Organometallics **2015**, *34*, 494−505
DOI: 10.1021/om5011269

Multimetallic alkenyl complexes bearing macrocyclic dithiocarbamate ligands

Anita Toscani, Eeva K. Heliövaara, Jubeda B. Hena, Andrew J. P. White and James D. E. T. Wilton-Ely*

Department of Chemistry, Imperial College London, South Kensington Campus, London SW7 2AZ (UK). E-mail: j.wilton-ely@imperial.ac.uk

Keywords: ruthenium, osmium, dithiocarbamate, sulfur ligands, alkenyl

Abstract

The aza-crown ether compounds, 1-aza-15-crown-5 and 1,10-diaza-18-crown-6 react with sodium hydroxide and carbon disulfide to provide the dithiocarbamates, [15]aneO_4-NCS_2Na and NaS_2CN-[18]aneO_4-NCS_2Na in good yield. The complexes [$MRCl(CO)(L)(PPh_3)_2$] (M = Ru, R = H, $CH=CHC_6H_4Me$-4, $CH=CHBu^t$, CH=CH-pyrenyl-1, C(C≡CPh)=CHPh; M = Os, R = H, CH=CH-pyrenyl-1); L = 2,1,3-benzothiadiazole or no ligand) undergo reaction with [15]aneO_4-NCS_2Na and NaS_2CN-[18]aneO_4-NCS_2Na to yield [$MR(S_2CN$-[15]ane$O_4)(CO)(PPh_3)_2$] and [$\{MR(CO)(PPh_3)_2\}_2(S_2CN$-[18]ane$O_4$-$NCS_2)$], respectively. In a similar manner, *cis*-[$RuCl_2(dppm)_2$] provides [$Ru(S_2CN$-[15]ane$O_4)(dppm)_2]^+$ and [$\{Ru(dppm)_2\}_2(S_2CN$-[18]aneO_4-$NCS_2)]^{2+}$, respectively. Reaction of [$Ru(CH=CHC_6H_4Me$-4)(S_2CN-[15]aneO_4)(CO)($PPh_3)_2$] with excess $HC≡CBu^t$ leads to the formation of the alkynyl complex, [$Ru(C≡CBu^t)(S_2CN$-[15]aneO_4)(CO)($PPh_3)_2$]. Treatment of [$OsHCl(CO)(BTD)(PPh_3)_2$] with [HC≡C-bpy$ReCl(CO)_3$] results in the bimetallic compound, [Os{CH=CH-bpy$ReCl(CO)_3$}$Cl(CO)(BTD)(PPh_3)_2$]. This reacts with [15]aneO_4-NCS_2Na and NaS_2CN-[18]aneO_4-NCS_2Na to yield [Os{CH=CH-bpy$ReCl(CO)_3$}(S_2CN-[15]aneO_4)(CO)($PPh_3)_2$] and [$\{Os\{CH=CH\text{-}bpyReCl(CO)_3\}(CO)(PPh_3)_2\}_2(S_2CN$-[18]ane$O_4$-$NCS_2)$], respectively. NMR studies provide information on the selectivity of binding of Li and Na ions. The structures of [$RuR(S_2CN$-[15]ane$O_4)(CO)(PPh_3)_2$] (R = H, $CH=CHC_6H_4Me$-4, CH=CH-pyrenyl-1) are also reported.

Introduction

It has been over a hundred years since the first report of a transition metal dithiocarbamate complex by Delépine.[1] Since this discovery, dithiocarbamate ($R_2NCS_2^-$) compounds of all the transition metals have been prepared in all common oxidation states.[2] While this observation reflects the versatility of this ligands class, the potential for exploiting the NR_2 substituents (frequently not expanded beyond R = Me, Et) in order to incorporate further functionality into the molecule has often been overlooked.[2] An exception to this is the use of dithiocarbamates as structural nodes in supramolecular frameworks by Beer and co-workers.[3] Our recent work[4] has attempted to exploit this potential in fundamental studies exploring the further reactivity of the NR_2 substituents (e.g., coordination to other metals,[4a-g] alkene metathesis[5]) as well as addressing potential applications such as medical imaging.[6] In the latter case, the incorporation of further metals in the system was achieved through the preference of lanthanide ions (such as trivalent gadolinium) for the harder oxygen and nitrogen donors of a macrocycle.

Ruthenium (and to a lesser extent osmium) alkenyl complexes[7] have received much attention over the last 25 years. They are readily accessible through hydrometallation of alkynes by the compounds $[RuHCl(CO)L_{2/3}]$ (L = PPr^i_3,[8] PPh_3[9]) and many properties of the resulting alkenyl complexes have been explored in pioneering work by the groups of Werner,[10] Esteruelas[11] Santos,[12] Caulton,[13] Hill[14] and others,[15] as well as by ourselves.[16] The most convenient triphenylphosphine-stabilized alkenyl complexes to use as starting materials are those of the form $[Ru(CR^1{=}CHR^2)Cl(CO)(PPh_3)_2]$[9] or $[Ru(CR^1{=}CHR^2)Cl(CO)(L)(PPh_3)_2]$ (L = BSD, 2,1,3-benzoselenadiazole or BTD, 2,1,3-benzothiadiazole),[14d] where L is a labile ligand. A significant advantage of the latter is that it avoids contamination with tris(phosphine) material. A key advantage offered by alkenyl complexes of this type is that two sites of reactivity are present in the complex. A vacant site at the metal center (or labile ligand, such as BTD) allows facile coordination of two-electron donors (e.g., CO),[12d] while the chloride and phosphine ligands are also readily replaced by polydentate chelates, such as thiacyles,[14g] pyrazolyborates,[14b,f] carboxylates[17] or 1,1-dithio ligands.[4c,i,5,15i,s,18] The facile generation of the alkenyl complexes themselves from insertion of both terminal and internal alkynes into the Ru-H bond allows for the introduction of alkenyl substituents known for their electrochemical (ferrocene)[4c] or photophysical (pyrene)[19,20]

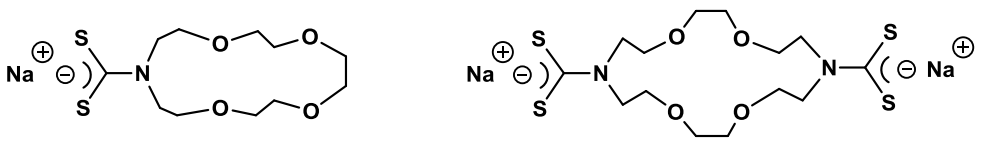
properties, for example. This route has been exploited by Winter and co-workers to join ruthenium alkenyl centers within a conjugated system.[21]

This report explores the functionalization of the alkenyl moiety to introduce a fluorophore or an addition transition metal unit, while exploiting the NR_2 substituents of the dithiocarbamate unit to incorporate a (bridging) macrocycle capable of interacting with cations.

Results and Discussion

Synthesis of dithiocarbamate alkenyl complexes

Green and co-workers reported the generation of the dithiocarbamate, [15]aneO_4-NCS_2Na (**1**), from the commercially available aza-crown ether, 1-aza-15-crown-5 (Fig.1).[22a,b] Since this work, which included the characterization of the complexes, [M{S_2CN-[15]aneO_4}$_n$] (Ni, Cu, n = 2; Cr, Fe, Co, n = 3) and [Cp_2Mo{S_2CN-[15]aneO_4}]PF_6, a number of studies have explored the coordination chemistry of this fascinating ligand. Homoleptic platinum[22c] and gold(I) complexes[22d] and, later, examples bearing phosphines and isocyanide co-ligands[22e] were reported. An application which emerged from a number of papers by Liu and co-workers was in technetium-based radiopharmaceuticals, where the crown ether unit was employed to help improve clearance from the liver.[22f,g] More recently, the [15]aneO_4-NCS_2^- ligand has also been utilized as a capping ligand for copper clusters.[22h] These sporadic reports over the last 25 years have not yet included examples of ruthenium and osmium. Similarly, the range of co-ligands found in these complexes has yet to contain σ-organyl functionality.



[15]aneO_4-NCS_2Na (**1**)

NaS_2CN-[18]aneO_4-NCS_2Na (**13**)

Figure 1. The crown ether ligands functionalized with dithiocarbamates used in this work.

Before exploring alkenyl functionality, the precursor hydride compound, [RuHCl(CO)(PPh_3)$_3$] was treated with a slight excess of [15]aneO_4-NCS_2Na (**1**) to yield a pale solution, from which a yellow solid was isolated in 88% yield. $^{31}P\{^1H\}$ NMR analysis confirmed that a new product had been formed with the presence of a singlet resonance at 50.5 ppm, while a hydride resonance was observed in the ^1H NMR spectrum at −10.94 ppm. This feature was observed as a triplet (J_{HP} = 19.9 Hz), indicating that two phosphines were present in a mutually *trans* arrangement. The product was formulated as [RuH(S_2CN-[15]aneO_4)(CO)(PPh_3)$_2$] (**2**) on the basis of this information and further analytical data. Structural characterization also proved possible once single crystals of **2** were grown by diffusion of ethanol into a dichloromethane solution of the complex. A crystal was chosen for a structural study (Fig. 2) – see Structural Discussion for further details.

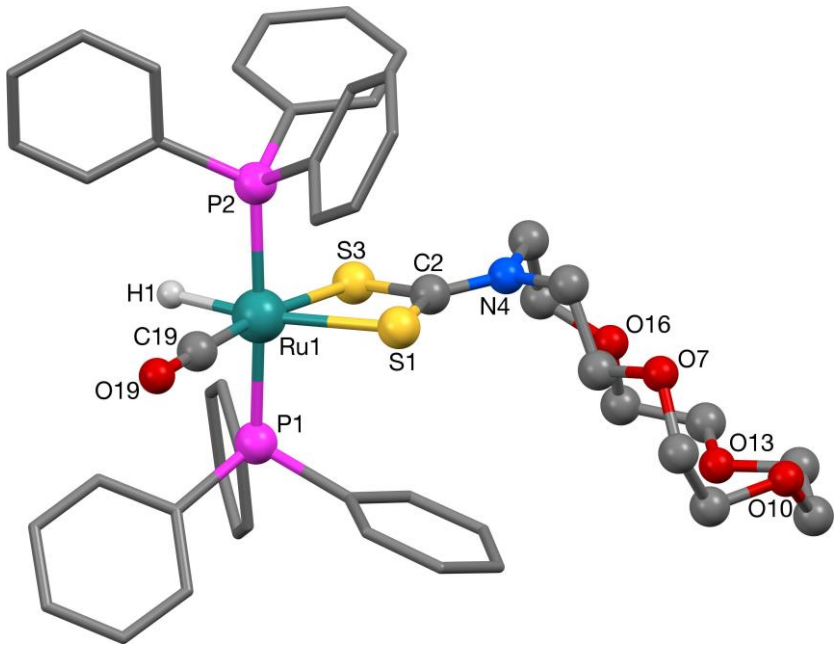
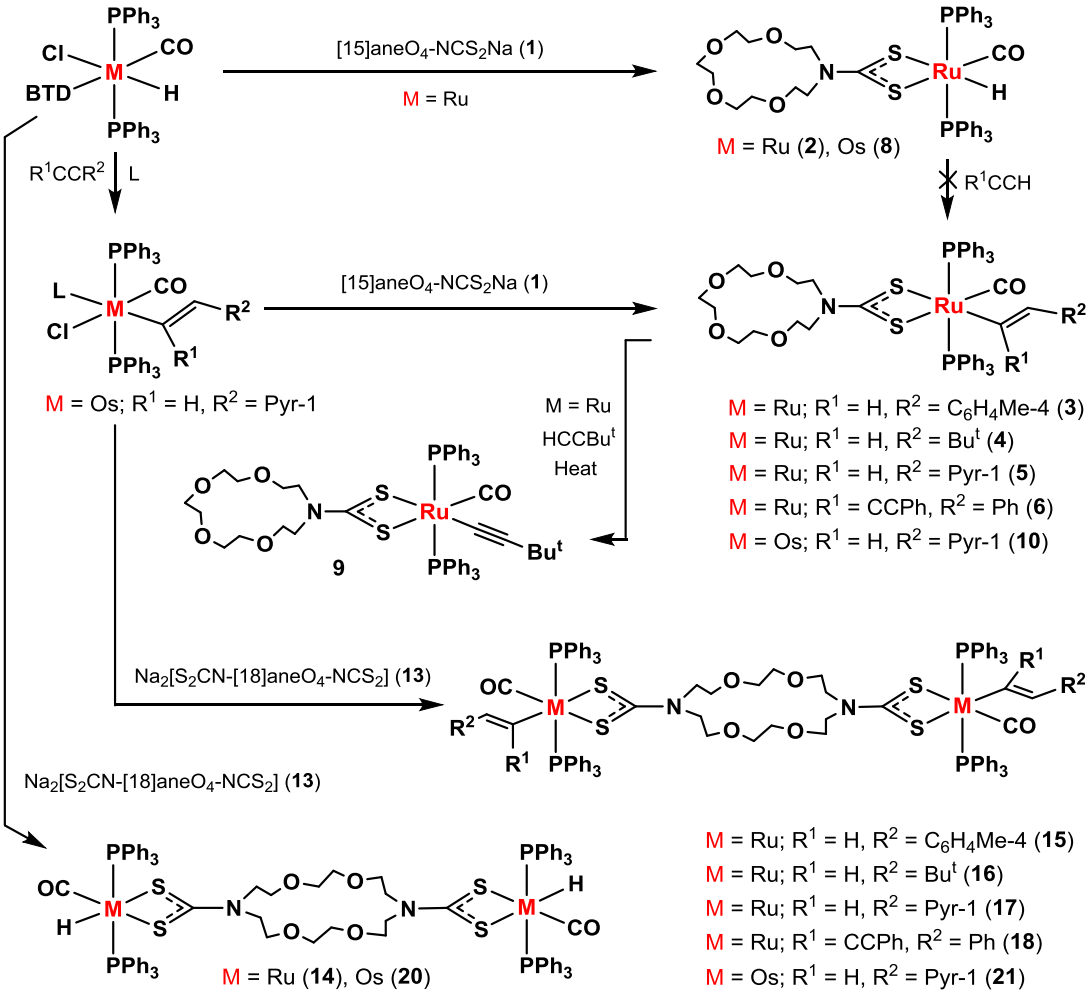


Figure 2. The molecular structure of [RuH(S_2CN-[15]aneO_4)(CO)(PPh_3)$_2$] (**2**). Selected bond lengths (Å) and angles (°): Ru(1)-C(19) 1.838(3), Ru(1)-P(1) 2.3368(5), Ru(1)-P(2) 2.3570(5), Ru(1)-S(3) 2.4700(6), Ru(1)-S(1) 2.4878(6), S(1)-C(2) 1.706(2), C(2)-N(4) 1.339(3), C(2)-S(3) 1.719(3), S(3)-Ru(1)-S(1) 70.645(19), S(1)-C(2)-S(3) 113.64(13).

A rapid reaction occurs between an orange solution of [Ru(CH=CHC_6H_4Me-4)Cl(CO)(BTD)(PPh_3)$_2$] and a slight excess of **1** dissolved in methanol to yield a pale yellow solution. The yellow solid isolated from this solution gave rise to a new singlet resonance in the $^{31}P\{^1H\}$ NMR spectrum at 39.7 ppm. ^1H NMR analysis revealed typical resonances for

the alkenyl ligand at 5.58 (d, Hβ, 1H, J_{HH} = 16.7 Hz) and 7.72 (dt, Hα, 1H, J_{HH}= 16.7 Hz, J_{HP} = 3.0 Hz) ppm. The latter resonance confirmed the mutually *trans* disposition of the phosphines. In addition to these features, new signals not observed in the ruthenium starting material were observed between 3.11 and 3.62 ppm corresponding to 20 protons. These were attributed to the ethylene protons of the crown ether ring, which appear in [15]aneO$_4$-NCS$_2$Na (**1**) at 3.66 (m, 12H), 3.93 (t, 4H, J_{HH} = 6.1 Hz) and 4.35 (t, 4H, J_{HH} = 6.1 Hz) ppm in CD$_3$OD. Additional evidence for the presence of the dithiocarbamate ligand was provided by absorptions at 1480 ($\nu_{C\text{-}N}$) and 840 ($\nu_{C\text{-}S}$) cm^{-1} in the solid state IR spectrum along with an intense absorption associated with the carbonyl ligand at 1910 cm^{-1}. An abundant molecular ion at *m/z* 1065 confirmed the overall formulation as [Ru(CH=CHC$_6$H$_4$Me-4)(S$_2$CN-[15]aneO$_4$)(CO)(PPh$_3$)$_2$] (**3**), as shown in Scheme 1.



Scheme 1. Synthesis of mono- and bimetallic dithiocarbamate complexes. L = BTD (2,1,3-benzothiadiazole) or no ligand depending on synthetic method.

It has recently been shown that the lability of 1,1-dithio ligands in ruthenium hydride compounds can be exploited to prepare alkenyl complexes.[18d] This is exemplified by the reaction of the dithiophosphate hydride complex $[RuH\{S_2P(OEt)_2\}(CO)(PPh_3)_2]$ with 4-ethynyltoluene to form $[Ru(CH{=}CHC_6H_4Me\text{-}4)\{S_2P(OEt)_2\}(CO)(PPh_3)_2]$. However, when the same reaction was attempted under identical conditions with $[RuH(S_2CN\text{-}[15]aneO_4)(CO)(PPh_3)_2]$ (**2**) to prepare **3**, no reaction took place.

The tertiary-butyl alkenyl analogue, $[Ru(CH{=}CHBu^t)(S_2CN\text{-}[15]aneO_4)(CO)(PPh_3)_2]$ (**4**), was prepared in 81% yield by an analogous procedure to that used to synthesize compound **3**. Similar resonances were again observed in the aliphatic region for the heterocycle, while a singlet absorption was observed for the 9 protons of the Bu^t group at 0.38 ppm.

Due to its properties as a fluorophore, pyrene has been widely used in a variety of applications.[23] Alkenyl complexes bearing 1-pyrenyl substituents have been studied and their electrochemical properties probed.[20,21] Our recent work has shown[19] that 1-pyrenylalkenyl complexes can be used as effective reporter units (both chromogenically and fluorogenically) in carbon monoxide sensing. It was thus decided to prepare $[Ru(CH{=}CHPyr\text{-}1)(S_2CN\text{-}[15]aneO_4)(CO)(PPh_3)_2]$ (**5**) by the same route as used above in order to generate a complex with both a fluorophore and the ability to coordinate ions through the macrocycle. This synthesis was achieved in 95% yield and spectroscopic analysis confirmed the formulation to be that desired. In order to complete the characterization and provide structural data, single crystals were grown diffusion of ethanol into a solution of **5** in dichloromethane. A crystal was chosen for a structural study (Fig. 3) – see Structural Discussion for further details.

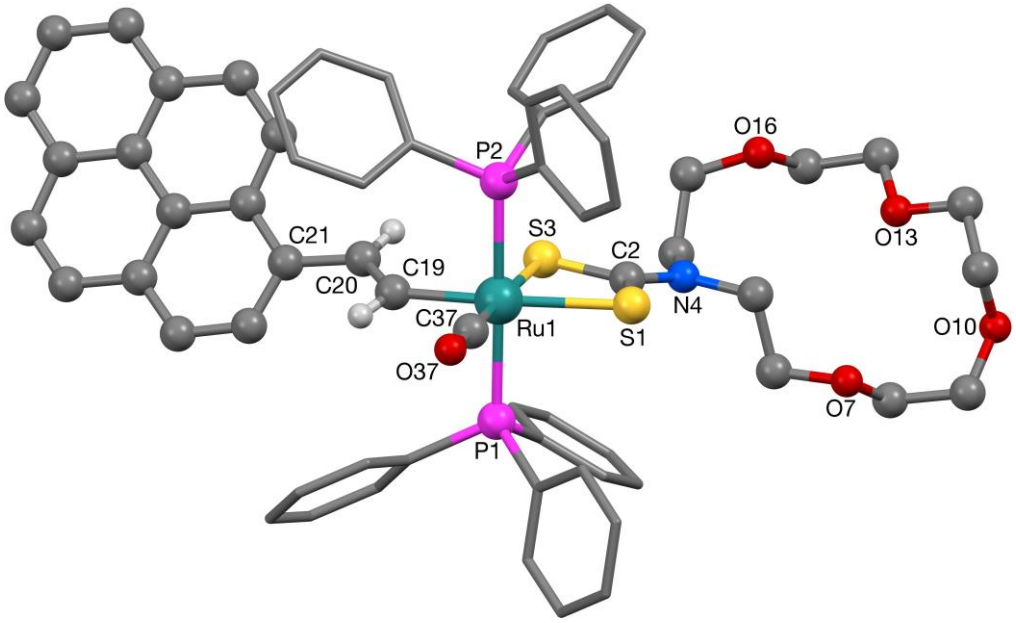


Figure 3. The molecular structure of [Ru(CH=CHPyr-1)(S_2CN-[15]aneO_4)(CO)(PPh_3)$_2$] (**5**). Selected bond lengths (Å) and angles (°): Ru(1)-C(37) 1.846(3), Ru(1)-C(19) 2.073(3), Ru(1)-S(3) 2.4550(6), Ru(1)-S(1) 2.5004(7), S(1)-C(2) 1.715(3), C(2)-N(4) 1.329(4), C(2)-S(3) 1.721(3), C(19)-C(20) 1.344(4), S(3)-Ru(1)-S(1) 70.77(2), P(2)-Ru(1)-P(1) 178.41(2), S(1)-C(2)-S(3)113.27(16).

In order to provide an example bearing a disubstituted alkenyl ligand, the complex, [Ru(C(C≡CPh)=CHPh)(S_2CN-[15]aneO_4)(CO)(PPh_3)$_2$] (**6**), was prepared in good yield (Scheme 1). The presence of the enynyl ligand was confirmed by the appearance of a singlet at 6.25 ppm for the β-proton in the ^{1}H NMR spectrum and a $\nu_{C\equiv C}$ absorption in the solid state infrared spectrum at 2138 cm^{-1}. Other features were found to be similar to those observed for the complexes **3** - **5**. Single crystals of **6** were grown by diffusion of ethanol into a solution of the complex in dichloromethane. A crystal was chosen for a structural study (Fig. 4) – see Structural Discussion for further details.

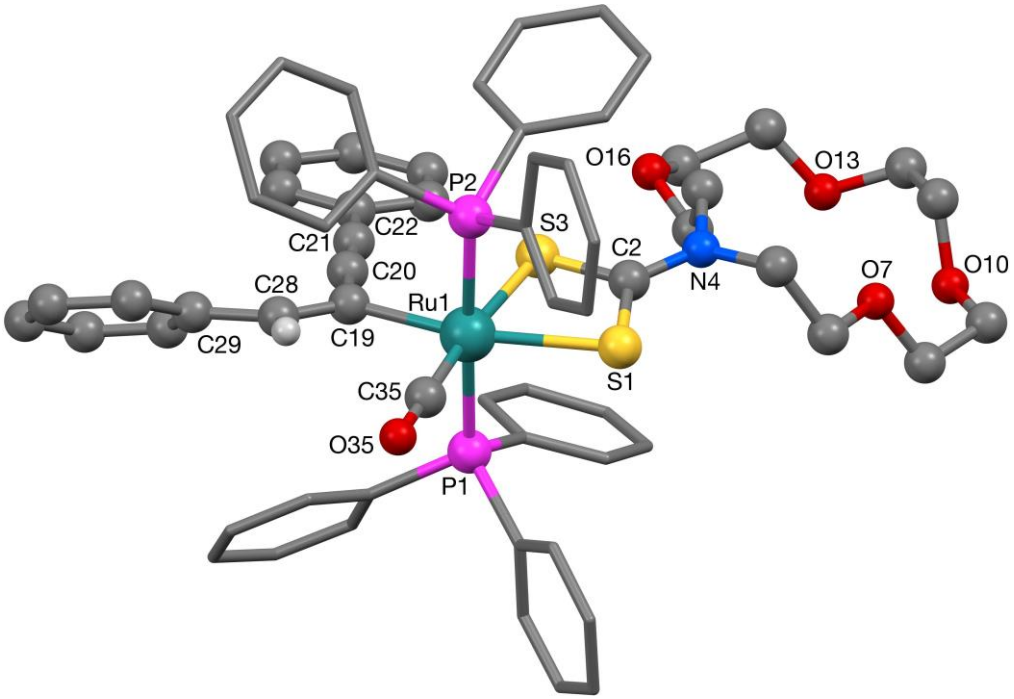
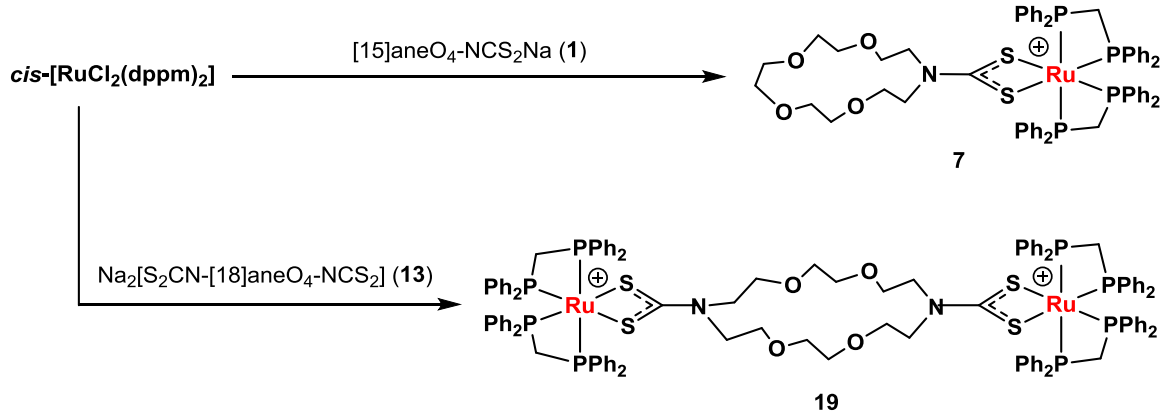


Figure 4. The molecular structure of [Ru(C(C≡CPh)=CHPh)(S_2CN-[15]aneO_4)(CO)(PPh_3)$_2$] (**6**). Selected bond lengths (Å) and angles (°): Ru(1)-C(35) 1.8444(16), Ru(1)-C(19) 2.1037(14), Ru(1)-S(3) 2.4647(4), Ru(1)-S(1) 2.4956(4), S(1)-C(2) 1.7179(16), C(2)-N(4) 1.338(2), C(2)-S(3) 1.7057(16), C(19)-C(28) 1.354(2), C(20)-C(21) 1.209(2), P(2)-Ru(1)-P(1) 178.268(12), S(3)-Ru(1)-S(1) 70.578(12), S(3)-C(2)-S(1) 113.66(8).

Non-alkenyl complexes were also prepared. Reaction of *cis*-[$RuCl_2$(dppm)$_2$] with [15]aneO_4-NCS_2Na (**1**) in the presence of ammonium hexafluorophosphate (Scheme 2) led to formation of [Ru(S_2CN-[15]aneO_4)(dppm)$_2$]PF_6 (**7**), while [OsH(S_2CN-[15]aneO_4)(CO)(PPh_3)$_2$] (**8**) was prepared from [OsHCl(CO)(BTD)(PPh_3)$_2$] (Scheme 1). It has been shown that reaction of [RuH{$S_2P(OEt)_2$}(CO)(PPh_3)$_2$] with terminal alkynes leads first to insertion of the alkyne into the Ru-H bond to form the alkenyl complex, [Ru(CH=CHR){$S_2P(OEt)_2$}(CO)(PPh_3)$_2$],[18d] while heating this product with excess HC≡CBu^t resulting in the isolation of [Ru(C≡CBu^t){$S_2P(OEt)_2$}(CO)(PPh_3)$_2$]. Under analogous conditions (room temperature stirring), no insertion of alkynes was observed into the M-H bond of **2** or **8**. However, heating complex **3** in toluene under reflux with 10 equivalents of HC≡CBu^t resulted in the formation of a new singlet at 38.5 ppm in the $^{31}P\{^1H\}$ NMR spectrum. Resonances for an alkenyl ligand were notably absent from the ^1H NMR spectrum, while a new singlet at 0.84 ppm integrating to 9 protons was observed. These data and the presence of a medium intensity $\nu_{C\equiv C}$ absorption at 2105 cm^{-1} in the solid state infrared

spectrum led to the formulation of the product (Scheme 2) as the alkynyl complex, $[Ru(C{\equiv}CBu^t)(S_2CN\text{-}[15]aneO_4)(CO)(PPh_3)_2]$ (**9**). This was confirmed by mass spectrometry and elemental analysis.

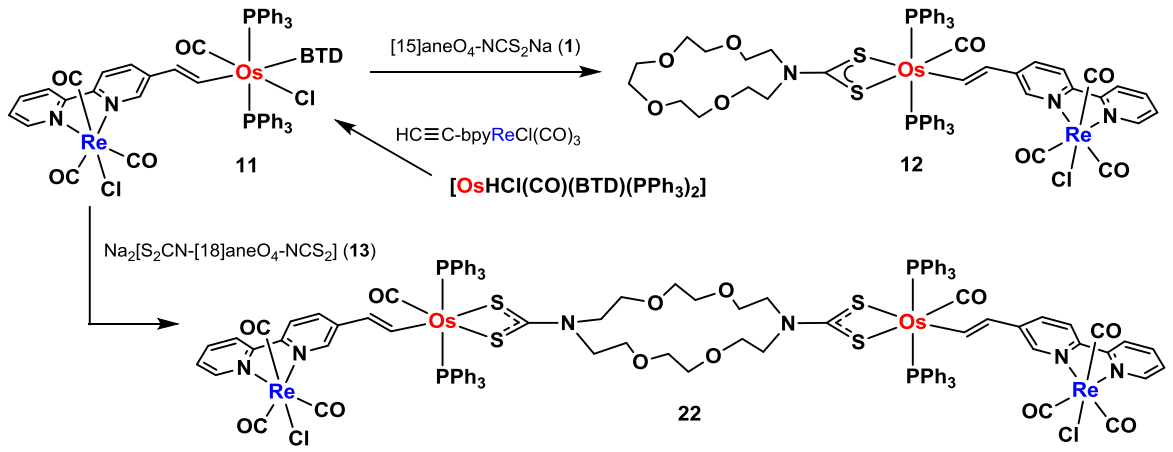


Scheme 2. Synthesis of mono- and bimetallic dithiocarbamate complexes bearing dppm ligands.

In order to provide further examples with the heaviest conger of group 8, the 1-pyrenyl alkenyl complex, $[Os(CH{=}CHPyr\text{-}1)Cl(CO)(BTD)(PPh_3)_2]$ was first prepared in good yield from $[OsHCl(CO)(BTD)(PPh_3)_2]$.[19] Treatment of this compound with $NaS_2CN\text{-}[15]aneO_4$ (**1**) led to formation of $[Os(CH{=}CHPyr\text{-}1)(S_2CN\text{-}[15]aneO_4)(CO)(PPh_3)_2]$ (**10**), which was characterized in the same way as the other compounds reported here. In the ^1H NMR spectrum, the chemicals shifts of the resonances assigned to the macrocylic ligand were found to be essentially unshifted from those found for **5**.

The rhenium(I) complex, $[ReCl(CO)_3(bpyC{\equiv}CH)]$[24a] is one of the versatile synthons employed in pioneering work on multimetallic systems by Lang and co-workers.[24] In these investigations, it was used to form alkynyl complexes, such as $[(dppf)CpRu(C{\equiv}CC_6H_4PPh_2\text{-}4)Au\{C{\equiv}C\text{-}bpyReCl(CO)_3\}]$.[24a] However, to our knowledge, no reports exist of the fragment being used to prepare alkenyl complexes. Treatment of $[OsHCl(CO)(BTD)(PPh_3)_2]$ with $[ReCl(CO)_3(bpyC{\equiv}CH)]$ led to isolation of the dark orange bimetallic complex, $[Os\{CH{=}CH\text{-}bpyRe(CO)_3Cl\}Cl(CO)(BTD)(PPh_3)_2]$ (**11**), as shown in Scheme 3. Formation of the alkenyl ligand was confirmed by the presence of resonances at 10.08 (dt, J_{HH} = 16.0 Hz, J_{HP} = 2.3 Hz) and 5.75 ppm (dt, J_{HH} = 16.0 Hz) for the Hα and Hβ protons, respectively. The retention of the rhenium fragment was supported by increased activity (compared to the hydride precursor) in the region 2017 – 1907 cm^{-1} in the infrared spectrum, in addition to an

absorption at 1878 cm^{-1} for the osmium-bonded carbonyl. The overall formulation was confirmed by good agreement of elemental analysis with calculated values. The lability of the chloride and BTD ligands was then exploited to introduce further functionality through reaction of **11** with NaS_2CN-[15]aneO_4 (**1**) to yield [Os{CH=CH-bpyRe$(CO)_3$Cl}(S_2CN-[15]aneO_4)$(CO)(PPh_3)_2$] (**12**). A new signal in the $^{31}P\{^1H\}$ NMR spectrum at 8.0 ppm, shifted substantially from the same feature in the precursor (0.1 ppm) was observed for **12**. Unusually, in both **11** and **12**, this resonance is observed as a doublet, showing a small coupling of between 5-6 Hz. This is attributed to slight inequivalence of the phosphorus environments due to the orientation of the mutually *trans* chloride and carbonyl ligands on the rhenium unit. The chemical shifts of the two resonances are almost identical, causing the doublets to overlap and so appear effectively as a single doublet resonance. The ^1H NMR spectroscopic data associated with the osmium unit in **12** did not change substantially compared to the precursor, however new resonances characteristic for the ethylene bridges within the crown ether ligand were noted between 3.01 and 3.54 ppm.



Scheme 3. Synthesis of bi- and tetrametallic dithiocarbamate complexes.

Our interest in multimetallic complexes has led to the preparation of a number of dinuclear ruthenium complexes, such as [{Ru(CR=CHR')$(CO)(PPh_3)_2$}$_2$($S_2CNC_4H_8NCS_2$)],[4c] [{Ru$(dppm)_2$}$_2$($S_2CNC_4H_8NCS_2$)]$(BF_4)_2$[4a,b] and [{Ru(CR=CHR')$(CO)(PPh_3)_2$}$_2$($S_2COCH_2C_6H_4CH_2OCS_2$)].[18a] Encouraged by the clean formation of the $[S_2$CN-[15]ane$O_4]^-$ complexes, it was decided to prepare a series of bimetallic compounds with a macrocyclic spacer. Commercially available, 1,10-diaza-18-crown-6 was treated with sodium hydroxide and just over two equivalents of carbon disulfide

to form the new bis(dithiocarbamate) ligand, NaS_2CN-[18]aneO_4-NCS_2Na (**13**) in 89% yield. ^1H NMR analysis revealed two triplets at 3.88 and 4.45 ppm (J_{HH} = 5.9 Hz) for the protons closest to the dithiocarbamate moiety, while the ethylene protons bonded solely to the oxygen atoms resonated as a singlet at 3.65 ppm. Direct evidence for the presence of the CS_2 unit was provided by a resonance at 210.7 ppm in the $^{13}C\{^1H\}$ NMR spectrum.

The ammonium analogue of **13** has been isolated and reported previously,[25a,b] however, no transition metal complexes of this ligand have been characterized, although some homoleptic species were generated in solution from various metal salts. Very recently, some tin examples have also been reported using **13** generated *in situ*.[25c] Thus, the transition metal compounds reported here are the first to be fully characterized for this bis(dithiocarbamate) ligand.

Treatment of two equivalents of [RuHCl(CO)(BTD)$(PPh_3)_2$] with one equivalent of **13** led to a slow reaction, which was complete after stirring for 5 hours. The colorless product isolated from this reaction was formulated as [{RuH(CO)$(PPh_3)_2$}$_2$(S_2CN-[18]aneO_4-NCS_2)] (**14**) on the basis of spectroscopic data such as a very similar $^{31}P\{^1H\}$ NMR chemical shift (50.2 ppm) to that found for **2**. The hydride resonance at −10.95 ppm was also essentially unchanged. The ^{13}C resonance associated with the CS_2 nucleus (210.8 ppm) was found to be unmoved from the chemical shift of the same unit in the precursor.

Using the same conditions, reaction of [Ru(CH=CHC_6H_4Me-4)Cl(CO)(BTD)$(PPh_3)_2$] with **13** led to a pale yellow solution, from which a cream precipitate was isolated in good yield. Similar absorptions were observed in the infrared spectrum to those observed for compound **3**, including intense bands at 1909 (ν_{CO}) and 1479 (ν_{C-N}) cm^{-1}. Retention of the alkenyl ligand was indicated in the ^1H NMR spectrum by the presence of resonances for the α- and β-protons at 5.52 and 7.71 ppm, respectively (showing a mutual J_{HH} coupling of 16.7 Hz). New features were observed between 3.06 and 3.50 ppm, integrating to 24 protons and were attributed to the macrocycle unit of the bis(dithiocarbamate) ligand. Further confirmation of the formulation as [{Ru(CH=CHC_6H_4Me-4)(CO)$(PPh_3)_2$}$_2$(S_2CN-[18]aneO_4-NCS_2)] (**15)** was provided by a molecular ion in the mass spectrum (*m/z* 1954) and good agreement of elemental analysis values with those calculated for this formulation.

Using the same preparative route, the bimetallic complexes [{Ru(CH=CHBu^t)(CO)$(PPh_3)_2$}$_2$(S_2CN-[18]aneO_4-NCS_2)] (**16**), [{Ru(CH=CHPyr-1)(CO)$(PPh_3)_2$}$_2$(S_2CN-[18]aneO_4-NCS_2)] (**17**) and {Ru(C(C≡CPh)=CHPh)(CO)$(PPh_3)_2$}$_2$(S_2CN-[18]aneO_4-NCS_2)] (**18**) were prepared in good

to excellent yield, bearing mono- and disubstituted alkenyl functionality. The pyrenyl fluorophore in complex **17** led to its consideration in later cation binding experiments. In order to complete the selection of compounds of this formulation, a dppm derivative, [{Ru(dppm)$_2$}$_2$(S$_2$CN-[18]aneO$_4$-NCS$_2$)](PF$_6$)$_2$ (**19**) and two osmium complexes, [{OsH(CO)(PPh$_3$)$_2$}$_2$(S$_2$CN-[18]aneO$_4$-NCS$_2$)] (**20**) and [{Os(CH=CHPyr-1)(CO)(PPh$_3$)$_2$}$_2$(S$_2$CN-[18]aneO$_4$-NCS$_2$)] (**21**) were also synthesized.

Following the same procedure, the tetrametallic complex, [{Os{CH=CH-bpyReCl(CO)$_3$}(CO)(PPh$_3$)$_2$}$_2$(S$_2$CN-[18]aneO$_4$-NCS$_2$)] (**22**) was prepared in 80% yield from reaction of **11** and **13**. The presence of the Re(CO)$_3$ units was supported by additional activity in the characteristic region for terminal carbonyl ligands in the solid-state spectrum, alongside the characteristic absorption at 1879 cm^{-1} for the carbonyl ligands attached to the osmium centers. The synthesis of this complex illustrates the complexity which can be readily introduced into these molecular assemblies using simple building blocks based on bifunctional linkers. Furthermore, such approaches enable the potential for combining units well known for their redox, photophysical or cation sensing properties to be exploited.

Cation binding experiments

Crown ethers are noted for their ability to interact with cations, with the number of available donors influencing the preference for particular cations.[26] Recent work has highlighted the binding abilities of these macrocyclic groups in both polar organic solvents (acetonitrile/dioxane)[27] and organic solvent/water mixtures (1,4-dioxane/H$_2$O)[28] and their applications as ion-specific receptors.[29] The crown ether, 12-crown-4, shows a greater affinity for lithium than for the larger group 1 cations, forming a 2:1 crown:Li complex; a combination of theoretical calculations and experimental techniques has confirmed that the Li$^+$ ion fits the cavity of 1-aza-12-crown-4,[29] whereas crown ring derivatives with more than 5 donor atoms do not provide suitable cavity dimensions for such a small alkali metal ion. In both the azacrown dithiocarbamate ligands investigated here (**1** and **13**), only four donor atoms are likely to be available for cation binding. Due to the contribution of the thioureide form, R$_2$N$^+$=CS$_2$$^{2-}$, the lone pair of the nitrogen in dithiocarbamate complexes shows negligible coordination ability.[2] This has been exploited in the successful ring-closing metathesis of [Ru(CH=CHC$_6$H$_4$Me-4){S$_2$CN(CH$_2$CH=CH$_2$)$_2$}(CO)(PPh$_3$)$_2$] to yield [Ru(CH=CHC$_6$H$_4$Me-4)(S$_2$CNC$_5$H$_{10}$)(CO)(PPh$_3$)$_2$], in contrast to diallylamine, which

deactivates the catalyst through coordination of the nitrogen lone pair. The substantial multiple bond character evident in the dithiocarbamate C-N bond in the crystal structures of **2**, **5** and **6** suggests that the nitrogen lone pair is unable to bind significantly to the cations in these experiments, leaving only the oxygen donors available.

Early studies[25,30] of **1** and **13** with transition metals involved the *in situ* formation of homoleptic complexes which were then examined spectrophotometrically on addition of alkali metal salts. A later study by Espinet and co-workers[22e] investigated the extraction efficiency of sodium picrate from aqueous solutions by gold(I) complexes of **1** in dichloromethane. The effect was observed to be even more pronounced when potassium picrate was used. In these cases it was suggested that the cations were being sandwiched between two crown ether units. Our recent investigations of the 1-pyrenyl-substituted complex, [Ru(CH=CHPyr-1)Cl(CO)(BTD)(PPh_3)$_2$] in sensing of carbon monoxide in air[19] has shown that the response can be measured in terms of visible color and fluorescence as well as other spectroscopies (IR and NMR). It was thus decided to explore whether any response could be determined for different cations using [Ru(CH=CHPyr-1)(S_2CN-[15]aneO_4)(CO)(PPh_3)$_2$] (**5**) and [{Ru(CH=CHPyr-1)(CO)(PPh_3)$_2$}$_2$(S_2CN-[18]aneO_4-NCS_2)] (**17**). Addition of potassium (KPF_6) and sodium ($NaBF_4$) ions in complex:cation ratios of 1:0.5, 1:1 and 1:1.5 to **5** led to no dramatic change in the resonances of the macrocyle protons (3.0 - 3.7 ppm). However, on addition of lithium ions ($LiClO_4$), a broadening of the azacrown methylene resonances in this region became apparent with significant loss of multiplicity.

Thus, the binding affinity of the azacrown pyrenyl ruthenium complex, [Ru(CH=CHPyr-1)(S_2CN-[15]aneO_4)(CO)(PPh_3)$_2$] (**5**), towards the group 1 alkali cations Li^+ and Na^+ was attempted. Trial titration experiments showed that NMR spectroscopy was the best technique to study this system, as UV-Vis and fluorescence spectroscopies were not found to display sufficiently diagnostic features. Indeed, upon addition of lithium and sodium perchlorate to a standard solution of the ruthenium complex, no variations in either optical or emission spectra were observed. Despite the fluorescence properties of the pyrenylalkenyl group, which were exploited successfully in CO sensing,[19] the emission of [Ru(CH=CHPyr-1)(S_2CN-[15]aneO_4)(CO)(PPh_3)$_2$] was too weak to be correlated to the increasing concentrations of lithium and sodium salts; the weak fluorescence signal of the complex suggests that the azacrown dithiocarbamate ligand quenches the pyrenyl emission as well as the metal-to-ligand charge transfer between the metal center and the fluorophore.

It was therefore decided to probe the interaction of lithium and sodium ions with a representative complex prepared during this work using ^{1}H NMR spectroscopy. Titrations

were performed in acetonitrile-d_3 by adding between 0 and 2.5 equivalents of sodium and lithium perchlorate stock solutions to a standard solution of complex **5** ($[H]_0$ = 0.003 M, host concentration). The resultant NMR spectra show a slight downfield shift (between 0.05 – 0.30 ppm) of the methylene 1-aza-15-crown-5 protons and a clear loss of fine structure. As is often observed for complexation with a crown ether or an azacrown ether, the host-guest complexation equilibrium is typical of a very fast exchange with the exchange rate being faster than the NMR spectroscopic time scale.[31]

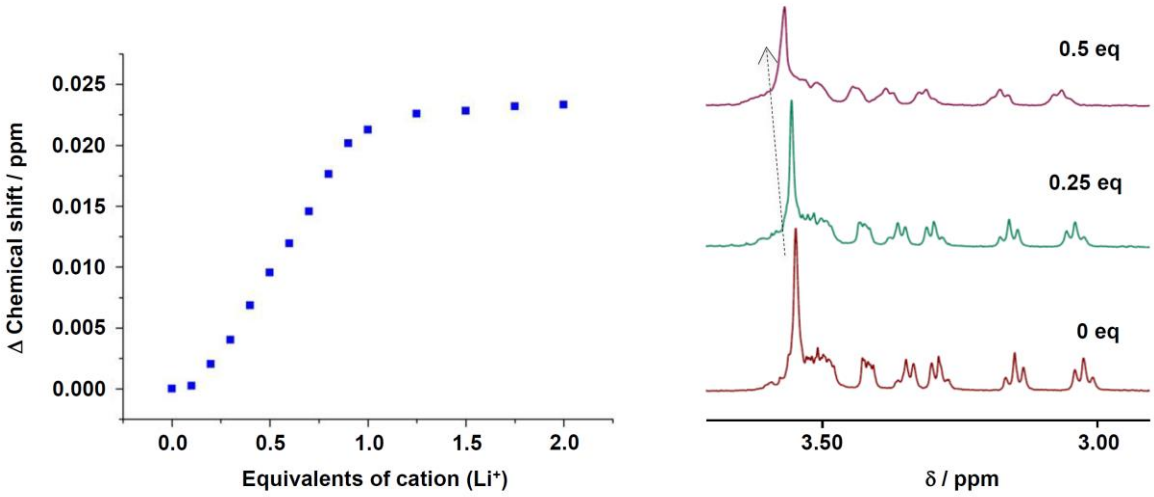


Figure 5. Isotherm generated from the titration of compound **5** with $LiClO_4$ (left) and three ^1H NMR spectra from the titration of compound **5** with 0, 0.25 and 0.5 equivalents of Li^+ (right).

The measurements of the binding constant were performed using 'local' and 'global' analysis methods and the values of K_a were found to be reasonable with respect to our observations. The 'local' analysis method is based on the analysis of only a single isotherm (single peak shift) whereas the 'global' method takes into account four isotherms (see Supporting Information). The K_a values were found to be 9.20 ± 1.50 M^{-1} (local method) and 9.75 ± 0.98 M^{-1} (global method) for Li^+ and 20.40 ± 1.45 M^{-1} (local method) and 20.10 ± 0.77 M^{-1} (global method) for Na^+ at the 95% confidence level, giving negative ΔG values of between –2.4 and –5.0 $kJmol^{-1}$, indicating that the dithiocarbamate azacrown spontaneously binds both alkali metal cations with a slight preference for sodium, which has a size well suited to the 1-aza-15-crown-5 cavity.[32] Despite this preference, the titration experiments confirm that these azacrown derivatives do not show substantial selectivity towards either of the two cations. The binding mode proposed is a 1:1 complex:cation ratio (see Supporting Information), however, the formation of sandwich-type multimetallic adducts might also to

be formed. Indeed, during the titrations, the precipitation of a bright yellow compound was observed when lithium or sodium were added in complex:cation ratios between 1:0.5 and 1:1, suggesting that the participation of the perchlorate anion in the formation of binary or ternary mixtures cannot also be excluded. A recent contribution by Stephenson *et al.*[32] reported evidence for the interaction of two perchlorate anions with two metal crown ether complexes in the presence of alkali metal cations, indicating the non-innocent character of the perchlorate anion.

The investigation of the bimetallic and multimetallic diazacrown compounds (such as **17**) was attempted but data could not be determined successfully due to precipitation issues caused by their low solubility.

Structural Discussion

The X-ray crystal structures of complexes [RuH(S_2CN-[15]aneO_4)(CO)(PPh_3)$_2$] (**2**), [Ru(CH=CHPyr-1)(S_2CN-[15]aneO_4)(CO)(PPh_3)$_2$] (**5**) and [Ru(C(C≡CPh)=CHPh)(S_2CN-[15]aneO_4)(CO)(PPh_3)$_2$] (**6**) all show the expected octahedral geometry at the ruthenium(II) centers with *cis*-interligand angles in the range 70.645(19) – 104.23(8)° for 2, 70.77(2) – 106.23(9)° for **5**, and 70.578(12) – 103.97(5)° for **6**. In each structure, the smallest angle is the S,S' bite of the chelating dithiocarbamate ligand, whilst the largest is that between the carbonyl ligand and S(1). In each structure the Ru–S bond *trans* to the carbonyl ligand [Ru–S(3)] is slightly shorter than that *trans* to the alkenyl ligand [Ru–S(1)], being 2.4700(6) and 2.4878(6) Å in **2**, 2.4450(6) and 2.5004(7) Å in **5**, and 2.4647(4) and 2.4956(4) Å in **6**, respectively. This is commonly observed in related dithiocarbamate complexes, such as [Ru(C(C≡CPh)=CHPh)($S_2CNC_4H_8NH_2$)(CO)(PPh_3)$_2$]Cl,[4c] and has been attributed to the superior *trans* influence of the alkenyl ligand compared to the carbon monoxide ligand. The $S_2C–NR_2$ distances in all three structures [C(2)–N(4) 1.339(3), 1.329(4) and 1.338(2) Å in **2**, **5** and **6** respectively] suggest distinct multiple bond character in each case.[33] The aryl substituents bound to the double bond of the alkenyl ligands take noticeably different conformations in **5** and **6**. In the former, the torsion angle across the linkage between the double bond and the pyrenyl moiety is ca. 37°, whilst in the latter the corresponding angle across the bond to the C(29) phenyl ring is ca. 25°. Additionally, the double bond itself has a different orientation with respect to the Ru(S_2CN-[15]aneO_4)(CO)(PPh_3)$_2$ unit in each structure. In **5** the other substituent on the first atom of the double bond [the hydrogen on

C(19)] is *syn* to the Ru–CO bond, whereas in **6** the equivalent substituent (the C≡CPh unit) is *anti* to the the Ru–CO bond. The [15]aneO_4 macrocycle adopts slightly different conformations in **5** and **6**, the former having a more elongated shape then the latter. The remaining features of both alkenyl and dithiocarbamate ligands are typical for these ligands coordinated to divalent ruthenium.[4c,5a,b]

Conclusions

Ruthenium and osmium alkenyl complexes possess great versatility through the reactivity they show both at the metal center (towards mono- or polydentate ligands) and through the functionality present on the alkenyl substituent. This contribution demonstrates the ease with which additional functionality can be incorporated into these complexes, such as fluorophores (pyrene), crown ether macrocycles or additional metal units (Re). The complexity of the assemblies can be increased to include 1-4 metals in a controlled, modular fashion by exploiting reliable, high-yielding and selective transformations. These compounds based on [15]aneO_4-NCS_2Na (**1**) and NaS_2CN-[18]aneO_4-NCS_2Na (**13**) greatly expand the range of non-homoleptic transition metal examples bearing these heterocylic dithiocarbamate ligands and constitute the first examples at all with ruthenium or osmium. In addition, NMR studies show that there are interactions between [Ru(CH=CHPyr-1)(S_2CN-[15]aneO_4)(CO)(PPh_3)$_2$] (**5**) and sodium cations, whereas a weaker binding is observed for lithium ions.

Experimental Section

General Comments. Unless otherwise stated, all experiments were carried out in air and the complexes obtained appear stable towards the atmosphere, whether in solution or in the solid state. Reagents and solvents were used as received from commercial sources. Petroleum ether is the fraction boiling in the 40–60 °C range. The following complexes were prepared as described elsewhere: [15]aneO_4-NCS_2Na (**1**),[22b] [RuHCl(CO)(PPh_3)$_3$],[34] [RuHCl(CO)(BTD)(PPh_3)$_2$],[35] [OsHCl(CO)(BTD)(PPh_3)$_2$],[14i] [Ru(C(C≡CPh)=CHPh)Cl(CO)(PPh_3)$_2$],[14a,b] [M(CH=CHPyr-1)Cl(CO)(BTD)(PPh_3)$_2$] (M = Ru, Os),[19] [Ru(CR^1=CHR^2)Cl(CO)(BTD)(PPh_3)$_2$] (R^1 = H, R^2 = C_6H_4Me-4, Bu^t)[36] and .[24a]

Electrospray (ES) and Liquid Secondary Ion Mass Spectrometry (LSIMS) mass data were obtained using Micromass LCT Premier and Autospec Q instruments, respectively. Infrared data were obtained using a Perkin-Elmer Spectrum 100 FT-IR spectrophotometer and characteristic triphenylphosphine-associated infrared data are not reported. NMR spectroscopy was performed at 25 °C using Varian Mercury 300 and Bruker AV400 spectrometers in $CDCl_3$ unless stated otherwise. All coupling constants are in Hertz. Resonances in the $^{31}P\{^1H\}$ NMR spectrum due to the hexafluorophosphate counteranion were observed where the formulation indicates but are not included below. Elemental analysis data were obtained from London Metropolitan University. Solvates were confirmed by integration of the ^1H NMR spectra. The procedures given provide materials of sufficient purity for synthetic and spectroscopic purposes.

[RuH(S_2CN-[15]aneO_4)(CO)(PPh_3)$_2$] (2)

[RuHCl(CO)(PPh_3)$_3$] (50 mg, 0.053 mmol) was dissolved in dichloromethane (17 mL) and 2,1,3-benzothiadiazole (17.8 mg, 0.131 mmol) added, resulting in an orange yellow coloration. [15]aneO_4-NCS_2Na (18 mg, 0.057 mmol) was added in methanol (10 mL) and the reaction stirred at room temperature for 1 hour. All solvent was removed (rotary evaporator) and a pale yellow crude product was obtained. This was dissolved in dichloromethane (15 mL) and filtered through Celite. Addition of methanol (15 mL) followed by slow reduction of the solvent volume (rotary evaporator) resulted in a pale yellow product, which was washed with methanol (10 mL), petroleum ether (10 mL) and dried. Yield: 44 mg (88%). IR: 1917 (ν_{CO}), 1478 (ν_{C-N}), 1111, 1089 (ν_{C-O}), 849 (ν_{C-S}), 744, 694 cm^{-1}. ^1H NMR: δ −10.94 (t, RuH, 1H, J_{HP} = 19.9 Hz), 3.21 (m, CH_2, 8H), 3.49 (m, CH_2, 4H), 3.63 (m, CH_2, 8H), 7.33 (m, C_6H_5, 18H), 7.74 (m, C_6H_5, 12H) ppm. ^{13}C NMR (CD_2Cl_2): δ 210.8 (s, CS_2), 206.0 (t, CO, J_{CP} = 14.3 Hz), 135.7 (t, *ipso*-C_6H_5, J_{CP} = 20.9 Hz), 134.7 (t, *o/m*-C_6H_5, J_{CP} = 5.9 Hz), 129.4 (s, *p*-C_6H_5), 127.8 (t, *o/m*-C_6H_5, J_{CP} = 4.6 Hz), 71.1 (s, OCH_2), 70.4, 70.3, 70.2, 70.1 (s x 4, OCH_2), 68.1, 67.9 (s x 2, NCCH_2), 52.2, 51.8 (s x 2, NCH_2) ppm. $^{31}P\{^1H\}$ NMR: δ 50.5 (s, PPh_3) ppm. MS (ES +ve): *m/z* (abundance %): 949 (72) $[M]^+$. Calcd. for $C_{48}H_{51}NO_5P_2RuS_2$: C 60.8, H 5.4, N 1.5%. Found: C 60.7, H 5.5, N 1.6%.

[Ru(CH=CH_6H_4Me-4)(S_2CN-[15]aneO_4)(CO)(PPh_3)$_2$] (3)

[Ru(CH=CH_6H_4Me-4)Cl(BTD)(CO)(PPh_3)$_2$] (50 mg, 0.053 mmol) was dissolved in dichloromethane (15 mL) to give a dark orange solution. The addition of [15]aneO_4-NCS_2Na (19 mg, 0.060 mmol) in methanol (5 mL) resulted in a color change to pale yellow. After

stirring for 1 hour at room temperature, all solvent was removed by rotary evaporation. The crude product was dissolved in dichloromethane (15 mL) and filtered through Celite. Methanol (15 mL) was added and the solvent volume reduced (rotary evaporator) until precipitation of the pale yellow product occurred. Yield: 38 mg (67%). IR: 1910 (ν_{CO}), 1480 (ν_{C-N}), 1123, 1089 (ν_{C-O}), 840 (ν_{C-S}), 692 cm^{-1}. ^{1}H NMR: δ 2.23 (s, CH_3, 3H), 3.11 (t, CH_2, 2H, J_{HH} = 6.5 Hz), 3.21 (t, CH_2, 2H, J_{HH} = 5.8 Hz), 3.31 (t, CH_2, 2H, J_{HH} = 6.0 Hz), 3.39 (t, CH_2, 2H, J_{HH} = 5.6 Hz), 3.47 (m, CH_2, 2H), 3.54 (m, CH_2, 2H), 3.62 (m, CH_2, 8H), 5.58 (d, Hβ, 1H, J_{HH} = 16.7 Hz), 6.41, 6.82 (AB, C_6H_4, 4H, J_{AB}= 8.0 Hz), 7.32 (m, C_6H_5, 20H), 7.55 (m, C_6H_5, 10H), 7.72 (dt, Hα, 1H, J_{HH}= 16.7 Hz, J_{HP} = 3.0 Hz) ppm. $^{31}P\{^{1}H\}$ NMR: δ 39.7 (s, PPh_3) ppm. MS (LSIMS): *m/z* (abundance %): 1065 (25) $[M]^+$. Calcd. for $C_{57}H_{59}NO_5P_2RuS_2 \cdot 0.25CH_2Cl_2$: C 63.3, H 5.5, N 1.3%. Found: C 63.5, H 5.3, N 1.6%.

[Ru(CH=CHBu^t)(S_2CN-[15]aneO_4)(CO)(PPh_3)$_2$] (4)

The same procedure was employed as used for the preparation of **3**, using [Ru(CH=CHBu^t)Cl(BTD)(CO)(PPh_3)$_2$] (50 mg, 0.055 mmol) and [15]aneO_4-NCS_2Na (19 mg, 0.060 mmol) to yield a pale yellow product. Yield: 46 mg (81%). IR: 1897 (ν_{CO}), 1477 (ν_{C-N}), 1122, 1089 (ν_{C-O}), 841 (ν_{C-S}), 740, 693 cm^{-1}. ^{1}H NMR: δ 0.38 (s, ^{t}Bu, 9H), 3.03 (m, CH_2, 4H), 3.36 (m, CH_2, 4H), 3.50 (m, CH_2, 4H), 3.61 (m, CH_2, 8H), 4.58 (dt, Hβ, 1H, J_{HH} =16.3 Hz), 6.30 (dt, Hα, 1H, J_{HH} = 16.3 Hz, J_{HP} = 3.0 Hz), 7.31 (m, C_6H_5, 20H), 7.56 (m, C_6H_5, 10H) ppm. $^{31}P\{^{1}H\}$ NMR: δ 40.2 (s, PPh_3) ppm. MS (ES +ve): 1031 (37) $[M]^+$. Calculated for $C_{54}H_{61}NO_5P_2RuS_2$: C 62.9, H 6.0, N 1.4%. Found: C 62.8, H 5.9, N 1.5%.

[Ru(CH=CHPyr-1)(S_2CN-[15]aneO_4)(CO)(PPh_3)$_2$] (5)

The same procedure was employed as used for the preparation of **3**, using [Ru(CH=CHPyr-1)Cl(BTD)(CO)(PPh_3)$_2$] (52 mg, 0.049 mmol) and [15]aneO_4-NCS_2Na (17 mg, 0.054 mmol) to yield a bright yellow product. Yield: 44 mg (95%). IR: 1908 (ν_{CO}), 1480 (ν_{C-N}), 1118, 1091 (ν_{C-O}), 850 (ν_{C-S}), 744, 692 cm^{-1}. ^{1}H NMR: δ 3.14 (t, CH_2, 2H, J_{HH} = 6.2 Hz), 3.23 (t, CH_2, 2H, J_{HH} = 5.7 Hz), 3.33 (m, CH_2, 2H), 3.39 (m, CH_2, 2H), 3.51 (m, CH_2, 2H), 3.57 (m, CH_2, 2H), 3.63 (m, CH_2, 8H), 6.87 (d, Hβ, 1H, J_{HH} = 16.4 Hz), 6.94 (d, pyrenyl-CH, 1H, J_{HH} = 8.1 Hz), 7.32 (m, C_6H_5, 20H), 7.64 (m, C_6H_5, 10H), 7.84 - 8.05 (m, pyrenyl-CH, 8H), 8.33 (dt, Hα, 1H, J_{HH} =16.4 Hz, J_{HP} = 3.0 Hz) ppm. $^{31}P\{^{1}H\}$ NMR: 39.7 (s, PPh_3) ppm. MS: *m/z* (abundance %): 1175 (10) $[M]^+$. Calcd. for $C_{66}H_{61}NO_5P_2RuS_2$: C 67.4, H 5.2, N 1.2%. Found: C 67.3, H 5.0, N 1.2%.

[Ru(C(C≡CPh)=CHPh)(S_2CN-[15]aneO_4)(CO)(PPh_3)$_2$] (6)

The same procedure was employed as used for the preparation of **3**, using [Ru(C(C≡CPh)=CHPh)Cl(CO)(PPh_3)$_2$] (100 mg, 0.112 mmol) and [15]aneO_4-NCS_2Na (40.0 mg, 0.126 mmol) to yield a light yellow product. Yield: 103 mg (80%). IR: 2138 ($\nu_{C\equiv C}$), 1907 (ν_{CO}), 1471 (ν_{C-N}), 1114, 1088 (ν_{C-O}), 864 (ν_{C-S}), 740, 692 cm^{-1}. ^{1}H NMR: δ 3.14 (m, CH_2, 2H), 3.23 (m, CH_2, 6H), 3.50 (m, CH_2, 2H), 3.55 (m, CH_2, 2H), 3.63 (m, CH_2, 8H), 6.25 (s, Hβ, 1H), 7.06 (m, CC_6H_5, 5H), 7.18 – 7.30 (m, PC_6H_5 + CC_6H_5, 23H), 7.59 (m, C_6H_5, 12H) ppm. ^{31}P{^{1}H} NMR: δ 38.0 (s, PPh_3) ppm. MS (LSIMS): 866 (100) $[M - CO - PPh_3 + 4H]^+$. Calcd. for $C_{64}H_{61}NO_5P_2RuS_2$: C 66.8, H 5.3, N 1.2%. Found: C 66.7, H 5.2, N 1.4%.

[Ru(S_2CN-[15]aneO_4)(dppm)$_2$]PF_6 (7)

Cis-[$RuCl_2$(dppm)$_2$] (40 mg, 0.043 mmol) was dissolved in dichloromethane (10 mL) and NH_4PF_6 (13.9 mg, 0.085 mmol) added in methanol (5 mL). Addition of [15]aneO_4-NCS_2Na (15 mg, 0.047 mmol) in methanol (3 mL) was followed by stirring the reaction for 1 hour at room temperature. All solvent was removed (rotary evaporator) and the crude product was dissolved in the minimum volume of dichloromethane and filtered through Celite. Ethanol (20 mL) was added and slow reduction of the solvent volume (rotary evaporator) used to obtain a pale yellow product. This was washed with ethanol (10 mL), petroleum ether (10 mL) and dried. Yield: 29 mg (52%). IR: 1485 (ν_{C-N}), 1435, 1098 (ν_{CO}), 836 (ν_{PF}), 698 cm^{-1}. NMR: ^{1}H NMR: δ 3.60 – 3.75 (m, CH_2, 20H), 4.60, 4.94 (m x 2, PCH_2P, 2 x 2H), 6.51 (m, C_6H_5, 4H), 6.97 (m, C_6H_5, 8H), 7.18 (m, C_6H_5, 2H), 7.35 (m, C_6H_5, 22H), 7.63 (m, C_6H_5, 4H) ppm. ^{31}P{^{1}H} NMR: δ –18.7 (t, J_{PP}= 34.2 Hz), −5.8 (t, J_{PP}= 34.3 Hz) ppm. MS (LSIMS): *m/z* (abundance %): 1164 (100) $[M]^+$. Calcd. for $C_{61}H_{64}F_6NO_4P_5RuS_2$: C 56.0, H 4.9, N 1.1%. Found: C 55.9, H 4.7, N 1.2%.

[OsH(S_2CN-[15]aneO_4)(CO)(PPh_3)$_2$] (8)

[15]aneO_4-NCS_2Na (25 mg, 0.079 mmol) was dissolved in methanol (5 mL) and added to a dichloromethane solution of [OsHCl(CO)(BTD)(PPh_3)$_2$] (70 mg, 0.077 mmol), resulting in an orange coloration. The reaction was stirred at room temperature for 3 hours. All solvent was removed under reduced pressure and a white crude product was obtained. This was dissolved in dichloromethane (10 mL) and filtered through Celite. Addition of methanol (15 mL) followed by slow reduction of the solvent volume (rotary evaporator) resulted in a brown product, which was washed with methanol (10 mL), petroleum ether (10 mL) and dried. Yield: 62 mg (76%). IR: 1978 (ν_{OsH}), 1903 (ν_{CO}), 1479 (ν_{C-N}), 1478, 1433, 1111 (ν_{C-O}),

845 (ν_{C-S}), 692 cm^{-1}. ^{1}H NMR: δ –12.77 (s, OsH, 1H, J_{HH} = 18.2 Hz), 3.02 (m, CH_2, 4H), 3.20, 3.25 (t x 2, CH_2, 2 x 2H, J_{HH} = 6.3 Hz), 3.41 – 3.46 (m, CH_2, 4H), 3.53 – 3.57 (m, CH_2, 8H), 7.35, 7.71 (m x 2, C_6H_5, 30H) ppm. $^{31}P\{^{1}H\}$ NMR: δ 18.6 (s, PPh_3) ppm. MS (ES +ve): *m/z* (abundance %): 1038 (12) $[M]^+$. Calcd. for $C_{48}H_{51}NO_5OsP_2S_2 \cdot 0.5CH_2Cl_2$: C 53.9, H 4.9, N 1.3%. Found: C 53.8, H 4.7, N 1.2%.

[Ru(C≡CBu^t)(S_2CN-[15]aneO_4)(CO)(PPh_3)$_2$] (9)

Complex **3** (48 mg, 0.051 mmol) was dissolved in toluene (10 mL) and HC≡CBu^t (0.060 mL, 0.49 mmol) added. The reaction was heated at reflux for 3 hours and then all solvent removed (rotary evaporator). The residue was dissolved in diethyl ether (5 mL). The addition of hexane (10 mL) led to precipitation of a pale brown solid, which was filtered and washed with hexane (2 x 10 mL) and dried. Yield: 21 mg (40 %). IR: 2860, 2105 ($\nu_{C\equiv C}$), 1931 (ν_{CO}), 1481, 1434 (ν_{C-N}), 1120, 1093 (ν_{C-O}), 842 (ν_{C-S}), 693 cm^{-1}. ^{1}H NMR: δ 0.84 (s, CH_3, 9H), 2.95 – 3.05 (m, CH_2, 4H), 3.31 (m, CH_2, 4H), 3.48 (m, CH_2, 4H), 3.60 – 3.68 (m, CH_2, 8H), 7.32, 7.93 (m x 2, C_6H_5, 30H) ppm. $^{31}P\{^{1}H\}$ NMR: δ 38.5 (s, PPh_3) ppm. MS (ES, +ve): *m/z* (abundance %): 1002 (7) $[M - CO]^+$. Calcd. for $C_{54}H_{59}NO_5P_2RuS_2$: C 63.0, H 5.8, N 1.4%. Found: C 62.6, H 5.5, N 1.0%.

[Os(CH=CHPyr-1)(S_2CN-[15]aneO_4)(CO)(PPh_3)$_2$] (10)

The same procedure was employed as used for the preparation of **3**, stirring [Os(CH=CHPyr-1)Cl(CO)(BTD)(PPh_3)$_2$] (54 mg, 0.047 mmol) and [15]aneO_4-NCS_2Na (15 mg, 0.047 mmol) for 4 hours to yield a brown yellow product. Yield: 42 mg (71%). IR: 1889 (ν_{CO}), 1479 (ν_{C-N}), 1432, 1090 (ν_{C-O}), 845 (ν_{C-S}), 691 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 2.97, 3.17 (t x 2, CH_2, 2 x 2H, J_{HH} = 6.3 Hz), 3.31 (m, CH_2, 4H), 3.44 – 3.58 (m, CH_2, 12H), 6.81 (dt, Hβ, 1H, J_{HH} = 16.8 Hz, J_{HP} = 1.8 Hz), 7.00 (d, pyrenyl-CH, 1H, J_{HH} = 8.2 Hz), 7.34, 7.63 (m x 2, C_6H_5, 30H), 7.74 (d, pyrenyl-CH, 1H, J_{HH} = 8.2 Hz), 7.87 (m, pyrenyl-CH, 4H), 7.90 (d, pyrenyl-CH, 1H, J_{HH} = 7.6 Hz), 8.04 (d, pyrenyl-CH, 2H, J_{HH} = 7.6 Hz), 9.04 (dt, Hα, 1H, J_{HH} =16.8 Hz, J_{HP} = 2.5 Hz) ppm. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 7.7 (s, PPh_3) ppm. MS (ES +ve) *m/z* (abundance %): 1306 (100) $[M + MeCN]^+$. Calcd. for $C_{66}H_{61}NO_5OsP_2S_2 \cdot 1.75CH_2Cl_2$: C 57.6, H 4.6, N 1.0%. Found: C 57.7, H 4.3, N 1.4%.

[Os{CH=CH-bpyReCl(CO)$_3$}Cl(CO)(BTD)(PPh$_3$)$_2$] (11)

[OsHCl(CO)(BTD)(PPh$_3$)$_2$] (565 mg, 0.617 mmol) was dissolved in dichloromethane (15 mL) to give a dark orange solution. After the addition of [ReCl(CO)$_3$(bpyC≡CH)] (283 mg, 0.618 mmol) in dichloromethane (10 mL) the color changed to dark red. The solution was stirred at room temperature for 6 h and then concentrated to dryness (rotary evaporator). Diethyl ether (30 mL) was added and a precipitate obtained by ultrasonic trituration, which was then filtered under vacuum and washed with diethyl ether (2 x 20 mL). The resulting product was a dark orange solid. Yield: 849 mg (98%). IR: 2017 (ν_{CO}), 1937 (ν_{CO}), 1907 (ν_{CO}), 1878 (ν_{CO}), 1587, 1536, 1472, 1434, 1094 ($\nu_{C–O}$), 846 ($\nu_{C–S}$), 745, 695 cm^{-1}. ^{1}H NMR: δ 5.75 (d, Hβ, 1H, J_{HH} = 16.0 Hz), 7.10 – 8.08 (m, C$_6$H$_5$ + BTD + bpy, 30H + 4H + 6H), 8.96 (d, bpy, 1H, J_{HH} = 8.0 Hz), 10.08 (dt, Hα, 1H, J_{HH} = 16.0 Hz, J_{HP} = 2.3 Hz) ppm. ^{31}P{^{1}H} NMR: δ 0.1 (d, PPh$_3$, J_{PP} = 14.2 Hz) ppm. MS (ES +ve) *m/z* (abundance): 1311 (100) [M – BTD + 2Na]$^+$. Calcd. for C$_{58}$H$_{43}$Cl$_2$N$_4$O$_4$OsP$_2$ReS: C, 49.7; H, 3.1; N, 4.0 %. Found: C, 49.5; H, 3.0; N, 3.9 %.

[Os{CH=CH-bpyReCl(CO)$_3$}(S$_2$CN-[15]aneO$_4$)(CO)(PPh$_3$)$_2$] (12)

The same procedure was employed as used for the preparation of **3**, using **11** (40 mg, 0.029 mmol) and **1** (10 mg, 0.032 mmol) to yield a red product. Yield: 32 mg (72%). IR: 2020 (ν_{CO}), 1927 (ν_{CO}), 1903 (ν_{CO}), 1882 (ν_{CO}), 1482, 1434 (ν_{C-N}), 1115, 1093 (ν_{C-O}), 845 (ν_{C-S}), 745, 693 cm^{-1}. ^{1}H NMR: δ 3.01 – 3.54 (m x 5, 20H, CH$_2$), 5.56 (d, 1H, Hβ, J_{HH} = 17.3 Hz), 6.87 (d, 1H, bpy, J_{HH} = 8.5 Hz), 7.37, 7.52 (m x 2, 30H + 1H, C$_6$H$_5$ + bpy), 7.65 (d, 1H, bpy, J_{HH} = 8.5 Hz), 7.94 – 7.98 (m, 3H, bpy), 8.97 (d, 1H, bpy, J_{HH} = 5.5 Hz), 9.38 (dt, 1H, Hα, J_{HH} = 17.3 Hz, J_{HP} unresolved) ppm. ^{31}P{^{1}H} NMR: δ 8.0 (d, PPh$_3$, J_{PP} = 5.6 Hz) ppm. MS (ES +ve) *m/z* (abundance): 1546 (100) [M + Na]$^+$. Calcd. for C$_{63}$H$_{59}$ClN$_3$O$_8$OsP$_2$ReS$_2$: C, 49.7; H, 3.9; N, 2.8 %. Found: C, 49.6; H, 3.7; N, 2.8 %.

NaS$_2$CN-[18]aneO$_4$-NCS$_2$Na (13)

1,10-Diaza-18-crown-6 (50.0 mg, 0.191 mmol) was dissolved in water (5 mL) and sodium hydroxide (22 mg, 0.39 mmol) was added in water (3 mL). Carbon disulfide (0.025 mL, 0.42 mmol) was added and the reaction stirred for 6 hours in an ice bath. All water was removed under reduced pressure and the crude product dissolved in methanol (5 mL), to which diethyl ether was added until precipitation of the colorless product was complete. The solid was washed with diethyl ether (10 mL) and dried. The solid is hygroscopic. Yield: 78 mg (89%).

IR: 3379, 1666, 1475, 1405, 1350, 1275, 1218, 1180, 1111 ($\nu_{C\text{-}O}$), 1027, 980, 948, 877, 848 ($\nu_{C\text{-}S}$) cm^{-1}. ^{1}H NMR (CD_3OD): δ 3.65 (s, CH_2, 8H), 3.88 (t, CH_2, 8H, J_{HH} = 5.9 Hz), 4.45 (t, CH_2, 8H, J_{HH} = 5.9 Hz) ppm. $^{13}C\{^{1}H\}$ NMR (D_2O, 500 MHz): δ 210.7 (s, CS_2), 69.8, 67.9 (s x 2, NCH_2CH_2O), 54.8 (s, OCH_2CH_2O) ppm. MS (ES −ve): *m/z* (abundance %): 412 (22) $[M]^+$. Calcd. for $C_{14}H_{24}N_2Na_2O_4S_4{\cdot}6H_2O$: C 29.7, H 6.4, N 4.9%. Found: C 29.5, H 6.7, N 5.2%.

[{RuH(CO)(PPh_3)$_2$}$_2$(S_2CN-[18]aneO_4-NCS_2)] (14)

[RuHCl(CO)(PPh_3)$_3$] (57 mg, 0.060 mmol) was dissolved in dichloromethane (15 mL) and **13** (14 mg, 0.031 mmol) was added as a methanolic solution, resulting in a pale orange coloration. After 5 hours, a white precipitate formed, which was filtered, washed with cold methanol (10 mL), petroleum ether (10 mL) and dried. Yield: 39 mg (76%). IR: 1909 (ν_{CO}), 1477 (ν_{C-N}), 1093 (ν_{C-O}), 844 ($\nu_{C\text{-}S}$), 692 cm^{-1}. NMR: ^{1}H NMR (CD_2Cl_2): δ −10.95 (t, RuH, 2H, J_{HP} = 19.9 Hz), 3.21, 3.16, 3.26, 3.38 (m x 4, CH_2, 24H), 7.33, 7.75 (m x 2, C_6H_5, 60H) ppm. $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 210.8 (s, CS_2), 205.8 (t, CO, J_{CP} = 14.3 Hz), 135.7 (t, *ipso*-C_6H_5, J_{CP} = 21.2 Hz), 134.7 (t, *o/m*-C_6H_5, J_{CP} = 5.9 Hz), 129.4 (s, *p*-C_6H_5), 127.8 (t, *o/m*-C_6H_5, J_{CP} = 4.6 Hz), 71.1 (s, OCH_2), 70.4, 70.3, 70.2, 70.1 (s x 4, OCH_2), 68.1, 67.9 (s x 2, $NCCH_2$), 52.2, 51.8 (s x 2, NCH_2) ppm. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 50.2 (s, PPh_3) ppm. MS (MALDI): 1787 (5) $[M + MeCN + Na]^+$. Calcd. for $C_{88}H_{86}N_2O_6P_4Ru_2S_4$: C 61.4, H 5.0, N 1.6%. Found: C 61.3, H 4.9, N 1.7%.

[{Ru(CH=CHC$_6$H$_4$Me-4)(CO)(PPh_3)$_2$}$_2$(S_2CN-[18]aneO_4-NCS_2)] (15)

[Ru(CH=CHC$_6$H$_4$Me-4)Cl(BTD)(CO)(PPh_3)$_2$] (50 mg, 0.053 mmol) was dissolved in dichloromethane (15 mL) to give a dark orange solution. The addition of **13** (12 mg, 0.026 mmol) in methanol (15 mL) resulted in a color change to pale yellow. After stirring for 1 hour at room temperature, all solvent was removed by rotary evaporation. The crude product was dissolved in dichloromethane (20 mL) and filtered through Celite. Methanol (20 mL) was added and the solvent volume reduced (rotary evaporator) until precipitation of the cream product occurred. This was washed with ethanol (10 mL), petroleum ether (10 mL) and dried. Yield: 34 mg (66 %). IR: 1909 (ν_{CO}), 1479 (ν_{C-N}), 1432, 1278 (ν_{C-O}), 1109, 829 ($\nu_{C\text{-}S}$) cm^{-1}. ^{1}H NMR: δ 2.24 (s, CH_3, 6H), 3.06 (m, CH_2, 4H), 3.17 – 3.24 (m, CH_2, 8H), 3.38 (d, CH_2, 8H, J_{HH} = 6.0 Hz), 3.50 (t, CH_2, 4H, J_{HH} = 5.6 Hz), 5.52 (d, Hβ, 2H, J_{HH} = 16.7 Hz), 6.41, 6.84 (AB, C_6H_4, 8H, J_{AB}= 7.9 Hz), 7.31, 7.56 (m x 2, C_6H_5, 60H), 7.71 (dt, Hα, 2H,

J_{HH}= 16.7 Hz, J_{HP} = 3.0 Hz) ppm. $^{31}P\{^{1}H\}$ NMR: δ 39.5 (s, PPh_3) ppm. MS (MALDI): *m/z* (abundance %): 1954 (4) $[M]^+$. Calcd. for $C_{106}H_{102}N_2O_6P_4Ru_2S_4$: C 65.2, H 5.3, N 1.4%. Found: C 64.8, H 5.1, N 1.2%.

[{Ru(CH=CHBu^t)(CO)(PPh$_3$)$_2$}$_2$(S$_2$CN-[18]aneO$_4$-NCS$_2$)] (16)

The same procedure was employed as used for the preparation of **15**, using [Ru(CH=CHBu^t)Cl(BTD)(CO)(PPh_3)$_2$] (54 mg, 0.059 mmol) and **13** (10 mg, 0.022 mmol) to yield a white powder. Yield: 38 mg (68%). IR: 1891 (ν_{CO}), 1475 (ν_{C-N}), 1432, 1089 (ν_{C-O}), 850 (ν_{C-S}), 691 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 0.36 (s, Me, 18H), 2.85, 3.00, 3.19, 3.34, 3.43 (m x 5, CH_2, 24H), 4.48 (dt, Hβ, 2H, J_{HH} = 16.3 Hz, J_{HP} = 1.6 Hz), 6.31 (dt, Hα, 2H, J_{HH} = 16.3 Hz, J_{HP} = 2.3 Hz), 7.31, 7.56 (m x 2, C_6H_5, 60H) ppm. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 39.9 (s, PPh_3) ppm. MS (MALDI): 1625 (3) $[M - PPh_3]^+$. Calcd. for $C_{100}H_{106}N_2O_6P_4Ru_2S_4$: C 63.7, H 5.7, N 1.5%. Found: C 63.5, H 5.5, N 1.4%.

[{Ru(CH=CHPyr-1)(CO)(PPh$_3$)$_2$}$_2$(S$_2$CN-[18]aneO$_4$-NCS$_2$)] (17)

The same procedure was employed as used for the preparation of **15**, using [Ru(CH=CHPyr-1)Cl(BTD)(CO)(PPh_3)$_2$] (50 mg, 0.048 mmol) and **13** (11 mg, 0.024 mmol) to yield a bright yellow product. Yield: 44 mg (84%). IR: 1906 (ν_{CO}), 1482 (ν_{C-N}), 1433, 1226, 1121 (ν_{C-O}), 844 (ν_{C-S}) cm^{-1}. ^1H NMR: δ 3.11 (m, CH_2, 4H), 3.21 – 3.28 (m, CH_2, 8H), 3.43 (m, CH_2, 8H), 3.51 (m, CH_2, 4H), 6.83 (d, Hβ, 2H, J_{HH} = 16.6 Hz), 6.95 (d, pyrenyl-CH, 2H, J_{HH} = 8.2 Hz), 7.32, 7.63 (m x 2, C_6H_5, 60H), 7.75 – 8.06 (m, pyrenyl-CH, 16H), 8.32 (dt, Hα, 2H, J_{HH} = 16.6 Hz, J_{HP} unresolved) ppm. $^{31}P\{^{1}H\}$ NMR: δ 39.2 (s, PPh_3) ppm. MS (MALDI): 2310 (18) $[M + 3K + H_2O]^+$. Calcd. for $C_{124}H_{106}N_2O_6P_4Ru_2S_4$: C 68.5, H 4.9, N 1.3%. Found: C 68.3, H 4.8, N 1.2%.

[{Ru(C(C≡CPh)=CHPh)(CO)(PPh$_3$)$_2$}$_2$(S$_2$CN-[18]aneO$_4$-NCS$_2$)] (18)

The same procedure was employed as used for the preparation of **15**, using [Ru(C(C≡CPh)=CHPh)Cl(CO)(PPh_3)$_2$] (50 mg, 0.056 mmol) and **13** (13 mg, 0.028 mmol) to yield a pale yellow product. Yield: 38 mg (64%). IR: 2142 ($\nu_{C\equiv C}$), 1919 (ν_{CO}), 1481 (ν_{C-N}), 1432, 1226, 1090 (ν_{C-O}), 841 (ν_{C-S}) cm^{-1}. ^1H NMR: δ 3.11 (m, CH_2, 4H), 3.18 (m, CH_2, 8H), 3.31 (m, CH_2, 4H), 3.41 (m, CH_2, 8H), 6.19 (s, Hβ, 2H), 6.96 (t, CC_6H_5, 2H, J_{HH}= 7.1 Hz), 7.01 – 7.10 (m, CC_6H_5, 8 H), 7.18 - 7.33 (m, PC_6H_5 + CC_6H_5, 40H + 10H), 7.59 (m, PC_6H_5, 20H) ppm. $^{31}P\{^{1}H\}$ NMR: δ 37.9 (s, PPh_3) ppm. MS (LSIMS): *m/z* (abundance %): 2073 (8)

$[M– 2CO + 3H]^+$. Calcd. for $C_{120}H_{106}N_2O_6P_4Ru_2S_4$: C 67.8, H 5.0, N 1.3%. Found: C 67.7, H 4.9, N 1.3%.

[{Ru(dppm)$_2$}$_2$(S$_2$CN-[18]aneO$_4$-NCS$_2$)](PF$_6$)$_2$ (19)

The same procedure as used for the preparation of **7** was employed using *cis*-$[RuCl_2(dppm)_2]$ (50 mg, 0.053 mmol), **13** (12 mg, 0.026 mmol) and NH_4PF_6 (18.0 mg, 0.110 mmol) to yield a pale yellow product. Yield: 28 mg (43%). IR: 1484 ($\nu_{C–N}$), 1435, 1228, 1095, 1000, 834 ($\nu_{P–F}$) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 3.58 (m, CH_2, 8H), 3.65 (m, CH_2, 8H), 3.80, 3.90 (m x 2, CH_2, 2 x 4H), 4.50, 4.95 (m x 2, PCH_2P, 2 x 4H), 6.49 (t, C_6H_5, 8H, J_{HH}= 9.0 Hz), 6.98 (t, C_6H_5, 8H, J_{HH}= 7.6 Hz), 7.09 (m, C_6H_5, 8H), 7.29 - 7.50 (m, C_6H_5, 48H), 7.68 (m, C_6H_5, 8H) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ – 18.5 (t, dppm, J_{PP} = 34.0 Hz), – 5.3 (m, dppm) ppm. MS (LSIMS): *m/z* (abundance %): 2241 (9) $[M–2CO+PF_6]^+$. Calcd. for $C_{114}H_{112}F_{12}N_2O_4P_{10}Ru_2S_4 \cdot 1.5CH_2Cl_2$: C 54.0, H 4.5, N 1.1%. Found: C 54.4, H 4.6, N 1.2%.

[{OsH(CO)(PPh$_3$)$_2$}$_2$(S$_2$CN-[18]aneO$_4$-NCS$_2$)] (20)

The same procedure was employed as used for the preparation of **14**, $[OsHCl(CO)(BTD)(PPh_3)_2]$ (66 mg, 0.072 mmol) and **13** (16 mg, 0.035 mmol) were stirred for 3 hours to yield a pale lilac product. Yield: 37 mg (54%). IR: 2016, 1980 (ν_{OsH}), 1893 (ν_{CO}), 1480 ($\nu_{C–N}$), 1434, 1093 ($\nu_{C–O}$), 845 (ν_{C-S}), 693 cm^{-1}. ^1H NMR (CD_2Cl_2): δ –12.75 (s, OsH, 2H, J_{HH} = 18.4 Hz), 3.09 – 3.15 (m, CH_2, 16H), 3.38 (t, CH_2, 8H, J_{HH} = 11.5 Hz), 7.37, 7.74 (m x 2, C_6H_5, 60H) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 18.5 (s, PPh_3) ppm. MS (MALDI): *m/z* (abundance %): 1376 (29) $[M–2PPh_3]^+$. Calcd. for $C_{88}H_{86}N_2O_6Os_2P_4S_4$: C 55.6, H 4.6, N 1.5%. Found: C 55.5, H 4.6, N 1.4%.

[{Os(CH=CHPyr-1)(CO)(PPh$_3$)$_2$}$_2$(S$_2$CN-[18]aneO$_4$-NCS$_2$)] (21)

The same procedure was employed as used for the preparation of **15**, stirring $[Os(CH=CHPyr\text{-}1)Cl(CO)(BTD)(PPh_3)_2]$ (54 mg, 0.047 mmol) and **13** (11 mg, 0.024 mmol) for 3 hours to yield a green product. Yield: 40 mg (72%). IR: 1887 (ν_{CO}), 1481 ($\nu_{C–N}$), 1432, 1090 ($\nu_{C–O}$), 844 (ν_{C-S}), 692 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 3.13 (m, CH_2, 6H), 3.30 (m, CH_2, 4H), 3.44 (m, CH_2, 10H), 3.69 (m, CH_2, 4H), 6.80 (d, Hβ, 2H, J_{HH}= 17.3 Hz), 7.05 (d, pyrenyl-CH, 2H, J_{HH}= 8.3 Hz), 7.38, 7.67 (m x 2, C_6H_5, 60H), 7.78 – 8.09 (m, pyrenyl-CH, 16H), 9.07 (dt, Hα, 2H, J_{HH}= 17.3 Hz, J_{HP} unresolved) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 7.4

(s, PPh_3) ppm. MS (LSIMS): *m/z* (abundance %): 2034 (12) $[M - 2CO - PPh_3]^+$. Calcd. for $C_{124}H_{106}N_2O_6Os_2P_4S_4 \cdot 3CH_2Cl_2$: C 58.5, H 4.3, N 1.1%. Found: C 58.7, H 4.1, N 1.2%.

[{Os{CH=CH-bpyRe(CO)$_3$Cl}(CO)(PPh$_3$)$_2$}$_2$(S$_2$CN-[18]aneO$_4$-NCS$_2$)] (22)

Compound **11** (30 mg, 0.021 mmol) was dissolved in dichloromethane (15 mL) to give a red solution. On addition of **13** (5.0 mg, 0.011 mmol) dissolved in methanol (5 mL), the solution darkened. After 2 h stirring at room temperature, all solvent was removed (rotary evaporator) and the crude product was dissolved in dichloromethane (20 mL). This was filtered through Celite and the solvent again removed by rotary evaporation. Diethyl ether (30 mL) was added followed by trituration in an ultrasonic bath to yield a dark red precipitate. This was filtered under vacuum and washed with diethyl ether (2 x 20 mL) and dried. Yield: 24 mg (80%). IR: 2013 (ν_{CO}), 1879 (ν_{CO}), 1739, 1468 (ν_{C-N}), 1433, 1366, 1229, 1217, 1091 (ν_{C-O}), 840 (ν_{C-S}), 744, 693 cm^{-1}. ^1H NMR: δ 3.07 – 3.20, 3.35 – 3.43 (m x 2, CH_2, 24H), 5.52 (d, 2H, Hβ, J_{HH} = 16.0 Hz), 6.85 (d, 2H, bpy, J_{HH} = 8.8 Hz), 7.38, 7.52 (m x 2, 60 H, C_6H_5), 7.64 – 7.72, 7.92 – 7.98 (m x 2, 2 x 5H, bpy), 8.97 (d, 2H, bpy, J_{HH} = 5.6 Hz), 9.36 (dt, 2H, Hα, J_{HH} = 16.0 Hz, J_{HP} unresolved) ppm. $^{31}P\{^1H\}$ NMR: δ 7.9 (s, PPh_3) ppm. MS (LSIMS, MALDI +ve): not diagnostic. Calcd. for $C_{118}H_{102}Cl_2N_6O_{12}Os_2P_4Re_2S_4$: C, 49.4; H, 3.6; N, 2.9 %. Found: C, 49.2; H, 3.6; N, 3.0 %.

Crystallography

Crystals of compounds **2**, **5** and **6** were grown by slow diffusion of ethanol into a dichloromethane solution of the complex in each case. Data were collected using an Oxford Diffraction Xcalibur 3 diffractometer, and the structures were refined based on F^2 using the SHELXTL and SHELX-97 program systems.[37]

Crystal data for **2**: $C_{48}H_{51}NO_5P_2RuS_2$, M = 949.02, monoclinic, $P2_1/n$ (no. 14), a = 12.28308(12), b = 20.7454(2), c = 18.0165(2) Å, β = 106.4116(11)°, V = 4403.88(8) $Å^3$, Z = 4, D_c = 1.431 g cm^{-3}, μ(Cu-Kα) = 4.836 mm^{-1}, T = 173 K, pale yellow needles, Agilent Xcalibur PX Ultra A diffractometer; 8436 independent measured reflections (R_{int} = 0.0208), R_1(obs) = 0.0298, wR_2(all) = 0.0775, 7684 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 148°], 545 parameters. CCDC 968702.

Crystal data for **5**: $C_{66}H_{61}NO_5P_2RuS_2 \cdot 1.5(CH_2Cl_2)$, M = 1302.67, monoclinic, $I2/a$ (no. 15), a = 21.8965(5), b = 17.9869(5), c = 31.6196(10) Å, β = 98.962(3)°, V = 12301.3(6) Å^3, Z = 8, D_c = 1.407 g cm^{-3}, μ(Cu-Kα) = 4.794 mm^{-1}, T = 173 K, yellow plates, Agilent Xcalibur PX Ultra A diffractometer; 11839 independent measured reflections (R_{int} = 0.0293), R_1(obs) = 0.0405, wR_2(all) = 0.1131, 9948 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 147°], 775 parameters. CCDC 968703.

Crystal data for **6**: $C_{64}H_{61}NO_5P_2RuS_2$, M = 1151.26, monoclinic, $P2_1/c$ (no. 14), a = 13.03464(8), b = 19.81564(10), c = 21.39853(12) Å, β = 101.6426(6)°, V = 5413.30(5) Å^3, Z = 4, D_c = 1.413 g cm^{-3}, μ(Cu-Kα) = 4.041 mm^{-1}, T = 173 K, pale yellow needles, Agilent Xcalibur PX Ultra A diffractometer; 10924 independent measured reflections (R_{int} = 0.0213), R_1(obs) = 0.0237, wR_2(all) = 0.0631, 10036 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 149°], 676 parameters. CCDC 968704.

Acknowledgements

We thank Johnson Matthey Ltd for a generous loan of ruthenium salts. We gratefully acknowledge the support of the Leverhulme Trust (Grant RPG-2012-634) for a studentship (A. T.). Prof. P. J. Blower (KCL), Prof. R. Vilar (IC) and A. Shivalingam (IC) are thanked for helpful discussions.

References

1 Delépine, M. *Compt. Rend.* **1907**, *144*, 1125-1127.

2 (a) Coucouvanis, D. *Prog. Inorg. Chem.* **1970**, *11*, 233–371; (b) Coucouvanis, D. *Prog. Inorg. Chem.* **1979**, *26*, 301–469; c) Burns, R. P.; McCullough, F. P.; McAuliffe, C. A. *Adv. Inorg. Chem. Radiochem.* **1980**, *23*, 211–280; d) Hogarth, G. *Prog. Inorg. Chem.* **2005**, *53*, 71–561; e) Cookson, J.; Beer, P. D. *Dalton Trans*. **2007**, 1459–1472.

3 a) Beer, P. D.; Berry, N. G.; Cowley, A. R.; Hayes, E. J.; Oates, E. C.; Wong, W. W. H.; *Chem. Commun.* **2003**, 2408-2409; b) Wong, W. W. H.; Curiel, D.; Cowley, A. R.; Beer, P. D.; *Dalton Trans.* **2005**, 359-364; c) Beer, P. D.; Cheetham, A. G.; Drew, M. G. B.; Fox, O. D.; Hayes, E. J.; Rolls, T. D.; *J. Chem. Soc., Dalton Trans.* **2003**,

603-611; d) Beer, P. D.; Berry, N.; Drew, M. G. B.; Fox, O. D.; Padilla-Tosta, M. E.; Patell, S.; *Chem. Commun.* **2001**, 199-200; e) Padilla-Tosta, M. E.; Fox, O. D.; Drew, M. G. B.; Beer, P. D.; *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 4235-4239; f) Fox, O. D.; Drew, M. G. B.; Beer, P. D.; *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 135-140; g) Vickers, M. S.; Cookson, J.; Beer, P. D.; Bishop, P. T.; Thiebaut, B,; *J. Mater. Chem.*, **2006**, *16*, 209–215; h) Cookson, J.; Beer, P. D.; *Dalton Trans*. **2007**, 1459-1472.

4 a) Wilton-Ely, J. D. E. T.; Solanki, D.; Hogarth, G. *Eur. J. Inorg. Chem.* **2005**, 4027-4030; b) Knight, E. R.; Solanki, D.; Hogarth, G.; Holt, K. B.; Thompson, A. L.; Wilton-Ely, J. D. E. T. *Inorg. Chem.* **2008**, *47*, 9642-9653; c) Macgregor, M. J.; Hogarth, G.; Thompson, A. L.; Wilton-Ely, J. D. E. T. *Organometallics* **2009**, *28*, 197-208; d) Knight, E. R.; Cowley, A. R.; Hogarth, G.; Wilton-Ely, J. D. E. T. *Dalton Trans.* **2009**, 607-609; e) Knight, E. R.; Leung, N. H.; Lin, Y. H.; Cowley, A. R.; Watkin, D. J.; Thompson, A. L.; Hogarth, G.; Wilton-Ely, J. D. E. T. *Dalton Trans.* **2009**, 3688-3697; f) Knight, E. R.; Leung, N. H.; Thompson, A. L.; Hogarth, G.; Wilton-Ely, J. D. E. T. *Inorg. Chem.* **2009**, *48*, 3866-3874; g) Oliver, K.; White, A. J. P.; Hogarth, G.; Wilton-Ely, J. D. E. T. *Dalton Trans.* **2011**, *40*, 5852-5864; h) Hogarth, G.; Rainford-Brent, E.-J. C.-R. C. R.; Kabir, S. E.; Richards, I.; Wilton-Ely, J. D. E. T.; Zhang, Q. *Inorg. Chim. Acta*, **2009**, *362*, 2020–2026; i) Naeem, S.; Ogilvie, E.; White, A. J. P.; Hogarth, G.; Wilton-Ely, J. D. E. T. *Dalton Trans.* **2010**, *39*, 4080-4089.

5 a) Naeem, S.; White, A. J. P.; Hogarth, G.; Wilton-Ely, J. D. E. T. *Organometallics* **2010**, *29*, 2547–2556; b) Naeem, S.; White, A. J. P.; Hogarth, G.; Wilton-Ely, J. D. E. T. *Organometallics*, **2011**, *30*, 2068–2069; c) Naeem, S.; Serapian, S. A.; Toscani, A.; White, A. J. P.; Hogarth, G.; Wilton-Ely, J. D. E. T. *Inorg. Chem.* **2014**, *53*, 2404–2416.

6 Sung, S.; Holmes, H.; Wainwright, L.; Toscani, A.; Stasiuk, G. J.; White, A. J. P.; Bell, J. D.; Wilton-Ely, J. D. E. T. *Inorg. Chem.* **2014**, *53*, 1989-2005.

7 For an overview of alkenyl chemistry of ruthenium(II), see: a) Whittlesey, M. K. in *Comprehensive Organometallic Chemistry III*; Crabtree, R. H.; Mingos, D. M. P.; Bruce, M. I.; Eds.; Elsevier: Oxford, U.K., 2006; Vol. 6; b) Hill, A. F. in *Comprehensive Organometallic Chemistry II*; Abel, E. W.; Stone, F. G. A.; Wilkinson, G.; Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 7.

8 Werner, H.; Esteruelas, M. A.; Otto, H.; *Organometallics* **1986**, *5*, 2295-2299.

9 Torres, M. R.; Vegas, A.; Santos, A.; Ros, J.; *J. Organomet. Chem.* **1986**, *309*, 169-177.

10 a) Jung, S.; Ilg, K.; Brandt, C. D.; Wolf, J.; Werner, H.; *Eur. J. Inorg. Chem.* **2004**, 469-480; b) Jung, S.; Brandt, C. D.; Wolf, J.; Werner, H.; *Dalton Trans.* **2004**, 375-383; c) Werner, H.; Jung, S.; Gonzalez-Herrero, P.; Ilg, K.; Wolf, J.; *Eur. J. Inorg. Chem.* **2001**, 1957-1961; d) Jung, S.; Ilg, K.; Wolf, J.; Werner, H.; *Organometallics* **2001**, *20*, 2121-2123; e) Werner, H.; Stüer, W.; Jung, S.; Weberndörfer, B.; Wolf, J.; *Eur. J. Inorg. Chem.* **2002**, 1076-1080; f) Werner, H.; Stark, A.; Steinert, P.; Grunwald, C.; Wolf, J.; *Chem. Ber.* **1995**, *128*, 49-62.

11 a) Esteruelas, M. A.; López, A. M.; Oñate, E.; *Organometallics* **2007**, *26*, 3260-3263; b) Bolano, T.; Castarlenas, R.; Esteruelas, M. A.; Oñate, E.; *J. Am. Chem. Soc.* **2006**, *128*, 3965-3973; c) Eguillar, B.; Esteruelas, M. A.; Oliván, M.; Oñate, E.; *Organometallics* **2005**, *24*, 1428-1438; d) Castarlenas, R.; Esteruelas, M. A.; Oñate, E.; *Organometallics* **2001**, *20*, 3283-3292; e) Castarlenas, R.; Esteruelas, M. A.; Oñate, E.; *Organometallics* **2001**, *20*, 2294-2302; f) Esteruelas, M. A.; García-Yebra, C.; Oliván, M.; Oñate, E.; Tajada, M.; *Organometallics* **2000**, *19*, 5098-5106; g) Castarlenas, R.; Esteruelas, M. A.; Oñate, E.; *Organometallics* **2000**, *19*, 5454-5463; h) Buil, M. L.; Esteruelas, M. A.; García-Yebra, C.; Gutiérrez-Puebla, E.; Oliván, M.; *Organometallics* **2000**, *19*, 2184-2193;i) Bohanna, C.; Buil, M. L.; Esteruelas, M. A.; Oñate, E.; Valero, C.; *Organometallics* **1999**, *18*, 5176-5179; j) Bohanna, C.; Callejas, B.; Edwards, A.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Ruiz, N.; Valero, C.; *Organometallics* **1998**, *17*, 373-381; k) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oñate, E.; *Organometallics* **1998**, *17*, 3567-3573; l) Esteruelas, M. A.; Liu, F.; Oñate, E.; Sola, E.; Zeier, B.; *Organometallics* **1997**, *16*, 2919-2928; m) Buil, M. L.; Elipe, S.; Esteruelas, M. A.; Oñate, E.; Peinado, E.; Ruiz, N.; *Organometallics* **1997**, *16*, 5748-5755; n) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Sola, E.; *J. Am. Chem. Soc.* **1996**, *118*, 89-99; o) Bohanna, C.; Esteruelas, M. A.; Herrero, J.; López, A. M.; Oro, L. A.; *J. Organomet. Chem.* **1995**, *498*, 199-206; p) Bohanna, C.; Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Sola, E.; *Organometallics* **1995**, *14*, 4825-4831; q) Bohanna, C.; Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; *Organometallics* **1995**, *14*, 4685-4696; Crochet, P.; r) Esteruelas, M. A.; López, A. M.; Martínez, M.-P.; Oliván, M.; Oñate, E.; Ruiz, N.; *Organometallics* **1998**, *17*, 4500-4509.

12 a) Gómez-Lor, B.; Santos, A.; Ruiz, M.; Echavarren, A. M.; *Eur. J. Inorg. Chem.* **2001**, 2305-2310; b) Castaño, A. M.; Echavarren, A. M.; López, J.; Santos, A.; *J. Organomet. Chem.* **1989**, *379*, 171-175; c) Montoya, J.; Santos, A.; Echavarren, A. M.; Ros, J.; *J. Organomet. Chem.* **1990**, *390*, C57-C60; d) Loumrhari, H.; Ros, J.; Torres, M. R.; Santos, A.; Echavarren, A. M.; *J. Organomet. Chem.* **1991**, *411*, 255-261; e) Montoya, J.; Santos, A.; López, J.; Echavarren, A. M.; Ros, J.; Romero, A.; *J. Organomet. Chem*. **1992**, *426*, 383-398; f) López, J.; Romero, A.; Santos, A.; Vegas, A.; Echavarren, A. M.; Noheda, P.; *J. Organomet. Chem.* **1989**, *373*, 249-258; g) Echavarren, A. M.; López, J.; Santos, A.; Montoya, J.; *J. Organomet. Chem.* **1991**, *414*, 393-400; h) Torres, M. R.; Vegas, A.; Santos, A.; Ros, J.; *J. Organomet. Chem.* **1987**, *326*, 413-421; i) Torres, M. R.; Santos, A.; Ros, J.; Solans, X.; *Organometallics* **1987**, *6*, 1091-1095; j) Santos, A.; Lopez, J.; Matas, L.; Ros, J.; Galan, A.; Echavarren, A. M.; *Organometallics* **1993**, *12*, 4215-4218.

13 a) Huang, D. J.; Renkema, K. B.; Caulton, K. G.; *Polyhedron* **2006**, *25*, 459-468; b) Marchenko, A. V.; Gérard, H.; Eisenstein, O.; Caulton, K. G.; *New. J. Chem.* **2001**, *25*, 1382-1388; c) Marchenko, A. V.; Gérard, H.; Eisenstein, O.; Caulton, K. G.; *New. J. Chem.* **2001**, *25*, 1244-1255; d) Coalter, J. N.; Streib, W. E.; Caulton, K. G.; *Inorg. Chem.* **2000**, *39*, 3749-3756; e) Pedersen, A.; Tilset, M.; Folting, K.; Caulton, K. G.; *Organometallics* **1995**, *14*, 875-888.

14 a) Hill, A. F.; Melling, R. P.; *J. Organomet. Chem.* **1990**, *396*, C22-C24; (b) Alcock, N. W.; Hill, A. F.; Melling, R. P. *Organometallics* **1991**, *10*, 3898-3903; c) Hill, A. F.; Harris, M. C. J.; Melling, R. P.; *Polyhedron* **1992**, *11*, 781-787; d) Harris, M. C. J.; Hill, A. F.; *Organometallics* **1991**, *10*, 3903-3906; e) Bedford, R. B.; Hill, A. F.; Thompsett, A. R.; White, A. J. P.; Williams, D. J.; *Chem. Commun.* **1996**, 1059-1060; f) Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T.; *Organometallics* **1998**, *17*, 4249-4258; g) Cannadine, J. C.; Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T.; *Organometallics* **1996**, *15*, 5409-5415; h) Hill, A. F.; Ho, C. T.; Wilton-Ely, J. D. E. T.; *Chem. Commun.* **1997**, 2207-2208; i) Hill, A. F.; Wilton-Ely, J. D. E. T.; *J. Chem. Soc., Dalton Trans.* **1998**, 3501-3510; j) Cowley, A. R.; Hector, A. L.; Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T.; *Organometallics*, **2007**, *26*, 6114-6125.

15 a) El Guaouzi, M.; Ros, J.; Solans, X.; Font-Bardía, M.; *Inorg. Chim. Acta* **1995**, *231*, 181-186; b) Matas, L.; Muniente, J.; Ros, J.; Alvarez-Larena, A.; Piniella, J. F.; *Inorg. Chem. Comm.* **1999**, *2*, 364-367; c) El Guaouzi, M.; Yáñez, R.; Ros, J.; Alvarez-

Larena, A.; Piniella, J. F.; *Inorg. Chem. Comm.* **1999**, *2*, 288-291; d) Torres, M. R.; Perales, A.;Loumrhari, H.; Ros, J.; *J. Organomet. Chem.* **1990**, *385*, 379-386; e) Matas, L.; Moldes, I.; Soler, J.; Ros, J.; Alvarez-Larena, A.; Piniella, J. F.; *Organometallics* **1998**, *17*, 4551-4555; f) Loumrhari, H.; Ros, J.; Torres, M. R.; Perales, A.; *Polyhedron* **1990**, *9*, 907-911; g) Maddock, S. M.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J.; *Organometallics* **1996**, *15*, 1793-1803; h) Deshpande, S. S.; Gopinathan, S.; Gopinathan, C.; *J. Organomet. Chem.* **1991**, *415*, 265-270; i) Bedford, R. B.; Cazin, C. S. J.; *J. Organomet. Chem.* **2000**, *598*, 20-23; j) Jia, G.; Wu, W. F.; Yeung, R. C. Y.; Xia, H. P.; *J. Organomet. Chem.*, **1997**, *539*, 53-59; k) Liu, S. H.; Chen, Y.; Wan, K. L.; Wen, T. B.; Zhou, Z.; Lo, M. F.; Williams, I. D.; Jia, G.; *Organometallics* **2002**, *21*, 4984-4992; l) Liu, S. H.; Xia, H.; Wen, T. B.; Zhou, Z.; Jia, G.; *Organometallics* **2003**, *22*, 737-743; m) Liu, S. H.; Hu, Q. Y.; Xue, P.; Wen, T. B.; Williams, I. D.; Jia, G.; *Organometallics* **2005**, *24*, 769-772; n) Liu, S. H.; Xia, H.; Wan, K. L.; Yeung, R. C. Y.; Hu, Q. Y.; Jia, G.; *J. Organomet. Chem.* **2003**, *683*, 331-336; o) Xia, H.; Wen, T. B.; Hu, Q. Y.; Wang. X.; Chen, X.; Shek, L. Y.; Williams, I. D.; Wong, K. S.; Wong, G. K. L.; Jia, G.; *Organometallics* **2005**, *24*, 562-569; p) Maurer, J.; Sarkar, B.; Schwederski, B.; Kaim, W.; Winter, R. F.; Záliš, S.; *Organometallics* **2006**, *25*, 3701-3712; q) Loumrhari, H.; Ros, J.; Torres, M. R.; *Polyhedron* **1991**, *10*, 421-427.

16 a) Wilton-Ely, J. D. E. T.; Wang, M.; Benoit, D.; Tocher, D. A.; *Eur. J. Inorg. Chem.* **2006**, 3068-3078; b) Wilton-Ely, J. D. E. T.; Pogorzelec, P. J.; Honarkhah, S. J.; Tocher, D. A.; *Organometallics* **2005**, *24*, 2862-2874; c) Wilton-Ely, J. D. E. T.; Honarkhah, S. J.;Wang, M.; Tocher, D. A.; *Dalton Trans.* **2005**, 1930-1939; d) Wilton-Ely, J. D. E. T.; Wang, M.; Honarkhah, S. J.; Tocher, D. A.; *Inorg. Chim. Acta.* **2005**, *358*, 3218-3226; e) Cowley, A. R.; Hector, A. L.; Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *Organometallics* **2007**, *26*, 6114-6125; f) Green, J. C.; Hector, A. L.; Hill, A. F.; Lin, S.; Wilton-Ely, J. D. E. T. *Organometallics* **2008**, *27*, 5548-5558.

17 a) Naeem, S.; Ribes, A.; White, A. J. P.; Haque, M. N.; Holt, K. B.; Wilton-Ely, J. D. E. T. *Inorg. Chem.* **2013**, *52*, 4700-4713; b) Lin, Y. H.; Duclaux, L.; Gonzàlez de Rivera, F.; Thompson, A. L.; Wilton-Ely, J. D. E. T. *Eur. J. Inorg. Chem.* **2014**, 2065-2072.

18 a) Lin, Y. H.; Leung, N. H.; Holt, K. B.; Thompson, A. L.; Wilton-Ely, J. D. E. T. *Dalton Trans.* **2009**, 7891-7901; b) Naeem, S.; Thompson, A. L.; Delaude, L.;

Wilton-Ely, J. D. E. T. *Chem. Eur. J.* **2010**, *16*, 10971–10974; c) Naeem, S.; Thompson, A. L.; White, A. J. P.; Delaude, L.; Wilton-Ely, J. D. E. T. *Dalton Trans.* **2011**, *40*, 3737–3747; d) Patel, P.; Naeem, S.; White, A. J. P.; Wilton-Ely, J. D. E. T. *RSC Advances* **2012**, *2*, 999–1008.

19 Moragues, M. E.; Toscani, A.; Sancenón, F.; Martínez-Mañez, R.; White, A. J. P.; Wilton-Ely, J. D. E. T. *J. Am. Chem. Soc.* **2014**, *136*, 11930−11933.

20 Maurer, J.; Linseis, J. M.; Sarkar, B.; Schwederski, B.; Niemeyer, M.; Kaim, W.; Záliš, S.; Anson, C.; Zabel, M.; Winter, R. F. *J. Am. Chem. Soc.* **2008**, *130*, 259-268.

21 Záliš, S.; Winter, R. F.; Kaim, W. *Coord. Chem. Rev.* **2010**, *254*, 1383–1396.

22 a) Green, M. L. H.; Marder, S. R.; Saunders, G. C.; Walker, N. M.; *J. Chem. Soc., Dalton Trans.* **1988**, 1697-1699; b) Granell, J.; Green, M. L. H.; Lowe, V. J.; Marder, S. R.; Mountford, P.; Saunders, G. C.; Walker, N. M.; *J. Chem. Soc., Dalton Trans.* **1990**, 605-614; c) Castellato, U.; Graziani, R. *Z. Kristallogr. - New Cryst. Struct.* **1999**, *214*, 495-496; d) Tzeng, B.-C.; Liu, W.-H.; Liao, J.-H.; Lee, G.-H.; Peng, S.-M. *Cryst. Growth Des.* **2004**, *4*, 573-577; e) Arias, J.; Bardají, M.; Espinet, P. *Inorg. Chem.* **2008**, *47*, 1597-1606; f) Kim, Y.-S.; He, Z.; Hsieh, W.-Y.; Liu, S. *Bioconjugate Chem.* **2006**, *17*, 473-484; g) Liu, S.; He, Z.; Hsieh, W.-Y.; Kim, Y.-S. *Nucl. Med. Biol.* **2006**, *33*, 419–432; h) Liao, P.-K.; Fang, C.-S.; Edwards, A. J.; Kahlal, S.; Saillard, J.-Y.; Liu, C. W. *Inorg. Chem.* **2012**, *51*, 6577−6591; i) Edwards, A. J.; Dhayal, R. S.; Liao, P.-K.; Liao, J.-H.; Chiang, M.-H.; Piltz, R. O.; Kahlal, S.; Saillard, J.-Y.; Liu, C. W. *Angew. Chem. Int. Ed.* **2014**, *53*, 7214−7218.

23 a) Manandhar, E.; Wallace, K. J. *Inorg. Chim. Acta* **2012**, *381*, 15–43; b) Karuppannan, S.; Chambron, J.-C. *Chem. Asian J.* **2011**, *6*, 964–984.

24 a) Packheiser, R.; Ecorchard, P.; Rüffer, T.; Walfort, B.; Lang, H. *Eur. J. Inorg. Chem.* **2008**, 4152–4165; b) Packheiser, R.; Jakob, A.; Ecorchard, P.; Walfort, B.; Lang, H. *Organometallics* **2008**, *27*, 1214–1226; c) Packheiser, R.; Ecorchard, P.; Rüffer, T.; Lang, H. *Chem. Eur. J.* **2008**, *14*, 4948–4960; d) Packheiser, R.; Ecorchard, P.; Walfort, B.; Lang, H. *J. Organomet. Chem.* **2008**, *693*, 933–946; e) Packheiser, R.; Ecorchard, P.; Rüffer, T.; Lohan, M.; Bräuer, B.; Justaud, F.; Lapinte, C.; Lang, H. *Organometallics* **2008**, *27*, 3444–3457; f) Packheiser, R.; Ecorchard, P.; Rüffer, T.; Lang, H. *Organometallics* **2008**, *27*, 3534–3546; g) Lang, H.; Zoufalá, P.; Klaib, S.; del Villar, A.; Rheinwald, G. *J. Organomet. Chem.* **2007**, *692*, 4168–4176; h) Packheiser, R.; Lang, H. *Eur. J. Inorg. Chem.* **2007**, 3786–3788; i) Packheiser, R.; Walfort, B.; Lang, H. *Organometallics* **2006**, *25*, 4579–4587.

25 a) Uehara, N.; Honzawa, H.; Aratake, S.; Shimizu, T. *Chem. Lett.* **1999**, 709-710; b) Uehara, N.; Honzawa, H.; Shimizu, T. *Anal. Sci.* **2001**, *17*, 199-203; c) Celis, N. A.; Villamil-Ramos, R.; Höpfl, H.; Hernández-Ahuactzi, I. F.; Sánchez, M.; Zamudio-Rivera, L. S.; Barba, V. *Eur. J. Inorg. Chem.* **2013**, 2912–2922.

26 Tsukanov, A. V.; Dubonosov, A. D.; Bren, V. A.; Minkin, V. I. *Chem. Heterocyc. Compd.*, **2008**, *44*, 899-923.

27 Parlayan, S.; Basoglu, A.; Gobel, Y.; Ocak, M.; Alp, H.; Kantekin, H.; Ocak, U. *J. Incl. Phenom. Macrocycl. Chem.* **2010**, *67*, 451-460.

28 Cicek, B.; Cakir, U.; Azizoglu, A. *J. Incl. Phenom. Macrocycl. Chem.* **2012**, *72*, 121-125.

29 Hori, K.; Tsukube, H. *J. Incl. Phenom. Mol. Recog. Chem.* **1998**, *32*, 311-329.

30 Uehara, N.; Togashi, H.; Shimizu, T. *Bunseki Kagaku* **2002**, *51*, 533-538.

31 Hirose, K. *J. Incl. Phenom. Macrocycl. Chem*. **2001**, *39*, 193-209.

32 Stephenson, G. R.; Anson, C. E.; Creaser, C. S.; Daul, C. A. *Eur. J. Inorg. Chem.* **2011**, 2086-2097.

33 Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans.* **1987**, S1-S19.

34 Laing, K. R.; Roper, W. R.; *J. Chem. Soc. A* **1970**, 2149-2153.

35 Alcock, N. W.; Hill, A. F.; Roe, M. S.; *J. Chem. Soc., Dalton Trans.* **1990**, 1737-1740.

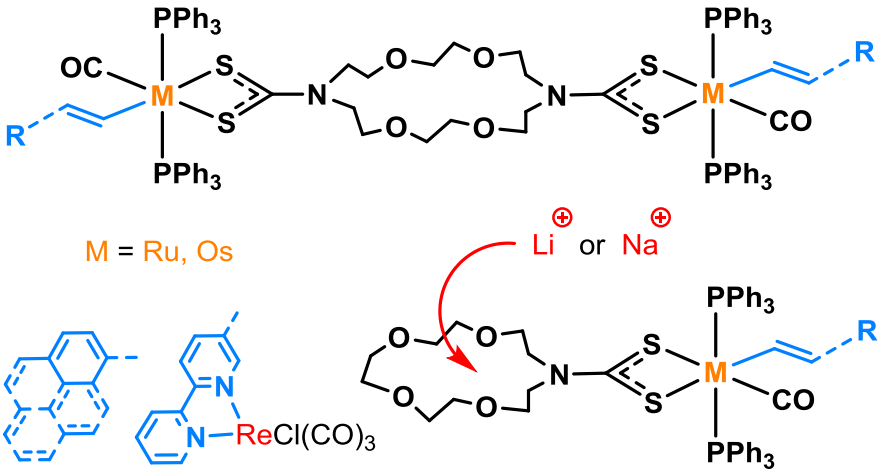
36 Procedure modified substituting BTD for BSD from reference 14d.

37 SHELXTL PC version 5.1, Bruker AXS, Madison, WI, 1997; SHELX-97, Sheldrick, G.; Institut Anorg. Chemie, Tammannstr. 4, D37077 Göttingen, Germany, 1998.

For Table of Contents:

Multimetallic alkenyl complexes bearing macrocyclic dithiocarbamate ligands

Anita Toscani, Eeva Heliövaara, Jubeda B. Hena, Andrew J. P. White and James D. E. T. Wilton-Ely*



Polyether-functionalized dithiocarbamate ligands are employed to create multimetallic ruthenium and osmium vinyl complexes bearing 2-4 metal centers. Additional functionality (fluorophore or rhenium center) can be incorporated through the generation of the vinyl ligand from the appropriate alkynes. The interaction of selected vinyl examples with cations is also explored.

Supporting Information

Multimetallic alkenyl complexes bearing macrocyclic dithiocarbamate ligands

Anita Toscani, Eeva K. Heliövaara, Jubeda B. Hena, Andrew J. P. White and James D. E. T. Wilton-Ely*

Department of Chemistry, Imperial College London, South Kensington Campus, London SW7 2AZ (UK).

Crystallography

The O(16)–C(17) O–CH_2 portion of the polyether macrocycle in the structure of **2** was found to be disordered. Two orientations were identified of ca. 54 and 46% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically). The Ru–H hydrogen atom was located from a ΔF map and refined freely.

Both of the included dichloromethane solvent molecules in the structure of **5** were found to be disordered. For the C(80)-based molecule three orientations were identified of ca. 65, 18 and 17% occupancy (with the 18% occupancy orientation sitting near to a C_2 axis), their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically). The C(90)-based was found to be disordered across a C_2 axis, and this was modelled by using one, complete, 50% occupancy orientation, with the operation of the C_2 axis generating a second orientation. The geometry of the unique orientation was optimised, the thermal parameters of adjacent atoms were restrained to be similar, and the non-hydrogen atoms were refined anisotropically.

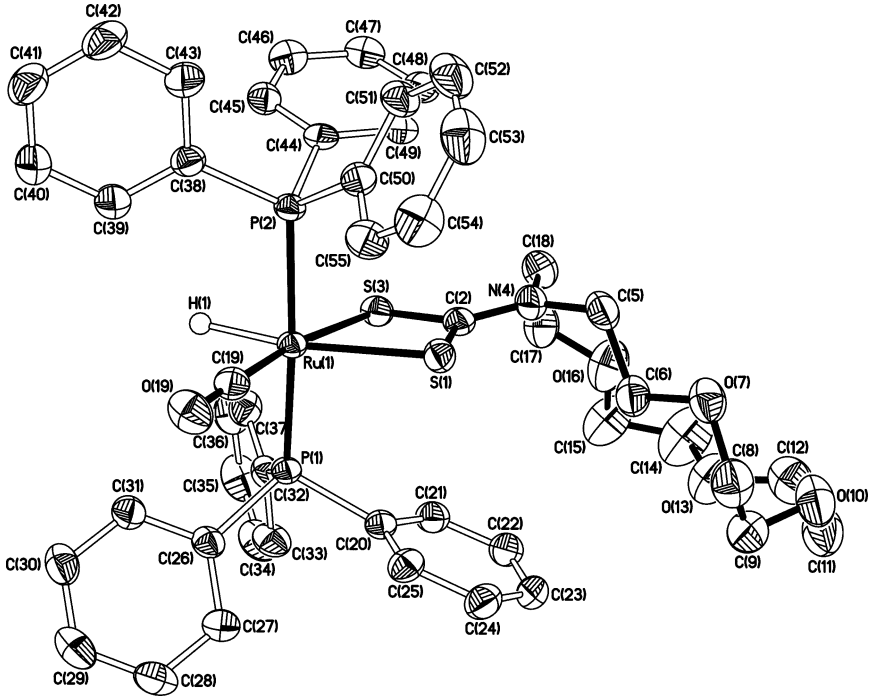


Figure S1. The crystal structure of **2** (50% probability ellipsoids).

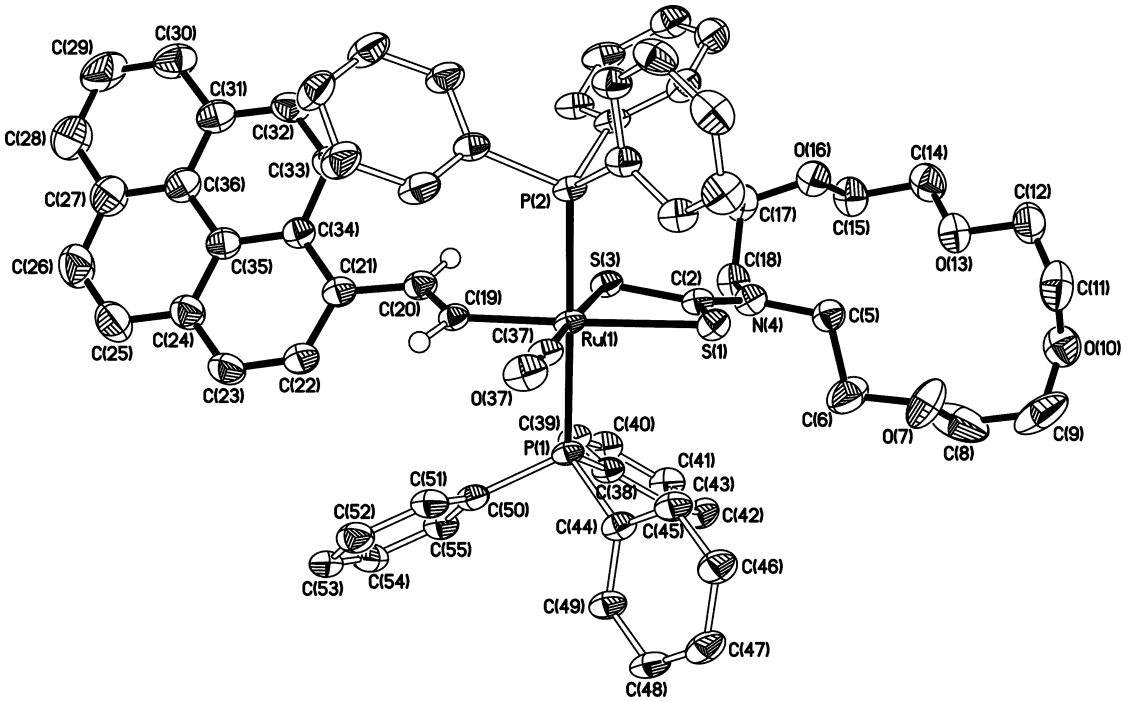


Figure S2. The crystal structure of **5** (50% probability ellipsoids).

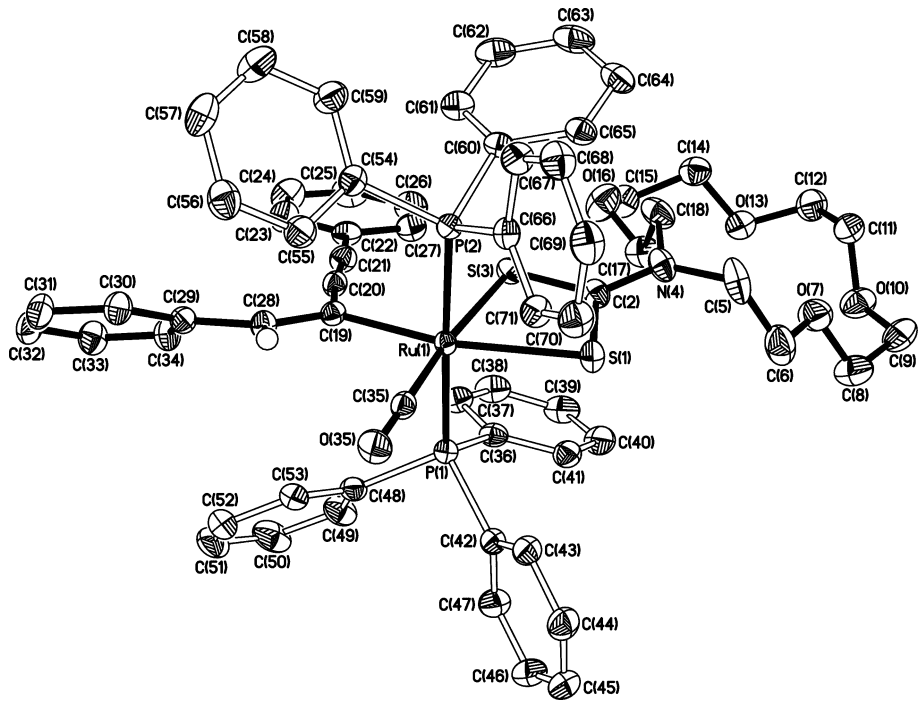


Figure S3. The crystal structure of **6** (50% probability ellipsoids).

NMR titrations, binding constants and thermodynamic parameters

The cation binding experiments were performed at 298 K using a Bruker AV400 NMR spectrometer in acetonitrile-d^3. The chemicals $NaClO_4$ (ACS grade, ≥98.0%) and $LiClO_4$ (purum p.a., ≥98.0%) and the deuterated acetonitrile were purchased from Sigma-Aldrich and were used as received without further purification. **Warning:** Perchlorates must be handled with care as they can be explosive when dry.

All titrations were performed with the starting concentration of [Ru(CH=CHPyr-1)(S_2CN-[15]aneO_4)(CO)(PPh_3)$_2$] (**5**) at 0.003 M and appropriate aliquots (from 0.1 to 2.5 eq) of freshly prepared guest solutions (0.3 M) of $NaClO_4$ and $LiClO_4$ were added with a micropipette. The initial volume of the host solution increased by only 3% during the titrations, therefore the host concentration was considered effectively constant during the whole experiment. The azacrown methylene protons (**a**, **b**, **c**, and **d**) were monitored during the course of the ^{1}H NMR titrations and the binding constants (K_a) were obtained by the analysis of a single isotherm (local method, proton **a**) and by the analysis of all four isotherms (global method, all protons). No sonication or heating of the solution was applied in order to minimise the volume variations and avoid systematic errors.

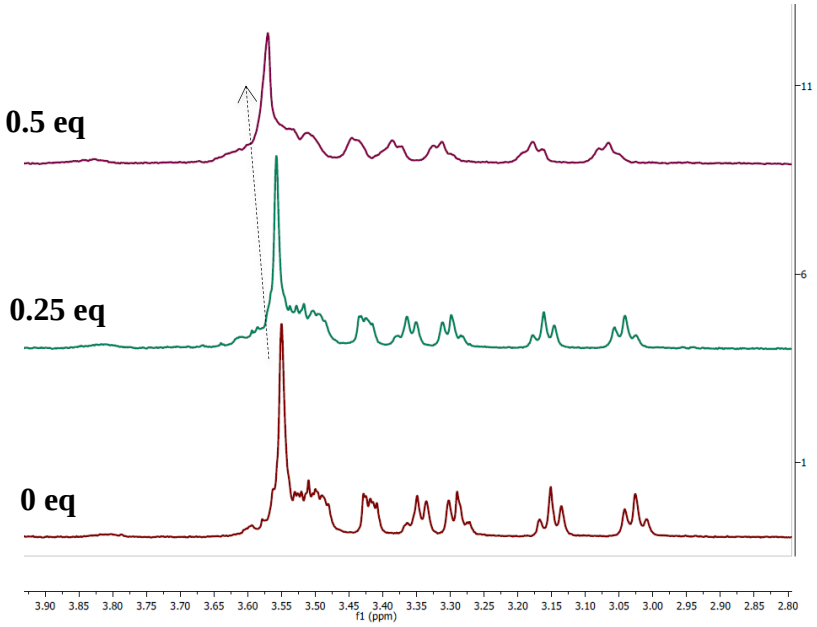


Figure S4. Titration spectra of **5** with 0, 0.25 and 0.5 eq of sodium perchlorate and the downfield shift of peaks a, b, c and d.

The spectra revealed that the host-guest complexation equilibrium has a faster exchange than the NMR spectroscopy time scale (Case 2 of Hirose's method[S1]). The formula used to determine the host-guest complex concentrations and the K_a are reported below. The binding constants (K_a) for the complexation were obtained by analyzing the isotherms with a non-linear least-square data treatment method with 95% confidence interval applied by t-distribution.

$$\delta = \delta_h \cdot (1 - x) + \delta_c \quad where\ x = \frac{a \cdot [C]}{[H]_t}$$

$$[H]_t \cdot (\delta - \delta_h) = a \cdot [C] \cdot (\delta_c - \delta_h)$$

δ is the observed chemical shift

δh, δc are the chemical shifts of free and complexed host, respectively

x is the ratio of complexed host at equilibrium over total host.

The stoichiometry of 1:1 (cation : ruthenium complex) was determined from the *x*-coordinate at the maximum of the modified Job plot, where $[H]_t \cdot (\delta - \delta_h)$, which is proportional to [C] (host-guest complex concentration) plotted as *y*-coordinate.

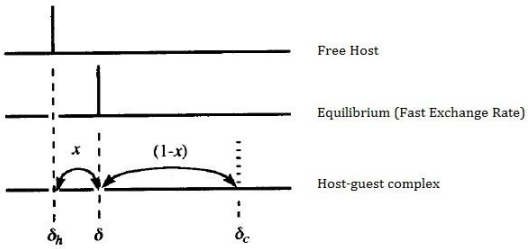


Figure S5. Schematic of the NMR spectra for a fast exchange host-guest complexation indicating the complexation ratio *x* and the variations of chemical shifts from the host to the host-guest complex.[S1]

The NMR titration curves and the results of the association constants and thermodynamic parameters are shown below.

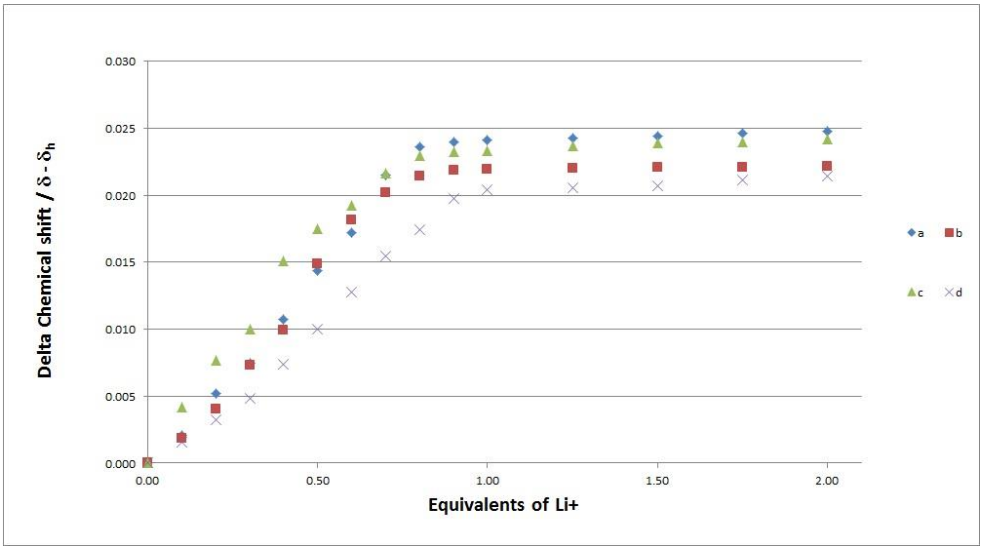


Figure S6. Isotherms resulting from the titration of **5** with $LiClO_4$ from 0 to 2 eq at 298 K.

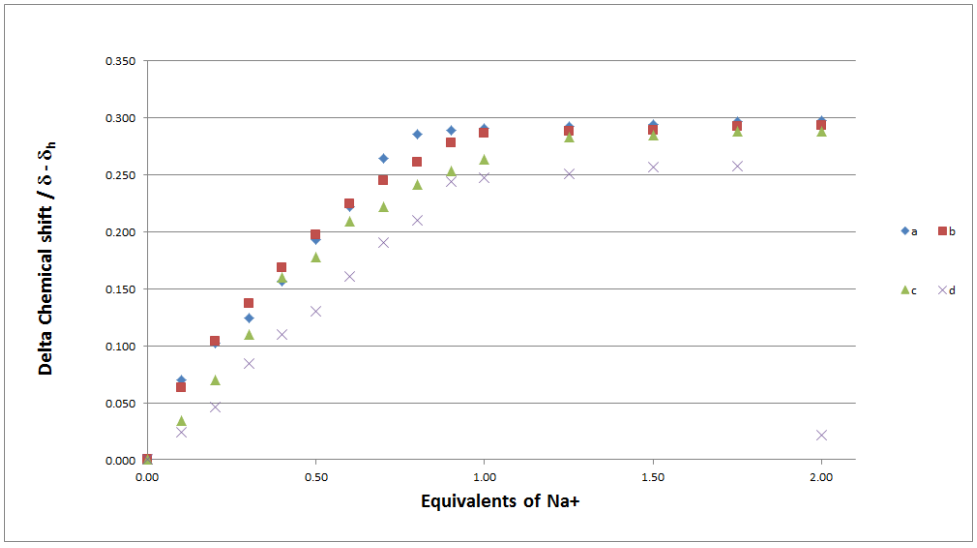


Figure S7. Isotherms resulting from the titration of **5** with $NaClO_4$ from 0 to 2 eq at 298 K.

Table S1. Association constants and thermodynamic parameters for the formation of the host-guest complexes between **5** and lithium and sodium cations.

Guest	K_a (M^{-1})[a]	K_a (M^{-1})[b]	ΔG (kJ mol^{-1})[c]
Li+	9.20 ± 1.5 M^{-1}	9.75 ± 0.98 M^{-1}	-5.5
Na+	20.4 ± 1.45 M^{-1}	20.1 ± 0.77 M^{-1}	-7.5

[a]Determined from the resonances of the methylene protons (a) of **5** in acetonitrile-d^3 at 298K based on the chemical shift change by the titration experiment followed by non-linear least square data treatment method reported by Hirose[S1]. The starting concentration of the host [**5**] = 3 mM. [b] Determined by the methylene protons (a, b, c, d) of **5** in acetonitrile-d^3at 298K based on the chemical shift change by the titration experiments and reported with 95% confidence interval applied by t-distribution [c]The free energies of host-guest complexation (ΔG_{298K}) were calculated from the Ka values using the equation $\Delta G_{298K} = - R T \ln(K_a)$ with concentrations equal to activities.

The Job plot revealing the ruthenium azacrown/cations binding stoichiometry is reported below. The plot (Figure S5) was obtained by plotting [H]/([H]+[G]) vs Δδ·[H]/([H]+[G]), indicating a 1:1 host:guest stoichiometry.

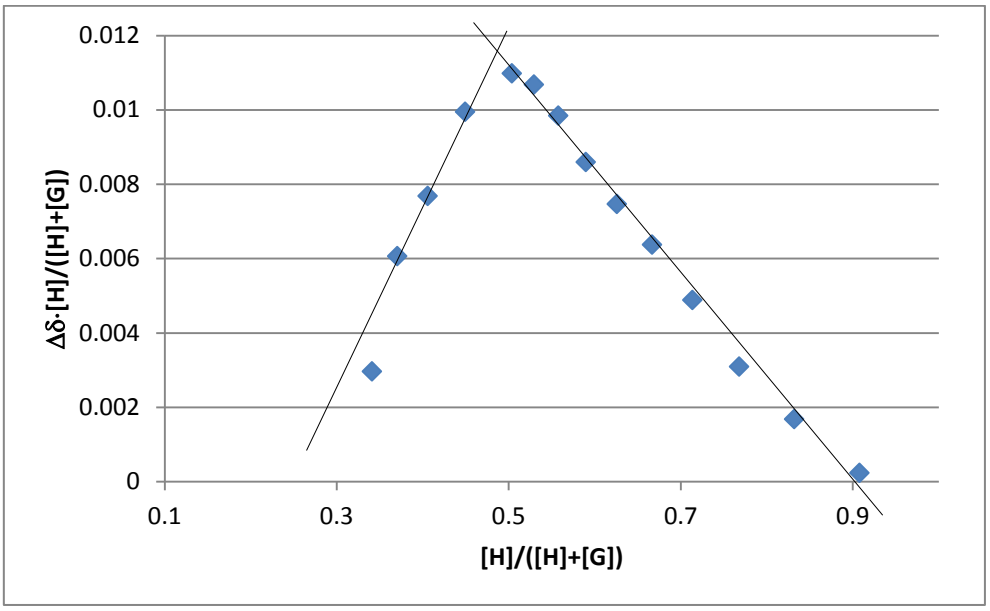


Figure S8. Job plot of compound **5** with $NaClO_4$ in acetonitrile-d^3 at 298 K showing a maximum at 0.5 mole fraction of compound **5**.

References

S1 Hirose, K. *J. Incl. Phenom. Macrocycl. Chem*. **2001**, *39*, 193-209.