Citterio, S. Ozawa, K. Suzuki, *J. Chem. Soc. Perkin Trans. 2* **2001**, 2309–2313.
[44] M. Boiocchi, L. Del Boca, D. Esteban-Gomez, L. Fabbrizzi, M. Licchelli, E. Monzani, *Chem. Eur. J.* **2005**, *11*, 3097–3104.
[45] D. Esteban-Gómez, L. Fabbrizzi, M. Liechelli, *J. Org. Chem.* **2005**, *70*, 5717–5720.
[46] D. E. Gómez, L. Fabbrizzi, M. Licchelli, E. Monzani, *Org. Biomol. Chem.* **2005**, *3*, 1495–1500.
[47] C. M. G. Dos Santos, M. Glynn, T. McCabe, J. S. S. De Melo, H. D. Burrows, T. Gunnlaugsson, *Supramol. Chem.* **2007**, *20*, 407–418.
[48] A. Westcott, C. J. Sumby, R. D. Walshaw, M. J. Hardie, *New J. Chem.* **2009**, *33*, 902–912.
[49] M. George, G. Tan, V. T. John, R. G. Weiss, *Chem. Eur. J.* **2005**, *11*, 3243–3254.
[50] S. Nishizawa, P. Bühlmann, K. P. Xiao, Y. Umezawa, *Anal. Chim. Acta* **1998**, *358*, 35–44.
[51] K. H. Choi, A. D. Hamilton, *Coord. Chem. Rev.* **2003**, *240*, 101–110.
[52] S. I. Sasaki, M. Mizuno, K. Naemura, Y. Tobe, *J. Org. Chem.* **2000**, *65*, 275–283.
[53] K. H. Lee, J.-I. Hong, *Tetrahedron Lett.* **2000**, *41*, 6083–6087.
[54] P. D. Beer, S. R. Bayly, *Top. Curr. Chem.* **2005**, *255*, 125–162.
[55] P. D. Beer, E. J. Hayes, *Coord. Chem. Rev.* **2003**, *240*, 167–189.
[56] M. G. Fisher, P. A. Gale, M. E. Light, S. J. Loeb, *Chem. Commun.* **2008**, 5695–5697.
[57] C. R. Bondy, P. A. Gale, S. J. Loeb, *J. Am. Chem. Soc.* **2004**, *126*, 5030–5031.
[58] C. R. Bondy, P. A. Gale, S. J. Loeb, *J. Supramol. Chem.* **2002**, *2*, 93–96.
[59] C. R. Bondy, P. A. Gale, S. J. Loeb, *Chem. Commun.* **2001**, 729–730.
[60] S. Nieto, J. Perez, L. Riera, V. Riera, D. Miguel, *Chem. Commun.* **2009**, 3279–3281.
[61] V. Amendola, L. Fabbrizzi, *Chem. Commun.* **2009**, 513–531.
[62] J. Pérez, L. Riera, *Chem. Soc. Rev.* **2008**, *37*, 2658–2667.
[63] J. Pérez, L. Riera, *Chem. Commun.* **2008**, 533–543.
[64] K. Sato, Y. Sadamitsu, S. Araib, T. Yamagishia, *Tetrahedron Lett.* **2007**, *48*, 1493–1496.
[65] J. T. Lenthall, J. W. Steed, *Coord. Chem. Rev.* **2007**, *251*, 1747–1760.
[66] C. R. Rice, *Coord. Chem. Rev.* **2006**, *250*, 3190–3199.
[67] E. J. O'Neil, B. D. Smith, *Coord. Chem. Rev.* **2006**, *250*, 3068–3080.

[68] R. Custelcean, B. A. Moyer, V. S. Bryantsev, B. P. Hay, *Cryst. Growth Des.* **2006**, *6*, 555–563.
[69] A. Channa, J. W. Steed, *Dalton Trans.* **2005**, 2455–2461.
[70] K. J. Wallace, R. Daari, W. J. Belcher, L. O. Abouderbala, M. G. Boutelle, J. W. Steed, *J. Organomet. Chem.* **2003**, *666*, 63–74.
[71] J. A. Tovilla, R. Vilar, A. J. P. White, *Chem. Commun.* **2005**, 4839–4841.
[72] C. Mendoza, J. Benet-Buchholz, M. A. Pericas, R. Vilar, *Dalton Trans.* **2009**, 2974–2985.
[73] P. Diaz, D. M. P. Mingos, R. Vilar, A. J. P. White, D. J. Williams, *Inorg. Chem.* **2004**, *43*, 7597–7604.
[74] R. Vilar, D. M. P. Mingos, A. J. P. White, D. J. Williams, *Angew. Chem.* **1998**, *110*, 1323–1326; *Angew. Chem. Int. Ed.* **1998**, *37*, 1258–1261.
[75] J. T. Lenthall, K. M. Anderson, S. J. Smith, J. W. Steed, *Cryst. Growth Des.* **2007**, *7*, 1858–1862.
[76] D. Griffiths, R. Hull, T. P. Seden, *J. Chem. Soc. Perkin Trans. 1* **1980**, 1240–1244.
[77] N. B. Ambati, V. Babu, V. Anand, P. Hanumanthu, *Synth. Commun.* **1999**, *29*, 289–294.
[78] S. J. Dickson, M. J. Paterson, C. E. Willans, K. M. Anderson, J. W. Steed, *Chem. Eur. J.* **2008**, *14*, 7296–7305.
[79] S. J. Dickson, S. C. G. Biagini, J. W. Steed, *Chem. Commun.* **2007**, 4955–4957.
[80] L. Ion, D. Morales, J. Pérez, L. Riera, V. Riera, R. A. Kowenicki, M. McPartlin, *Chem. Commun.* **2006**, 91–93.
[81] M. A. Bennett, A. K. Smith, *J. Chem. Soc. Dalton Trans.* **1974**, 233–241.
[82] M. Poyatos, A. Maisse-Francois, S. Bellemin-Laponnaz, E. Peris, L. H. Gade, *J. Organomet. Chem.* **2006**, *691*, 2713–2720.
[83] S. K. Mandal, A. R. Chakravarty, *J. Organomet. Chem.* **1991**, *417*, C59–C62.
[84] F. H. Allen, O. Kennard, *Chem. Des. Autom. News* **1993**, *8*, 31.
[85] CSD version 5.31 + 2 updates.
[86] J. Bernstein, R. E. Davis, L. Shimoni, N.-L. Chang, *Angew. Chem.* **1995**, *107*, 1689–1708; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1555–1573.
[87] D. R. Turner, B. Smith, A. E. Goeta, I. R. Evans, D. A. Tocher, J. A. K. Howard, J. W. Steed, *CrystEngComm* **2004**, *6*, 633–641.
[88] W. Henderson, B. K. Nicholson, M. B. Dinger, R. L. Bennett, *Inorg. Chim. Acta* **2002**, *338*, 210–218.
[89] S. D. Robinson, A. Sahajpal, J. W. Steed, *Inorg. Chim. Acta* **2000**, *306*, 205–210.
[90] W. Henderson, R. D. W. Kemmitt, S. Mason, M. R. Moore, J. Fawcett, D. R. Russell, *J. Chem. Soc. Dalton Trans.* **1992**, 59–66.
[91] S. Okeya, Y. Fujiwara, S. Kawashima, Y. Hayashi, K. Isobe, Y. Nakamura, H. Shimomura, Y. Kushi, *Chem. Lett.* **1992**, 1823–1826.
[92] X. Shen, X. Shi, B. Kang, Y. Liu, Y. Tong, H. Jiang, K. Chen, *Polyhedron* **1998**, *17*, 4049–4058.
[93] J. Marek, P. Kopel, Z. Travnicek, *Acta Crystallogr. Sect. C* **2003**, *59*, m558–m560.
[94] W. Henderson, C. E. F. Rickard, *Inorg. Chim. Acta* **2003**, *343*, 74–78.
[95] W. Henderson, B. K. Nicholson, E. R. T. Tiekink, *Inorg. Chim. Acta* **2006**, *359*, 204–214.
[96] M. Lipowska, L. Hansen, A. Taylor, L. G. Marzilli, *Inorg. Chem.* **1996**, *35*, 4484–4489.
[97] M. Lipowska, B. L. Hayes, L. Hansen, A. Taylor, L. G. Marzilli, *Inorg. Chem.* **1996**, *35*, 4227–4231.
[98] C. Bilton, J. A. K. Howard, N. N. L. Madhavi, A. Nangia, G. R. Desiraju, F. H. Allen, C. C. Wilson, *Chem. Commun.* **1999**, 1675–1676.
[99] J. W. Steed, *CrystEngComm* **2003**, *5*, 169–179.
[100] I. G. Dance, *Polyhedron* **1986**, *5*, 1037–1104.
[101] G. Belchem, J. W. Steed, D. A. Tocher, *J. Chem. Soc. Dalton Trans.* **1994**, 1949–1962.
[102] A. D. Burrows, M. D. Coleman, M. F. Mahon, *Polyhedron* **1999**, *18*, 2665–2671.
[103] J. Huang, R. L. Ostrander, A. L. Rheingold, M. A. Walters, *Inorg. Chem.* **1995**, *34*, 1090–1093.
[104] R. D. Adams, M. P. Pompeo, J. H. Yamamoto, *Organometallics* **1993**, *12*, 951–954.
[105] J. W. Kang, K. Moseley, P. M. Maitlis, *J. Am. Chem. Soc.* **1969**, *91*, 5970.
[106] M. R. Churchill, S. A. Julis, *Inorg. Chem.* **1977**, *16*, 1488–1494.
[107] P. Gans, HypNMR 2006, University of Leeds, Leeds, **2006**.
[108] C. Frassineti, S. Ghelli, P. Gans, A. Sabatini, M. S. Moruzzi, A. Vacca, *Anal. Biochem.* **1995**, *231*, 374–382.
[109] S. J. Brooks, P. R. Edwards, P. A. Gale, M. E. Light, *New J. Chem.* **2006**, *30*, 65–70.
[110] S. J. Brooks, P. A. Gale, M. E. Light, *CrystEngComm* **2005**, *7*, 586–591.
[111] Y. Tobe, S. Sasaki, M. Mizuno, K. Hirose, K. Naemura, *J. Org. Chem.* **1998**, *63*, 7481–7489.
[112] R. A. Walton, *Spectrochim. Acta* **1965**, *21*, 1795–1801.
[113] SHELXS-97, G. M. Sheldrick, University of Göttingen (Germany), **1997**.
[114] SHELXL-97, G. M. Sheldrick, University of Göttingen (Germany), **1997**.
[115] J. L. Atwood, L. J. Barbour, *Cryst. Growth Des.* **2003**, *3*, 3–8.
[116] L. J. Barbour, *J. Supramol. Chem.* **2001**, *1*, 189–191.

Received: May 18, 2010
Published online: August 16, 2010

