The functionalisation of ruthenium(II) and osmium(II) alkenyl complexes with amine- and alkoxy-terminated dithiocarbamates†

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The complex *cis*-[$RuCl_2(dppm)_2$] reacts with the amine-terminated dithiocarbamates $KS_2CN(CH_2CH_2NEt_2)_2$ and $KS_2CN(CH_2CH_2CH_2NMe_2)_2$ to form the compounds $[Ru\{S_2CN(CH_2CH_2NEt_2)_2\}(dppm)_2]^+$ and $[Ru\{S_2CN(CH_2CH_2CH_2NMe_2)_2\}(dppm)_2]^+$, respectively. The methoxy-terminated dithiocarbamate compound $[Ru\{S_2CN(CH_2CH_2OMe)_2\}(dppm)_2]^+$ was also prepared from the same precursor using $KS_2CN(CH_2CH_2OMe)_2$. The alkenyl complexes $[RuRCl(CO)(BTD)(PPh_3)_2]$ (R = CH=CHBu^t, CH=CHC_6H_4Me-4, CH=CHCPh$_2$OH), $[Ru(C(C{\equiv}CBu^t){=}CHBu^t)Cl(CO)(PPh_3)_2]$ and $[Os(CH{=}CHC_6H_4Me\text{-}4)Cl(CO)(BTD)(PPh_3)_2]$ also react cleanly with $KS_2CN(CH_2CH_2CH_2NMe_2)_2$ and $KS_2CN(CH_2CH_2NEt_2)_2$ to yield $[MR\{S_2CN(CH_2CH_2CH_2NMe_2)_2\}(CO)(PPh_3)_2]$ and $[MR\{S_2CN(CH_2CH_2NEt_2)_2\}(CO)(PPh_3)_2]$, respectively. In a similar fashion, the compounds $[RuR\{S_2CN(CH_2CH_2OMe_2)_2\}(CO)(PPh_3)_2]$ (R = CH=CHBu^t, CH=CHC_6H_4Me-4, C(C≡CBu^t)=CHBu^t) were also prepared. Treatment of $[Ru(CH{=}CHBu^t)\{S_2CN(CH_2CH_2CH_2NMe_2)_2\}(CO)(PPh_3)_2]$ and $[Ru\{S_2CN(CH_2CH_2NEt_2)_2\}(dppm)_2]^+$ with trifluoroacetic acid affords the ammonium complexes $[Ru(CH{=}CHBu^t)\{S_2CN(CH_2CH_2CH_2NHMe_2)_2\}(CO)(PPh_3)_2]^{2+}$ and $[Ru\{S_2CN(CH_2CH_2NHEt_2)_2\}(dppm)_2]^{2+}$, while the same reagent generates the tricationic vinylcarbene complex $[Ru(=CHCH{=}CPh_2)\{S_2CN(CH_2CH_2CH_2NHMe_2)_2\}(CO)(PPh_3)_2]^{3+}$ through loss of water from $[Ru(CH{=}CHCPh_2OH)\{S_2CN(CH_2CH_2CH_2NMe_2)_2\}(CO)(PPh_3)_2]$. The structures of $[Ru\{S_2CN(CH_2CH_2OMe)_2\}(dppm)_2]PF_6$ and $[Ru(CH{=}CHC_6H_4Me\text{-}4)\{S_2CN(CH_2CH_2OMe)_2\}(CO)(PPh_3)_2]$ were determined crystallographically.

Introduction

In the hundred years since the synthesis of the first dithiocarbamate complex of a transition metal by Delépine,[1] a huge range of derivatives has been prepared, including examples of all the d-block metals.[2] A major part of this widespread use is the ability of this ligand class to stabilise many different oxidation states and co-ligand sets. This first attribute is amply illustrated by the many electrochemical investigations that have been carried out on dithiocarbamate compounds in the intervening years.[3] Most dithiocarbamates are derived in a straightforward manner from secondary amines. The commercially available ligands, $[S_2CNR_2]^-$ (R = Me, Et), are still commonly used while the exploration of the potential afforded by dithiocarbamates with more diverse substituents is often neglected. This is surprising given the ease with which metals coordinate to the ligand, permitting the facile incorporation of additional functionality into the molecule.

Our recent research has focused on functionalised dithiocarbamates, with a view to coordinating a number of different metals within the same system.[4] This has provided access to fascinating multimetallic compounds which lie at the interface between coordination and materials chemistry. The structural and electrochemical properties of such materials allow them to be used for a diversity of applications, such as sensing or catalysis.

This report explores the incorporation of amine and methoxy functionality (Scheme 1)[5] into the dithiocarbamate skeleton as a means to extend the molecule, coordinate further metal centres and to change the physical properties of the complex as a whole. This latter aspect can be exploited through reversible protonation of the amine groups or using them to 'protect' acid-sensitive co-ligands from the presence of mildly acidic conditions.

Results and discussion

Ruthenium bis(diphenylphosphino)methane complexes

The bis(dppm) compound *cis*-[$RuCl_2(dppm)_2$][6] has been shown to be a versatile starting material for the addition of bidentate ligands[4,7] and, in particular, of dithiocarbamates.[4,8] This is due to the facile generation of a pair of active sites by removal of the chloride ligands, while the robustness of the remaining coordination sphere is maintained due to the inertness of the dppm ligands. The ligand $KS_2CN(CH_2CH_2CH_2NMe_2)_2$ (**A**) was generated *in situ* by treatment of a methanol solution of 3,3′-iminobis(*N*,*N*-dimethylpropylamine) with carbon disulfide in the presence of KOH. Treatment of *cis*-[$RuCl_2(dppm)_2$] with a slight excess of this ligand in the presence of NH_4PF_6 afforded the colourless cation $[Ru\{S_2CN(CH_2CH_2CH_2NMe_2)_2\}(dppm)_2]PF_6$ (**1**) in 82% yield (Scheme 2). Two new pseudotriplets were observed

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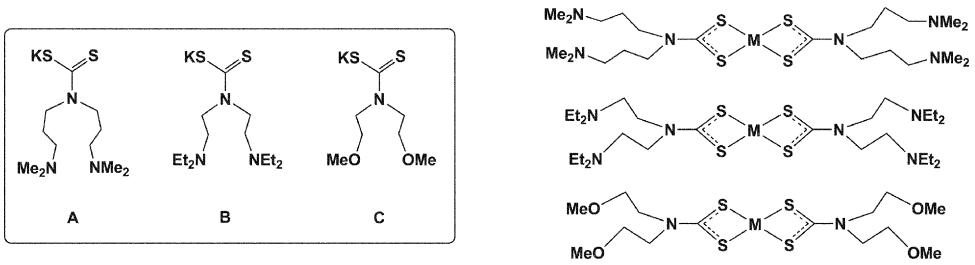
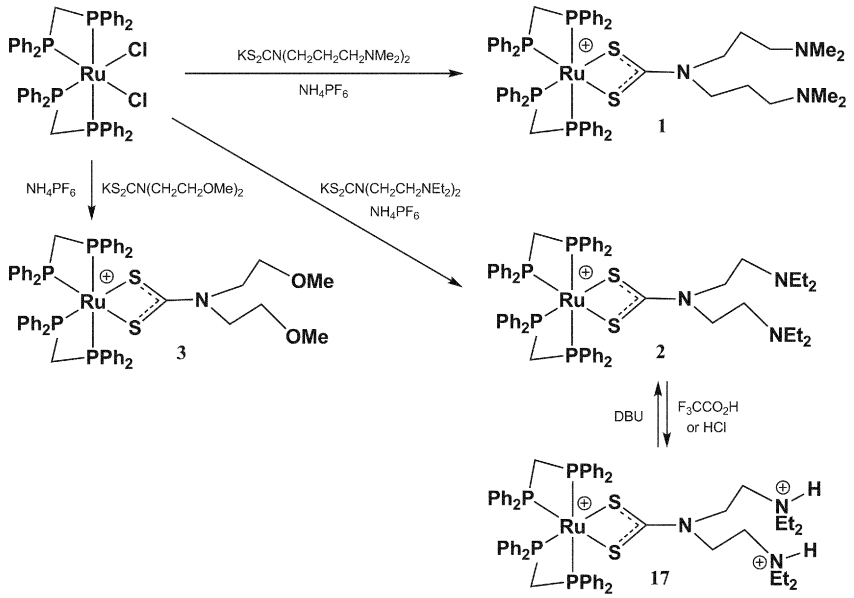


Scheme 1 The three functionalised dithiocarbamate ligands used in this work and homoleptic examples of previous complexes prepared using them (M = Ni, Cu, Zn).[5d]



Scheme 2 Preparation of dithiocarbamate complexes from *cis*-[$RuCl_2(dppm)_2$].

in the ^{31}P NMR spectrum at −15.5 and −2.1 ppm, showing coupling of 34.1 Hz. Further evidence for the presence of the dppm ligands was provided by the multiplet resonances for the methylene protons at 4.42 and 4.97 ppm in the ^1H NMR spectrum. The presence of the dithiocarbamate unit was confirmed by pairs of multiplets at 1.32, 1.40 ppm and 3.12, 3.64 ppm as well as a further broad multiplet at 1.87 ppm, all assigned to the propylene arms of the ligand. The methyl protons gave rise to distinct resonances at 1.95 ppm. The overall composition was supported by a molecular ion in the electrospray mass spectrum (+ve mode) at *m/z* 1132 and good agreement of elemental analysis with calculated values.

The ligand $KS_2CN(CH_2CH_2NEt_2)_2$ (**B**) shares many features with **A** but has shorter and less flexible pendant arms. In a similar manner to **A**, ligand **B** was generated *in situ* and then allowed to react with *cis*-[$RuCl_2(dppm)_2$] and NH_4PF_6 to yield [$Ru\{S_2CN(CH_2CH_2NEt_2)_2\}(dppm)_2$]$PF_6$ (**2**). The shorter ethylene bridge in the dithiocarbamate ligand gave rise to multiplets at 2.40, 3.28 and 3.81 ppm, while the ethyl substituents displayed resonances at 1.05 and 2.57 ppm, showing mutual J_{HH} coupling of 7.1 Hz. Again, a molecular ion at *m/z* 1160 Hz, was observed in 100% abundance in the mass spectrum (ES +ve).

A further related dithiocarbamate ligand with pendant functional groups has been reported recently - the methoxy-terminated ligand, $KS_2CN(CH_2CH_2OMe)_2$ (**C**).[9] This reacted smoothly (Scheme 2) with *cis*-[$RuCl_2(dppm)_2$] and NH_4PF_6 to yield the compound [$Ru\{S_2CN(CH_2CH_2OMe)_2\}(dppm)_2$]$PF_6$ (**3**). In contrast to the amino-terminated dithiocarbamate ligands, no duplication of resonances was observed in the ^1H NMR spectrum. Instead, a singlet at 3.38 ppm was present for the methyl protons while a multiplet was seen at 3.51 ppm for the methylene protons adjacent to the methoxy group and another at 3.79 ppm for the remaining methylene protons. Single crystals of **3** were grown by slow diffusion of ethanol into a dichloromethane solution of **3** and the structure was determined by X-ray diffraction (Fig. 1).

The structural study reveals a distorted octahedral geometry with *cis*-interligand angles in the range 71.444(19) to 103.630(19)°. The Ru–S distances of 2.4237(5) and 2.4351(5) Å are comparable to those found in the bimetallic complex $[\{(dppm)_2Ru\}_2(S_2CNC_4H_8NCS_2)]^{2+}$, which range between 2.426(2) and 2.452(2) Å.[4a] The S(1)–C(2)–S(3) angle of 112.03(12)° is also akin to those observed for the literature complex [112.3(5) and 113.1(4)°], while the S(1)–Ru–S(3) angle of 71.444(19)° is very similar to one of its counterparts in the literature species. The C–S and C(2)–N(4) distances are all indicative of considerable multiple bond character and, in the latter case, can be identified as the origin of the observed planarity of the RuS_2CNR_2 unit (the Ru, S(1), C(2), S(3), N(4), C(5) and C(9) atoms are coplanar to within *ca.* 0.12 Å).

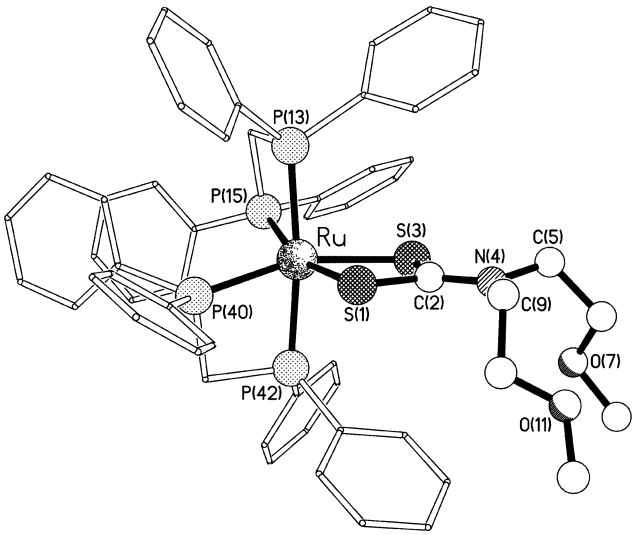


Fig. 1 The molecular structure of the cation in **3**. Selected bond lengths (Å) and angles (°); Ru–S(1) 2.4237(5), Ru–S(3) 2.4351(5), Ru–P(13) 2.3541(5), Ru–P(15) 2.3344(5), Ru–P(40) 2.3207(5), Ru–P(42) 2.3233(5), S(1)–C(2) 1.704(2), C(2)–S(3) 1.717(2), C(2)–N(4) 1.340(3), S(1)–Ru–S(3) 71.444(19), S(1)–C(2)–S(3) 112.03(12). Protons and the hexafluorophosphate counteranion have been omitted for clarity.

Ruthenium and osmium alkenyl complexes

Having demonstrated the coordination chemistry of the three ligands **A-C** with the Ru(dppm)$_2$ unit, the focus of the research shifted to the use of the ligands with group 8 alkenyl complexes.[10] These compounds have enjoyed great interest, principally stemming from the preparation of the complexes [Ru(CR^1=CHR^2)Cl(CO)L$_2$] (L = PPr$^i_3$,[11] PPh$_3$[12]) in the 1980s. The rich reactivity of these compounds, both in terms of transformation of the alkenyl group as well as coordination chemistry at the metal centre, makes them ideal choices for exploring new mono-, bi- and tridentate ligands.[11-20] The compounds [Ru(CR^1=CHR^2)Cl(CO)(PPh$_3$)$_2$][12] and [Ru(CR^1=CHR^2)Cl(CO)(BTD)(PPh$_3$)$_2$] (BTD = 2,1,3-benzothiadiazole - a labile ligand)[17c] are the most convenient triphenylphosphine-stabilised alkenyl complexes to use as starting points for this chemistry. Although many ruthenium (and to a lesser extent osmium) dithiocarbamates are known, no example has been reported with the amine- or methoxy-terminated ligands used here.

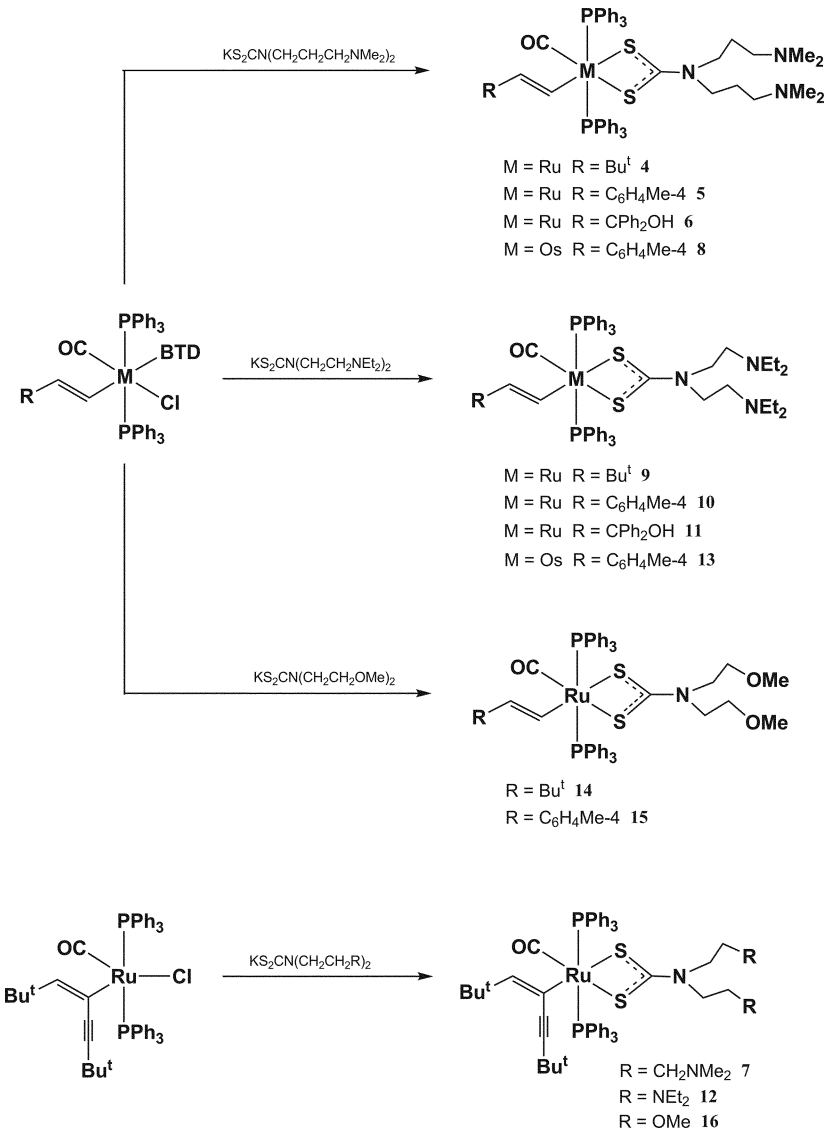
Addition of a slight excess of KS$_2$CN(CH$_2$CH$_2$CH$_2$NMe$_2$)$_2$ (**A**) to an orange dichloromethane solution of [Ru(CH=CHBu^t)Cl(CO)(BTD)(PPh$_3$)$_2$] led to a rapid decolourisation and formation of a pale yellow solution. Work up yielded a pale yellow microcrystalline material, which gave rise to a new singlet in the ^{31}P NMR spectrum at 39.5 ppm. Evidence for the retention of the alkenyl ligand was provided by a singlet at 0.40 ppm (^{t}Bu) in the ^{1}H NMR spectrum and alkenyl resonances at 4.60 and 6.30 ppm showing mutual coupling of 16.4 Hz. The downfield alkenyl signal was found to display coupling to the mutually *trans* phosphine ligands (J_{HP} = 2.7 Hz) and was assigned as Hα. In addition, singlets at 2.12 and 2.14 ppm were observed for the methyl protons of the terminal NMe$_2$ units along with pairs of multiplets for the propylene chain in the region 1.09 to 3.19 ppm. The CS$_2$ nucleus of the dithiocarbamate ligand gave rise to a singlet resonance at 206.1 ppm in the ^{13}C NMR spectrum, while the carbons of the (CH$_2$)$_3$ units were observed as pairs of resonances in the region 57.1 – 24.9 ppm. The methyl carbons resonated at 45.5 ppm, slightly downfield of the carbons of the *tert*-butyl unit. Infrared data displayed features typical of dithiocarbamate (ν_{CN} at 1457 cm^{-1}) and triphenylphosphine ligands as well as an intense absorption at 1905 cm^{-1} due to the carbonyl ligand. The overall formulation of [Ru(CH=CHBu^t){S$_2$CN(CH$_2$CH$_2$CH$_2$NMe$_2$)$_2$}(CO)(PPh$_3$)$_2$] (**4**) was confirmed by an abundant molecular ion in the electrospray (+ve ion) mass spectrum at *m*/*z* 1000 and good agreement of elemental analysis with calculated values (Scheme 3).

Two further ruthenium examples with ligand **A**, [Ru(CH=CHC$_6$H$_4$Me-4){S$_2$CN(CH$_2$CH$_2$CH$_2$NMe$_2$)$_2$}(CO)(PPh$_3$)$_2$] (**5**) and [Ru(CH=CHCPh$_2$OH){S$_2$CN(CH$_2$CH$_2$CH$_2$NMe$_2$)$_2$}(CO)(PPh$_3$)$_2$] (**6**), were prepared bearing aromatic and γ-hydroxy-substituted alkenyl ligands. These were found to exhibit similar spectroscopic features to **4**. The disubstituted alkenyl derivative [Ru{C(C≡CBu^t)=CHBu^t}{S$_2$CN(CH$_2$CH$_2$CH$_2$NMe$_2$)$_2$}(CO)(PPh$_3$)$_2$] (**7**) was also synthesised in the same manner from pentacoordinate [Ru{C(C≡CBu^t)=CHBu^t}Cl(CO)(PPh$_3$)$_2$]. The multiplets attributed to the amine arms of the dithiocarbamate ligand were found to be more closely spaced in the ^{1}H NMR spectrum of this compound than found in the other examples.

An osmium example, [Os(CH=CHC$_6$H$_4$Me-4){S$_2$CN(CH$_2$CH$_2$CH$_2$NMe$_2$)$_2$}(CO)(PPh$_3$)$_2$] (**8**), was prepared from [Os(CH=CHC$_6$H$_4$Me-4)Cl(CO)(BTD)(PPh$_3$)$_2$] to confirm that an analogous reaction ensued between the dithiocarbamate ligand and a representative alkenyl complex of the heaviest congener of group 8. Spectroscopic data were found to be similar to those for **5**, apart from the characteristically lower frequency of the ν_{CO} absorption at 1894 cm^{-1} in the solid state infrared spectrum.

In an analogous fashion, the diethylamino variant, KS$_2$CN(CH$_2$CH$_2$NEt$_2$)$_2$ (**B**), was used to prepare [Ru(CH=CHBu^t){S$_2$CN(CH$_2$CH$_2$NEt$_2$)$_2$}(CO)(PPh$_3$)$_2$] (**9**) from [Ru(CH=CHBu^t)Cl(CO)(BTD)(PPh$_3$)$_2$]. Features associated with the alkenyl, phosphine and carbonyl ligands were found to be similar to those observed for **4**. Pairs of multiplets were again seen in the ^{1}H NMR spectrum at 1.93, 2.21 and 2.83, 3.28 ppm for the ethylene units with overlapping multiplets identified for the diethylamino substituents at 0.95 and 2.43 ppm. Mass spectrometry and elemental analysis data were in good agreement with the above formulation. The complexes [Ru(CH=CHC$_6$H$_4$Me-4){S$_2$CN(CH$_2$CH$_2$NEt$_2$)$_2$}(CO)(PPh$_3$)$_2$] (**10**), [Ru(CH=CHCPh$_2$OH){S$_2$CN(CH$_2$CH$_2$NEt$_2$)$_2$}(CO)(PPh$_3$)$_2$] (**11**), [Ru{C(C≡C^{t}Bu)=CH^{t}Bu}{S$_2$CN(CH$_2$CH$_2$NEt$_2$)$_2$}(CO)(PPh$_3$)$_2$] (**12**) and [Os(CH=CHC$_6$H$_4$Me-4){S$_2$CN(CH$_2$CH$_2$NEt$_2$)$_2$}(CO)(PPh$_3$)$_2$] (**13**) were also prepared to confirm the generality of the coordination chemistry shown by [S$_2$CN(CH$_2$CH$_2$NEt$_2$)$_2$]$^-$ with the alkenyl precursors and to increase the options for structural determination through X-ray diffraction (Scheme 3).

The ligand, KS$_2$CN(CH$_2$CH$_2$OMe)$_2$ (**C**), was prepared as a methanol solution and added to the alkenyl complexes [Ru(alkenyl)Cl(CO)(BTD)(PPh$_3$)$_2$], however, these reactions did not lead to a single product but rather to an inseparable mixture which gave rise to two closely spaced resonances in the ^{31}P NMR spectrum in each case. The presence of two compounds was further supported by two sets of alkenyl



Scheme 3 Preparation of alkenyl dithiocarbamate complexes.

resonances in the ^{1}H NMR spectrum. A partially successful crystallographic investigation revealed a complex with the methyl xanthate ligand, $[S_2COMe]^-$, presumably formed by deprotonation of methanol and reaction with carbon disulfide. In order to confirm the nature of the contaminant, the complex $[Ru(CH{=}CHBu^t)(S_2COMe)(CO)(PPh_3)_2]$ was prepared in the same manner as the isopropyl xanthate analogue,[19b] and found to account for the remaining resonances (*e.g.*, S_2COMe resonance at around 3.20 ppm in the ^{1}H NMR spectra) in the product mixtures obtained initially. Elimination of methanol from both ligand preparation and work up of the complex allowed the complexes $[Ru(alkenyl)\{S_2CN(CH_2CH_2OMe)_2\}(CO)(PPh_3)_2]$ (alkenyl = $CH{=}CHBu^t$, **14**; $CH{=}CHC_6H_4Me$-4, **15**; $C(C{\equiv}CBu^t){=}CHBu^t$), **16**) to be prepared in high yield from an aqueous solution of **C**. ^{1}H NMR analysis of complex **14** revealed two singlets for the methoxy protons at 3.19 and 3.20 ppm as well as triplets for the protons of the pendant arms at 2.85, 3.07, 3.18 and 3.48 ppm (all showing coupling of around 6 Hz) alongside typical features for the alkenyl ligands. Similar spectroscopic and analytical data were obtained for **14 - 16** (Scheme 3). Single crystals of $[Ru(CH{=}CHC_6H_4Me\text{-}4)\{S_2CN(CH_2CH_2OMe)_2\}(CO)(PPh_3)_2]$ (**15**) were grown and the molecular structure determined by X-ray diffraction (Fig. 2).

A distorted octahedral geometry is found for the ruthenium centre with *cis*-interligand angles in the range 70.346(15) to 101.83(6)° while the P(1)–Ru–P(2) angle of 174.221(15)° approaches linearity. The Ru–S distances of 2.4661(4) and 2.4936(4) Å are longer than those found in complex **3**, reflecting the greater *trans* influence of the carbonyl and alkenyl ligands compared to the phosphorus donors of the dppm ligands. A similar elongation of the Ru–S distance opposite the alkenyl ligand over that *trans* to the carbonyl is also found in the complex $[Ru(C(C{\equiv}CPh){=}CHPh)(S_2CNC_4H_8NH_2)(CO)(PPh_3)_2]^+$.[4c] The S(1)–C(2)–S(3) angle of 113.47(10)° in **15** is slightly larger than that of 112.03(12)° observed for the same ligand in complex **3**, while the S(3)–Ru–S(1) angle of 70.346(15)° is smaller than in **3** [71.444(19)°]. These changes are associated with a longer Ru···C(2) separation in **15** [2.9628(18) Å] *cf.* that seen in **3**

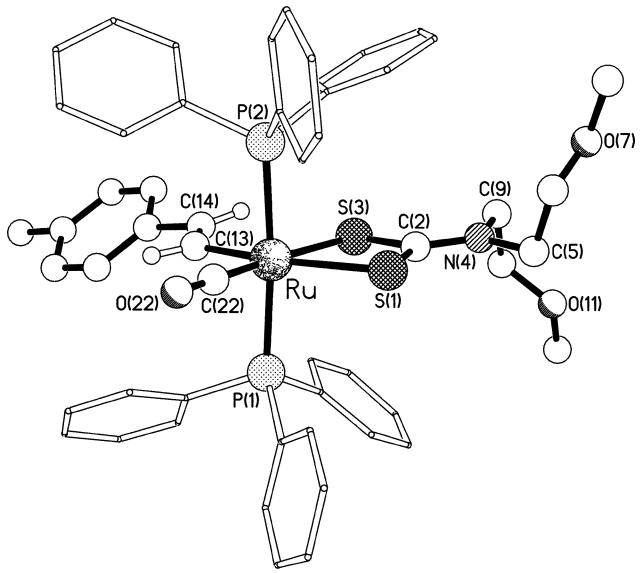


Fig. 2 The molecular structure of **15**. Selected bond lengths (Å) and angles (°); Ru–S(1) 2.4936(4), Ru–S(3) 2.4661(4), Ru–P(1) 2.3684(4), Ru–P(2) 2.3680(4), Ru–C(13) 2.0851(18), Ru–C(22) 1.860(2), S(1)–C(2) 1.7105(19), C(2)–S(3) 1.7066(19), C(2)–N(4) 1.337(2), C(13)–C(14) 1.328(3), S(1)–Ru–S(3) 70.346(15), P(1)–Ru–P(2) 174.221(15), S(1)–C(2)–S(3) 113.47(10), Ru–C(13)–C(14) 127.45(15).

[2.928(2) Å]. As noted in **3**, the RuS_2CNR_2 unit is again flat, the Ru, S(1), C(2), S(3), N(4), C(5) and C(9) atoms being coplanar to within *ca.* 0.09 Å.

Protonation studies

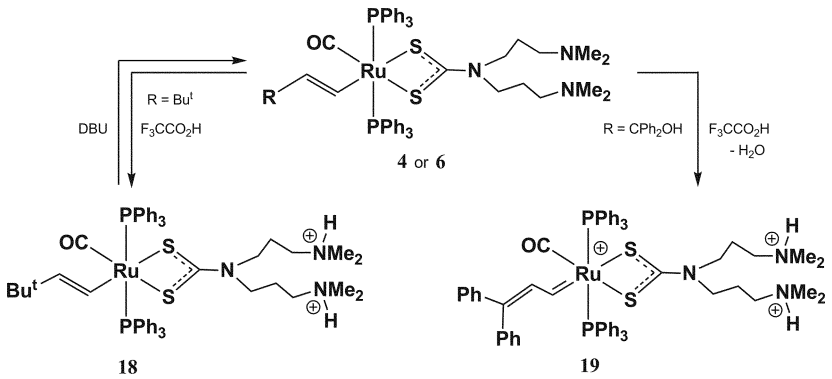
With the amine functionality now introduced into the complexes through the dithiocarbamate ligand, the reactivity of the pendant groups was probed. Given the sustained interest in solubility of metal complexes in aqueous media,[21] the first investigation attempted was the treatment of the complexes with acid to form ammonium functionalised metal compounds.

Due to the robustness of the dppm co-ligands, the complex $[Ru\{S_2CN(CH_2CH_2NEt_2)_2\}(dppm)_2]PF_6$ (**1**) was chosen for the first protonation attempt. Two equivalents of trifluoroacetic acid were added but little change was observed to the colour of the solution. After work up, ^{1}H NMR analysis revealed a shift and significant broadening in the chemical shift of the resonances of the ethyl substituents of the dithiocarbamate ligand. The multiplet resonances for the ethylene units were also displaced. A new, intense band was observed in the solid state infrared spectrum at 1670 cm^{-1} for the trifluoroacetate counteranions as well as a ν_{PF} absorption at 833 cm^{-1} for the hexafluorophosphate anion. These data led to the formulation of the product as $[Ru\{S_2CN(CH_2CH_2NHEt_2)_2\}(dppm)_2](PF_6)(O_2CCF_3)_2$ (**17**), as shown in Scheme 2. The retention of the PF_6^- counteranion suggested a relatively strong interaction with the ammonium units. Attempts to obtain NMR data for this material in D_2O were unsuccessful, however, treatment of **1** with two equivalents of dry HCl afforded **17** as the chloride salt, which showed modest water solubility. Aqueous solubility will undoubtedly be improved if more than one dithiocarbamate unit can be attached to the metal centre.

The parent alkenyl complexes, $[Ru(CR{=}CHR)Cl(CO)(BTD)(PPh_3)_2]$ are susceptible to cleavage of the organic ligand by acids such as HCl so it was not assumed that reaction with acid would be limited to straightforward protonation of the amine functionality. Again, addition of two equivalents of trifluoroacetic acid to $[Ru(CH{=}CHBu^t)\{S_2CN(CH_2CH_2CH_2NMe_2)_2\}(CO)(PPh_3)_2]$ (**4**) did not appear to cause any colour change and little difference was observed in the chemical shift of the ^{31}P NMR resonance. However, significant shifts in the resonances for the methyl (2.66 and 2.72 ppm) and propylene (1.42–3.51 ppm) protons with respect to the values for **4** clearly indicated that protonation had occurred. Negligible difference in the alkenyl and phosphine resonances in the same spectrum showed that the co-ligands had been unaffected by this transformation. The IR spectrum displayed a new peak at 1674 cm^{-1} attributed to the trifluoroacetate counteranions alongside the ν_{CO} absorption at 1915 cm^{-1}. The formulation of $[Ru(CH{=}CH^tBu)\{S_2CN(CH_2CH_2CH_2NHMe_2)_2\}(CO)(PPh_3)_2](OSO_2CF_3)_2$ (**18**) was further supported by mass spectrometry and elemental analysis (Scheme 4). This protonation was found to be reversible on addition of DBU, which regenerated **4**.

Following the successful protonation of the *tert*-butyl alkenyl complex **4**, the γ-hydroxy alkenyl complex $[Ru(CH{=}CHCPh_2OH)\{S_2CN(CH_2CH_2CH_2NMe_2)_2\}(CO)(PPh_3)_2]$ (**6**) was treated with excess trifluoroacetic acid causing an instant colour change from colourless to intense red. Since protonation of **4** had involved no discernible colour change, it was clear that a new chromophore had been generated in the molecule. A singlet was observed in the ^{31}P NMR spectrum of the compound at 32.0 ppm, shifted significantly from the value found for the precursor **6** (39.9 ppm). The ^{1}H NMR spectrum displayed two new downfield doublets at 8.10 and 14.68 ppm, showing a mutual coupling of 14.0 Hz, the latter typical of the chemical shift of a carbene proton. The signals due to the protons of the methyl substituents of the dithiocarbamate ligand were shifted from 2.11 and 2.15 ppm in **6** to 2.80 and 2.83 ppm in this complex, suggesting protonation had occurred also at the nitrogen lone pairs. The other protons of this ligand were apparent only as two broad multiplets centred at 1.41 and 2.98 ppm. The shift in frequency of the ν_{CO} absorption from 1913 cm^{-1} in **6** to 1952 cm^{-1} in **19** indicated a decrease in electron density at the metal centre, consistent with formation of a cation. On the basis of these data in conjunction with ^{13}C NMR spectroscopy (310.5 ppm, RuCH, J_{CP} = 8.6 Hz) mass spectrometry (molecular ion at m/z 1108 and peak for fragmentation of the vinylcarbene unit at m/z 916) and elemental analysis, the product was formulated as $[Ru(=CHCH=CPh_2)\{S_2CN(CH_2CH_2CH_2NHMe_2)_2\}(CO)(PPh_3)_2](O_2CCF_3)_3$ (**19**), formed through elimination of water after protonation (Scheme 4).

The formation of **18** and **19** bodes well for the use of these ligands in the construction of systems in which protection of acid-sensitive functionality is necessary. Thus, attack of small amounts of acid may occur preferentially at the amine functionality rather than elsewhere in the molecule. This was demonstrated in the reaction of **6** with one equivalent of trifluoroacetic acid. Initially, a slight red colouration was observed, however, ^{1}H NMR analysis revealed protonation of the amine groups rather than formation of the vinylcarbene compound. Formation of **19** only occurs on addition of more than two equivalents of F_3CCO_2H.



Scheme 4 Protonation reactions of alkenyl complexes **4** (R = Bu^t) and **6** (R = CPh_2OH).

Conclusion

Using bis(dppm) and σ-alkenyl compounds as model complexes, the first examples of ruthenium and osmium with the amine- or methoxy-terminated 'smart' dithiocarbamate ligands, $[S_2CN(CH_2CH_2CH_2NMe_2)_2]^-$, $[S_2CN(CH_2CH_2NEt_2)_2]^-$ and $[S_2CN(CH_2CH_2OMe)_2]^-$ have been prepared. They have been shown to yield coordinatively saturated complexes which can then be used as a starting point for further chemistry. Protonation of the amine-terminated compounds leads to clean formation of ammonium units rendering them moderately water soluble whereas, in the case of the γ-hydroxyalkenyl complex, a vinylcarbene ligand is also generated. The ammonium complexes discussed here have modest water solubility (the precursors are completely insoluble) due to the presence of only one dithiocarbamate unit. However, the commercial availability and low cost of the amines $HN(CH_2CH_2NEt_2)_2$ and $HN(CH_2CH_2CH_2NMe_2)_2$ and the simple preparation of the corresponding dithiocarbamates could make these ligands an attractive alternative to more complicated or expensive water solubilising ligands such as sulfonated phosphines. Furthermore, the amine units can also be employed to protect acid-sensitive co-ligands from cleavage or unwanted reaction during transformations in the presence of acid.

Experimental

General comments

All experiments were carried out under aerobic conditions and the majority of the complexes appear indefinitely stable towards the atmosphere in solution or in the solid state. Solvents were used as received from commercial sources. The complexes $[Ru(CH{=}CHBu^t)Cl(CO)(BTD)(PPh_3)_2]$, $[Ru(CH{=}CHC_6H_4Me\text{-}4)Cl(BTD)(CO)(PPh_3)_2]$ and $[Ru(CH{=}CHCPh_2OH)Cl(BTD)(CO)(PPh_3)_2]$ were prepared using the literature route,[17c] substituting 2,1,3-benzoselanadiazole (BSD) for the for the commercially available 2,1,3-benzothiadiazole (BTD) ligand. The compounds $[Os(CH{=}CHC_6H_4Me\text{-}4)Cl(BTD)(CO)(PPh_3)_2]$,[17h] $[Ru\{C(C{\equiv}CBu^t){=}CHBu^t\}Cl(CO)(PPh_3)_2]$,[22] and *cis*-$[RuCl_2(dppm)_2]$[15b] were synthesised as described in the indicated reports. Solutions (4.0 mmol) of the ligands, $KS_2CN(CH_2CH_2CH_2NMe_2)_2$ (methanol),[5] $KS_2CN(CH_2CH_2NEt_2)_2$,[5] $KS_2CN(CH_2CH_2OMe)_2$.[9b] were prepared in water unless otherwise stated, by literature methods. Electrospray mass spectrometry data were obtained using a Micromass LCT Premier instrument and infrared data were measured using a Perkin Elmer Spectrum 100 FT-IR spectrometer. Characteristic phosphine-associated infrared data have been omitted. NMR spectroscopy was performed at 25 °C using a Bruker AV400 spectrometer in $CDCl_3$ unless otherwise indicated. All couplings are in Hertz and ^{31}P NMR spectra are proton decoupled. Resonances for the hexafluorophosphate anion are not reported. Elemental analysis data were obtained from London Metropolitan University. The procedures given provide materials of sufficient purity for synthetic and spectroscopic purposes. Samples were recrystallised from a mixture of dichloromethane and ethanol for elemental analysis. Solvates were confirmed by integration of the ^1H NMR spectrum.

Reactions with *cis*-$[RuCl_2(dppm)_2]$

A solution of *cis*-$[RuCl_2(dppm)_2]$ (80 mg, 0.085 mmol) in dichloromethane (20 mL) was treated with two equivalents of the dithiocarbamate ligand and NH_4PF_6 (28 mg, 0.172 mmol) in methanol (10 mL) and stirred for 30 min. All solvent was removed and the residue dissolved in the minimum volume of dichloromethane and filtered through diatomaceous earth (celite). Ethanol (10 mL) was added and the solvent volume reduced (rotary evaporation) until precipitation was complete. The product was washed with ethanol (10 mL) and petroleum ether (10 mL). The product was dried under vacuum.

Reactions of alkenyl complexes with $KS_2CN(CH_2CH_2CH_2NMe_2)_2$

A solution of $KS_2CN(CH_2CH_2CH_2NMe_2)_2$ in water was prepared by a literature procedure[5d] and 0.129 mmol was added to a dichloromethane–methanol (10 mL:10 mL) solution of the metal alkenyl complex. The reaction was stirred for one hour. Reduction in solvent volume (rotary evaporator) led to precipitation of the product. This was washed with water (5 mL), ethanol (10 mL) and petroleum ether (10 mL). The product was dried under vacuum.

Reactions of alkenyl complexes with $KS_2CN(CH_2CH_2NEt_2)_2$

A solution of $KS_2CN(CH_2CH_2NEt_2)_2$ in methanol was prepared by a literature procedure[5d] and 0.132 mmol was added to a dichloromethane–methanol (10 mL:10 mL) solution of the metal alkenyl complex. The reaction was stirred for one hour. Reduction in solvent volume (rotary evaporator) led to precipitation of the

product. This was washed with water (5 mL), ethanol (10 mL) and petroleum ether (10 mL). The product was dried under vacuum.

Reactions of alkenyl complexes with $KS_2CN(CH_2CH_2OMe)_2$

A solution of $KS_2CN(CH_2CH_2OMe)_2$ in water was prepared by a literature procedure[9b] and 0.132 mmol was added to an acetone solution (20 mL) of the metal alkenyl complex. The reaction was stirred for one hour. All solvent was removed and diethyl ether (20 mL) added and the crude product triturated ultrasonically. The pale yellow precipitate was filtered and washed with water (5 mL) and diethyl ether (10 mL). The product was dried under vacuum.

$[Ru\{S_2CN(CH_2CH_2CH_2NMe_2)_2\}(dppm)_2]PF_6$ (1)

Reaction of two equivalents of $KS_2CN(CH_2CH_2CH_2NMe_2)_2$ with *cis*-$[RuCl_2(dppm)_2]$ (80 mg, 0.085 mmol) gave 88.8 mg of colourless product (82%). IR (solid state): 1504, 1358, 1309, 1258, 1231, 878, 833 (ν_{PF}) cm^{-1}. ^{31}P NMR (CD_2Cl_2): −15.5, −2.1 ($t^v \times 2$, dppm, $J_{PP} = 34.1$ Hz) ppm. ^1H NMR (CD_2Cl_2): 1.32, 1.40 (m × 2, 2 × 2H, $NCH_2CH_2CH_2N$); 1.87 (m, 4H, CH_2NMe_2); 1.95 (s, 12H, NMe_2); 3.12, 3.64 (m × 2, 2 × 2H, CH_2NCS_2); 4.42, 4.97 (m × 2, 2 × 2H, PCH_2P); 6.37, 6.77, 6.95, 7.07, 7.17, 7.25, 7.56 (m × 7, 40H, C_6H_5) ppm. MS (ES +ve) *m/z* (abundance) = 1132 (100) $[M]^+$. Analysis: Calculated for $C_{61}H_{68}F_6N_3P_5RuS_2$ (M_w = 1277.27): C 57.4%, H 5.4%, N 3.3%; Found: C 57.3%, H 5.2%, N 3.2%.

$[Ru\{S_2CN(CH_2CH_2NEt_2)_2\}(dppm)_2]PF_6$ (2)

Reaction of two equivalents of $KS_2CN(CH_2CH_2NEt_2)_2$ with *cis*-$[RuCl_2(dppm)_2]$ (80 mg, 0.085 mmol) gave 70 mg of colourless product (63%). IR (solid state): 1454 (ν_{CN}), 1382, 1356, 1311, 1246, 1173, 879, 835 (ν_{PF}) cm^{-1}. ^{31}P NMR ($CDCl_3$): −18.5, −6.0 ($t^v \times 2$, dppm, $J_{PP} = 34.1$ Hz) ppm. ^1H NMR ($CDCl_3$): 1.05 (t, 12H, NCH_2CH_3, $J_{HH} = 7.1$ Hz); 2.40 (m, 4H, CH_2NEt_2); 2.57 (q, 8H, NCH_2CH_3, $J_{HH} = 7.1$ Hz); 3.28, 3.81 (m × 2, 2 × 2H, CH_2NCS_2); 4.63, 4.99 (m × 2, 2 × 2H, PCH_2P); 6.54, 6.96, 7.04, 7.19, 7.26, 7.36, 7.61 (m × 7, 40H, C_6H_5) ppm. MS (ES +ve) *m/z* (abundance) = 1160 (100) $[M]^+$. Analysis: Calculated for $C_{63}H_{72}F_6N_3P_5RuS_2$ (M_w = 1305.33): C 58.0%, H 5.6%, N 3.2%; Found: C 57.8%, H 5.5%, N 3.1%.

$[Ru\{S_2CN(CH_2CH_2OMe)_2\}(dppm)_2]PF_6$ (3)

Reaction of two equivalents of $KS_2CN(CH_2CH_2OMe)_2$ with *cis*-$[RuCl_2(dppm)_2]$ (80 mg, 0.085 mmol) gave 90.7 mg of colourless product (87%). IR (solid state): 1424, 1359, 1310, 1284, 1243, 1194, 1116, 975, 920, 831 (ν_{PF}) cm^{-1}. ^{31}P NMR (CD_2Cl_2): −18.6, −5.2 ($t^v \times 2$, dppm, $J_{PP} = 34.3$ Hz) ppm. ^1H NMR (CD_2Cl_2): 3.38 (s, 6H, OCH_3); 3.51 (m, 4H, CH_2OMe); 3.79 (m, 4H, CH_2NCS_2); 4.48, 4.95 (m × 2, 2 × 2H, PCH_2P); 6.48, 6.99, 7.10, 7.32, 7.41, 7.49, 7.69 (m × 7, 40H, C_6H_5) ppm. MS (ES +ve) *m/z* (abundance) = 1078 (100) $[M]^+$. Analysis: Calculated for $C_{57}H_{58}F_6NO_2P_5RuS_2$ (M_w = 1223.14): C 56.0%, H 4.8%, N 1.2%; Found: C 55.9%, H 4.7%, N 1.1%.

$[Ru(CH{=}CH^tBu)\{S_2CN(CH_2CH_2CH_2NMe_2)_2\}(CO)(PPh_3)_2]$ (4)

$[Ru(CH{=}CH^tBu)Cl(CO)(BTD)(PPh_3)_2]$ (100 mg, 0.110 mmol) gave 66 mg of pale yellow product (60%). IR (solid state): 1905(ν_{CO}), 1572, 1457 (ν_{CN}), 1369, 1354, 1257, 1211, 1174, 1034, 981, 937 cm^{-1}. ^{31}P NMR ($CDCl_3$): 39.5 (s, PPh_3) ppm. ^{13}C NMR (CD_2Cl_2): 207.3 (t, CO, $J_{CP} = 15.9$ Hz); 206.1 (s, CS_2); 141.9 (t, Cβ, $J_{CP} = 3.5$ Hz); 135.0 (t^v, *o/m*-C_6H_5, $J_{CP} = 5.2$ Hz); 134.7 (t^v, *ipso*-C_6H_5, $J_{CP} = 20.9$ Hz); 134.2 (t, Cα, $J_{CP} = 12.5$ Hz); 129.2 (s, *p*-C_6H_5); 127.6 (t^v, *o/m*-C_6H_5, $J_{CP} = 4.5$ Hz); 57.1, 56.9 (s × 2, NCH_2); 48.3, 47.5 (s × 2, NCH_2), 45.5 (s, NMe_2); 35.7 (s, CMe_3); 29.7 (s, ^{t}Bu-Me); 25.2, 24.9 (s × 2, CCH_2C) ppm. ^1H NMR ($CDCl_3$): 0.40 (s, 9H, ^{t}Bu); 1.09, 1.36 (m × 2, 2 × 2H, $NCH_2CH_2CH_2N$); 1.97 (t, 2H, CH_2NMe_2; $J_{HH} = 6.9$ Hz); 2.07 (t, 2H, CH_2NMe_2; $J_{HH} = 7.1$ Hz); 2.12, 2.14 (s × 2, 2 × 6H, NMe_2); 2.79, 3.19 (m × 2, 2 × 2H, CH_2NCS_2); 4.60 (dt, 1H, Hβ, $J_{HH} = 16.4$ Hz; $J_{HP} = 1.8$ Hz); 6.30 (dt, 1H, Hα, $J_{HH} = 16.4$ Hz, $J_{HP} = 2.7$ Hz); 7.27–7.31, 7.55–7.60 (m × 2, 30H, C_6H_5) ppm. MS (ES +ve) *m/z* (abundance) = 1000 (74) $[M]^+$; 738 (85) $[M - PPh_3]^+$. Analysis: Calculated for $C_{54}H_{65}N_3OP_2RuS_2$ (M_w = 999.26): C 64.9%, H 6.6%, N 4.2%; Found: C 65.0%, H 6.6%, N 4.1%.

$[Ru(CH{=}CHC_6H_4Me\text{-}4)\{S_2CN(CH_2CH_2CH_2NMe_2)_2\}(CO)(PPh_3)_2]$ (5)

$[Ru(CH{=}CHC_6H_4Me\text{-}4)Cl(CO)(BTD)(PPh_3)_2]$ (100 mg, 0.106 mmol) gave 69 mg of pale yellow product (63%). IR (solid state): 1905 (ν_{CO}), 1540, 1500, 1462 (ν_{CN}), 1416, 1367, 1349, 1296, 1258, 1039, 830 cm^{-1}. ^{31}P NMR ($CDCl_3$): 39.2 (s, PPh_3) ppm. ^1H NMR ($CDCl_3$): 1.23, 1.33 (m × 2, 2 × 2H, $NCH_2CH_2CH_2N$); 2.05 (m, 4H, CH_2NMe_2); 2.12, 2.16 (s × 2, 2 × 6H, NMe_2); 2.24 (s, 3H, CCH_3); 2.94, 3.20 (m × 2, 2 × 2H, CH_2NCS_2); 5.55 (d, 1H, Hβ, $J_{HH} = 16.8$ Hz); 6.39, 6.83 (AB, 4H, C_6H_4, $J_{AB} = 8.0$ Hz); 7.27–7.34, 7.53–7.58 (m × 2, 30H, C_6H_5); 7.72 (dt, 1H, Hα, $J_{HH} = 16.8$ Hz, $J_{HP} = 3.3$ Hz) ppm. MS (ES +ve) *m/z* (abundance) = 1034 (68) $[M]^+$; 772 (69) $[M - PPh_3]^+$. Analysis: Calculated for $C_{57}H_{63}N_3OP_2RuS_2$ (M_w = 1033.28): C 66.3%, H 6.2%, N 4.1%; Found: C 66.2%, H 6.1%, N 3.9%.

$[Ru(CH{=}CHPh_2OH)\{S_2CN(CH_2CH_2CH_2NMe_2)_2\}(CO)(PPh_3)_2]$ (6)

$[Ru(CH{=}CHPh_2OH)Cl(CO)(BTD)(PPh_3)_2]$ (300 mg, 0.290 mmol) gave 215 mg of pale yellow product (66%). IR (solid state): 1913 (ν_{CO}), 1552, 1447(ν_{CN}), 1374, 1313, 1257(ν_{SCS}), 1236, 990, 892, 837 cm^{-1}. ^{31}P NMR ($CDCl_3$): 39.9 (s, PPh_3) ppm. ^1H NMR ($CDCl_3$): 1.09, 1.29 (m × 2, 2 × 2H, $NCH_2CH_2CH_2N$); 1.99 (t, 2H, CH_2NMe_2; $J_{HH} = 6.9$ Hz); 2.04 (t, 2H, CH_2NMe_2; $J_{HH} = 7.0$ Hz); 2.11, 2.15 (s × 2, 2 × 6H, NMe_2); 2.60 (s(br), 1H, OH); 2.77, 3.09 (m × 2, 2 × 2H, CH_2NCS_2); 5.51 (d, 1H, Hβ, $J_{HH} = 16.6$ Hz); 6.83 (m, 4H, CC_6H_5); 6.96 (dt, 1H, Hα, $J_{HH} = 16.6$ Hz, J_{HP} unresolved); 7.13 (m, 6H, CC_6H_5); 7.27–7.52 (m, 30H, PC_6H_5) ppm. MS (ES +ve) *m/z* (abundance) = 1126 (3) $[M]^+$; 1108 (68) $[M–OH_2]^+$; 846 (40) $[M–OH_2–PPh_3]^+$. Analysis: Calculated for $C_{63}H_{67}N_3O_2P_2RuS_2$ (M_w = 1125.38): C 67.2%, H 6.0%, N 3.7%; Found: C 67.3%, H 6.1%, N 3.8%.

$[Ru\{C(C{\equiv}C^tBu){=}CH^tBu\}\{S_2CN(CH_2CH_2CH_2NMe_2)_2\}(CO)(PPh_3)_2]$ (7)

$[Ru\{C(C{\equiv}C^tBu){=}CH^tBu\}Cl(CO)(PPh_3)_2]$ (100 mg, 0117 mmol) gave 17 mg of pale yellow product (13%). Product was soluble in methanol resulting in low yield. A further crop was obtained by ultrasonic trituration in diethylether. IR (solid state): 2221

($\nu_{C\equiv C}$), 1911 (ν_{CO}), 1574, 1785, 1459 (ν_{CN}), 1387, 1356, 1259, 915, 843, 825 cm^{-1}. ^{31}P NMR ($CDCl_3$): 38.2 (s, PPh_3) ppm. ^{1}H NMR ($CDCl_3$): 0.60 (s, 9H, ^{t}Bu); 1.22 (m, 4H, $NCH_2CH_2CH_2N$); 1.33 (s, 9H, ^{t}Bu); 2.02 (m, 4H, CH_2NMe_2); 2.10, 2.14 (s × 2, 2 × 6H, NMe_2); 2.87, 2.98 (m × 2, 2 × 2H, CH_2NCS_2); 5.19 (s, 1H, Hβ); 7.24–7.36, 7.59 (m × 2, 30H, C_6H_5) ppm. MS (ES +ve) *m*/*z* (abundance) = 1080 (42) [M]$^+$; 818 (95) [M – PPh_3]$^+$. Analysis: Calculated for $C_{60}H_{73}N_3OP_2RuS_2$ (M_w = 1079.39): C 66.8%, H 6.8%, N 3.9%; Found: C 66.7%, H 6.7%, N 4.0%.

[Os(CH=CHC$_6$H$_4$Me-4){S$_2$CN(CH$_2$CH$_2$CH$_2$NMe$_2$)$_2$}(CO)(PPh$_3$)$_2$] (8)

[Os(CH=CHC$_6$H$_4$Me-4)Cl(CO)(BTD)(PPh_3)$_2$] (20 mg, 0.019 mmol) gave 7 mg of pale yellow product (33%). The product was found to be partially soluble in ethanol and a further crop was obtained by ultrasonic trituration in diethylether. IR (solid state): 1894 (ν_{CO}), 1638, 1364, 1228, 1118 cm^{-1}. ^{31}P NMR ($CDCl_3$): 7.4 (s, PPh_3) ppm. ^{1}H NMR ($CDCl_3$): 1.21, 1.35 (m × 2, 2 × 2H, $NCH_2CH_2CH_2N$); 2.02 (t, 2H, CH_2NMe_2; J_{HH} = 7.5 Hz); 2.06 (t, 2H, CH_2NMe_2; J_{HH} = 7.3 Hz); 2.09, 2.15 (s × 2, 2 × 6H, NMe_2); 2.23 (s, 3H, CCH_3); 2.82, 3.11 (m × 2, 2 × 2H, CH_2NCS_2); 5.49 (d, 1H, Hβ, J_{HH} = 17.1 Hz); 6.38, 6.83 (AB, 4H, C_6H_4, J_{AB} = 8.0 Hz); 7.27–7.33, 7.53–7.59 (m × 2, 30H, C_6H_5); 8.34 (dt, 1H, Hα, J_{HH} = 17.1 Hz, J_{HP} = 2.5 Hz) ppm. MS (ES +ve) *m*/*z* (abundance) = 1124 (98) [M]$^+$; 862 (39) [M – PPh_3]$^+$. Analysis: Calculated for $C_{57}H_{63}N_3OOsP_2S_2$ (M_w = 1122.44): C 61.0%, H 5.7%, N 3.7%; Found: C 59.0%, H 5.6%, N 3.7%.

[Ru(CH=CH^{t}Bu){S$_2$CN(CH$_2$CH$_2$NEt$_2$)$_2$}(CO)(PPh$_3$)$_2$] (9)

[Ru(CH=CH^{t}Bu)Cl(CO)(BTD)(PPh_3)$_2$] (100 mg, 0.110 mmol) gave 59.8 mg of pale yellow product (53%). IR (solid state): 1898 (ν_{CO}), 1573, 1384, 1372, 1285, 1228, 1176, 984, 914 cm^{-1}. ^{31}P NMR ($CDCl_3$): 39.5 (s, PPh_3) ppm. ^{1}H NMR ($CDCl_3$): 0.38 (s, 9H, ^{t}Bu); 0.95 (m, 12H, NCH_2CH_3); 1.93, 2.21 (m × 2, 2 × 2H, CH_2NEt_2); 2.43 (m, 8H, NCH_2CH_3); 2.83, 3.28 (m × 2, 2 × 2H, CH_2NCS_2); 4.59 (d, 1H, Hβ, J_{HH} = 16.4 Hz); 6.28 (dt, 1H, Hα, J_{HH} = 16.4 Hz, J_{HP} = 2.7 Hz); 7.29–7.34, 7.55–7.59 (m × 2, 30H, C_6H_5) ppm. MS (ES +ve) *m*/*z* (abundance) = 1028 (100) [M]$^+$; 766 (60) [M – PPh_3]$^+$. Analysis: Calculated for $C_{56}H_{69}N_3OP_2RuS_2$ (M_w = 1027.32): C 65.5%, H 6.8%, N 4.1%; Found: C 65.3%, H 6.8%, N 4.0%.

[Ru(CH=CHC$_6$H$_4$Me-4){S$_2$CN(CH$_2$CH$_2$NEt$_2$)$_2$}(CO)(PPh$_3$)$_2$] (10)

[Ru(CH=CHC$_6$H$_4$Me-4)Cl(CO)(BTD)(PPh_3)$_2$] (100 mg, 0.106 mmol) gave 73 mg of pale yellow product (65%). IR (solid state): 1906(ν_{CO}), 1543, 1455(ν_{CN}), 1384, 1282, 1230, 1204, 1177, 969.6, 832.1 cm^{-1}. ^{31}P NMR ($CDCl_3$): 39.3 (s, PPh_3) ppm. ^{1}H NMR ($CDCl_3$): 0.94, 0.98 (t × 2, 2 × 6H, NCH_2CH_3, J_{HH} = 7.1 Hz); 2.07, 2.17 (m × 2, 2 × 2H, CH_2NEt_2); 2.24 (s, 3H, CCH_3); 2.43 (m, 8H, NCH_2CH_3); 2.98, 3.27 (m × 2, 2 × 2H, CH_2NCS_2); 5.53 (d, 1H, Hβ, J_{HH} = 16.6 Hz); 6.37, 6.83 (AB, 4H, C_6H_4, J_{AB} = 8.0 Hz); 7.27–7.34, 7.53–7.57 (m × 2, 30H, C_6H_5); 7.70 (dt, 1H, Hα, J_{HH} = 16.7 Hz, J_{HP} = 3.3 Hz) ppm. MS (ES +ve) *m*/*z* (abundance) = 1062 (100) [M]$^+$; 917 (6) [M–CO–alkenyl]$^+$; 800 (55) [M – PPh_3]$^+$. Analysis: Calculated for $C_{59}H_{67}N_3OP_2RuS_2$ (M_w = 1061.33): C 66.8%, H 6.4%, N 4.0%; Found: C 66.7%, H 6.2%, N 4.0%.

[Ru(CH=CHCPh$_2$OH){S$_2$CN(CH$_2$CH$_2$NEt$_2$)$_2$}(CO)(PPh$_3$)$_2$] (11)

[Ru(CH=CHCPh$_2$OH)Cl(CO)(BTD)(PPh_3)$_2$] (100 mg, 0.097 mmol) gave 34 mg of pale yellow product (30%). The product was found to be partially soluble in ethanol and a further crop was obtained by ultrasonic trituration in diethylether. IR (solid state): 1914 (ν_{CO}), 1550, 1446 (ν_{CN}), 1387, 1235, 1174, 988, 850 cm^{-1}. ^{31}P NMR ($CDCl_3$): 40.2 (s, PPh_3) ppm. ^{1}H NMR ($CDCl_3$): 0.94, 0.98 (t × 2, 2 × 6H, NCH_2CH_3, J_{HH} = 7.1 Hz); 1.93, 2.16 (m × 2, 2 × 2H, CH_2NEt_2); 2.44 (m, 8H, NCH_2CH_3); 2.81, 3.18 (m × 2, 2 × 2H, CH_2NCS_2); 5.51 (d, 1H, Hβ, J_{HH} = 16.6 Hz); 6.82–6.86 (m, 4H, CC_6H_5); 6.97 (dt, 1H, Hα, J_{HH} = 16.6 Hz, J_{HP} = 2.5 Hz); 7.08–7.15 (m, 6H, CC_6H_5); 7.28–7.38, 7.47–7.52 (m × 2, 30H, PC_6H_5) ppm. MS (ES +ve) *m*/*z* (abundance) = 1154 (12) [M]$^+$; 1136 (46) [M – OH_2]$^+$; 874 (47) [M–OH_2–PPh_3]$^+$. Analysis: Calculated for $C_{65}H_{71}N_3O_2P_2RuS_2$ (M_w = 1153.43): C 67.7%, H 6.2%, N 3.6%; Found: C 67.8%, H 6.1%, N 3.5%.

[Ru{C(C≡C^{t}Bu)=CH^{t}Bu}{S$_2$CN(CH$_2$CH$_2$NEt$_2$)$_2$}(CO)(PPh$_3$)$_2$] (12)

[Ru{C(C≡C^{t}Bu)=CH^{t}Bu}Cl(CO)(PPh_3)$_2$] (100 mg, 0.117 mmol) gave 60.3 mg of pale yellow product (47%). IR (solid state): 2164 ($\nu_{C\equiv C}$), 1912 (ν_{CO}), 1547, 1420, 1384, 1354, 1257, 1202, 1174, 916, 844, 826 cm^{-1}. ^{31}P NMR ($CDCl_3$): 38.0 (s, PPh_3) ppm. ^{1}H NMR ($CDCl_3$): 0.60 (s, 9H, ^{t}Bu); 0.92, 0.98 (t × 2, 2 × 6H, NCH_2CH_3, J_{HH} = 7.0 Hz); 1.32 (s, 9H, ^{t}Bu); 2.04 (m, 4H, CH_2NEt_2); 2.44 (m, 8H, NCH_2CH_3); 2.97, 3.04 (m × 2, 2 × 2H, CH_2NCS_2); 5.22 (s, 1H, Hβ); 7.24–7.35, 7.58 (m × 2, 30H, C_6H_5) ppm. MS (ES +ve) *m*/*z* (abundance) = 1108 (100) [M]$^+$; 846 (70) [M – PPh_3]$^+$; 817 (46) [M – CO – PPh_3]$^+$. Analysis: Calculated for $C_{62}H_{77}N_3OP_2RuS_2$ (M_w = 1107.44): C 67.2%, H 7.0%, N 3.8%; Found: C 67.4%, H 7.0%, N 3.7%.

[Os(CH=CHC$_6$H$_4$Me-4){S$_2$CN(CH$_2$CH$_2$NEt$_2$)$_2$}(CO)(PPh$_3$)$_2$] (13)

[Os(CH=CHC$_6$H$_4$Me-4)Cl(CO)(BTD)(PPh_3)$_2$] (20 mg, 0.019 mmol) gave 14 mg of pale yellow product (64%). IR (solid state): 1893 (ν_{CO}), 1495, 1453 (ν_{CN}), 1384, 1350, 1282, 1242, 974, 831 cm^{-1}. ^{31}P NMR ($CDCl_3$): 7.4 (s, PPh_3) ppm. ^{1}H NMR ($CDCl_3$): 0.93, 0.97 (t × 2, 2 × 6H, NCH_2CH_3, J_{HH} = 7.1 Hz); 2.08, 2.21 (m × 2, 2 × 2H, CH_2NEt_2); 2.23 (s, 3H, CCH_3); 2.43 (m, 8H, NCH_2CH_3); 2.86, 3.19 (m × 2, 2 × 2H, CH_2NCS_2); 5.50 (d, 1H, Hβ, J_{HH} = 17.1 Hz); 6.38, 6.83 (AB, 4H, C_6H_4, J_{AB} = 7.9 Hz); 7.29–7.31, 7.55–7.57 (m × 2, 30H, C_6H_5); 8.33 (dt, 1H, Hα, J_{HH} = 17.1 Hz, J_{HP} = 2.4 Hz) ppm. MS (ES +ve) *m*/*z* (abundance) = 1152 (100) [M]$^+$; 1007 (4) [M–CO–alkenyl]$^+$; 890 (8) [M – PPh_3]$^+$. Analysis: Calculated for $C_{59}H_{67}N_3OOsP_2S_2$ (M_w = 1150.49): C 61.6%, H 5.9%, N 3.7%; Found: C 61.7%, H 5.8%, N 3.6%.

[Ru(CH=CHBu^t){S$_2$CN(CH$_2$CH$_2$OMe)$_2$}(CO)(PPh$_3$)$_2$] (14)

Reaction of 1.2 equivalents of $KS_2CN(CH_2CH_2OMe)_2$ with [Ru(CH=CH^{t}Bu)Cl(CO)(BTD)(PPh_3)$_2$] (100 mg, 0.110 mmol) gave 99 mg of pale yellow product (95%). IR (solid state): 1896 (ν_{CO}), 1711, 1414, 1359, 1273, 1222, 1194, 1109, 913 cm^{-1}. ^{31}P NMR ($CDCl_3$): 39.7 (s, PPh_3) ppm. ^{1}H NMR ($CDCl_3$): 0.41 (s, 9H, Bu^t); 2.85 (t, 2H, CH_2, J_{HH} = 5.9 Hz); 3.07 (t, 2H, CH_2,

J_{HH} = 5.9 Hz); 3.18 (t, 2H, CH_2, J_{HH} = 6.0 Hz); 3.19, 3.20 (s × 2, 2 × 3H, OCH_3); 3.48 (t, 2H, CH_2, J_{HH} = 5.9 Hz); 4.56 (dt, 1H, Hβ, J_{HH} = 16.4 Hz, J_{HP} = 1.6 Hz); 6.31 (dt, 1H, Hα, J_{HH} = 16.4 Hz, J_{HP} = 2.6 Hz); 7.29–7.33, 7.56–7.61 (m × 2, 30H, C_6H_5) ppm. MS (ES +ve) *m/z* (abundance) = 968 (61) $[M + Na]^+$; 945 (3) $[M]^+$. Analysis: Calculated for $C_{50}H_{55}NO_3P_2RuS_2$ (M_w = 945.13): C 63.5%, H 5.9%, N 1.5%; Found: C 63.5%, H 5.8%, N 1.6%.

[Ru(CH=CHC$_6$H$_4$Me-4){S$_2$CN(CH$_2$CH$_2$OMe)$_2$}(CO)(PPh$_3$)$_2$] (15)

Reaction of 1.2 equivalents of $KS_2CN(CH_2CH_2OMe)_2$ with $[Ru(CH{=}CHC_6H_4Me\text{-}4)Cl(CO)(BTD)(PPh_3)_2]$ (100 mg, 0.106 mmol) gave 83 mg of pale yellow product (80%). IR (solid state): 1907 (ν_{CO}), 1712, 1541, 1506, 1413, 1361, 1274, 1179, 1110, 969, 829 cm^{-1}. ^{31}P NMR ($CDCl_3$): 39.3 (s, PPh_3) ppm. ^{1}H NMR ($CDCl_3$): 2.25 (s, 3H, CCH_3); 3.00 (t, 2H, CH_2, J_{HH} = 5.8 Hz); 3.14 (t, 2H, CH_2, J_{HH} = 5.7 Hz); 3.19, 3.24 (s × 2, 2 × 3H, OCH_3); 3.24 (t, 2H, CH_2, J_{HH} = 5.9 Hz); 3.50 (t, 2H, CH_2, J_{HH} = 5.7 Hz); 5.53 (d, 1H, Hβ, J_{HH} = 16.8 Hz); 6.43, 6.85 (AB, 4H, C_6H_4, J_{AB} = 7.9 Hz); 7.29–7.36, 7.55–7.59 (m × 2, 30H, C_6H_5); 7.72 (dt, 1H, Hα, J_{HH} = 16.8 Hz, J_{HP} = 3.2 Hz) ppm. MS (ES +ve) *m/z* (abundance) = 1002 (20) $[M + Na]^+$, 1002 (9) $[M]^+$, 862 (39) $[M - alkenyl]^+$. Analysis: Calculated for $C_{53}H_{53}NO_3P_2RuS_2$ (M_w = 979.14): C 65.0%, H 5.5%, N 1.4%; Found: C 65.1%, H 6.1%, N 1.7%.

[Ru{C(C≡C^{t}Bu)=CH^{t}Bu}{S$_2$CN(CH$_2$CH$_2$OMe)$_2$}(CO)(PPh$_3$)$_2$] (16)

Reaction of 1.2 equivalents of $KS_2CN(CH_2CH_2OMe)_2$ with $[Ru\{C(C{\equiv}C^tBu){=}CH^tBu\}Cl(CO)(PPh_3)_2]$ (100 mg, 0.117 mmol) gave 83 mg of pale yellow product (69%). IR (solid state): 2166 ($\nu_{C\equiv C}$), 1911 (ν_{CO}), 1413, 1387, 1356, 1305, 1275, 1260, 1232, 1195, 1111, 964 cm^{-1}. ^{31}P NMR ($CDCl_3$): 38.3 (s, PPh_3) ppm. ^{1}H NMR ($CDCl_3$): 0.61 (s, 9H, Bu^t); 3.01, 3.13 (m × 2, 2 × 4H, CH_2); 1.31 (s, 9H, Bu^t); 3.19, 3.22 (s × 2, 2 × 3H, OCH_3); 5.19 (s, 1H, Hβ); 7.26–7.36, 7.59 (m × 2, 30H, C_6H_5) ppm. MS (ES +ve) *m/z* (abundance) = 1048 (19) $[M + Na]^+$; 1026 (22) $[M]^+$. Analysis: Calculated for $C_{56}H_{63}NO_3P_2RuS_2$ (M_w = 1025.25): C 65.6%, H 6.2%, N 1.4%; Found: C 65.7%, H 6.3%, N 1.5%.

[Ru{S$_2$CN(CH$_2$CH$_2$NHEt$_2$)$_2$}(dppm)$_2$](PF$_6$)(O$_2$CCF$_3$)$_2$ (17)

A solution of $[Ru\{S_2CN(CH_2CH_2NEt_2)_2\}(dppm)_2](PF_6)$ (40 mg, 0.031 mmol) in dichloromethane (10 mL) was treated with 2 equivalents of trifluoroacetic acid in dichloromethane (0.8 mL) and stirred for 5 min. All solvent was removed (rotary evaporator) and the crude product triturated ultrasonically in diethyl ether (20 mL) to give a yellow product. This was washed with diethyl ether (10 mL) and dried to yield 37.8 mg of product (80%). IR (solid state): 2811 (ν_{NH}), 1670 ($\nu_{C=O}$), 1310, 1241, 1198, 1177, 1127, 1096, 833 (ν_{PF}) cm^{-1}. ^{31}P NMR ($CDCl_3$): –5.7, –17.5 (t^v × 2, dppm, J_{PP} = 34.4 Hz) ppm. ^{1}H NMR ($CDCl_3$): 1.29 (s(br), 12H, NCH_2CH_3); 2.66, 3.00 (m × 2, 2 × 2H, CH_2NEt_2); 3.14 (s(br), 8H, NCH_2CH_3); 3.65, 4.40 (m × 2, 2 × 2H, CH_2NCS_2); 4.45, 4.93 (m × 2, 2 × 2H, PCH_2P); 6.46, 6.95, 7.12, 7.22–7.42, 7.60 (m × 5, 40H, C_6H_5), 12.08 (s(br), 2H, $NHEt_2$) ppm. MS (ES +ve) *m/z* (abundance) = 1160 (100) $[M]^+$. Analysis: Calculated for $C_{67}H_{74}F_{12}N_3O_4P_5RuS_2$ (M_w = 1533.37): C 52.5%, H 4.9%, N 2.7%; Found: C 52.4%, H 4.9%, N 2.7%.

[Ru(CH=CH^{t}Bu){S$_2$CN(CH$_2$CH$_2$CH$_2$NHMe$_2$)$_2$}(CO)(PPh$_3$)$_2$]-(O$_2$CCF$_3$)$_2$ (18)

A solution of $[Ru(CH{=}CH^tBu)\{S_2CN(CH_2CH_2CH_2NMe_2)_2\}(CO)(PPh_3)_2]$ (40 mg, 0.040 mmol) in dichloromethane (10 mL) was treated with 2 equivalents of trifluoroacetic acid in dichloromethane (1 mL) and stirred for 5 min. All solvent was removed (rotary evaporator) and the crude product triturated ultrasonically in diethyl ether (20 mL) to give a pale yellow product. This was washed with diethyl ether (10 mL) and dried to yield 37.3 mg of product (76%). IR (solid state): 2776 (ν_{NH}), 1915 (ν_{CO}), 1674 ($\nu_{C=O}$), 1412, 1385, 1366, 1307, 1286, 1256, 1236, 1197, 1170, 1125, 1091, 1029, 999, 969, 951, 829 cm^{-1}. ^{31}P NMR ($CDCl_3$): 39.2 (s, PPh_3) ppm. ^{1}H NMR ($CDCl_3$): 0.41 (s, 9H, ^{t}Bu); 1.42, 1.73 (m × 2, 2 × 2H, $NCH_2CH_2CH_2N$); 2.66, 2.72 (s × 2, 2 × 6H, NMe_2); 2.80, 2.88 (m × 2, 2 × 2H, CH_2NMe_2); 3.28, 3.51 (m × 2, 2 × 2H, CH_2NCS_2); 4.60 (dt, 1H, Hβ, J_{HH} = 16.4 Hz; J_{HP} = 1.6 Hz); 6.31 (dt, 1H, Hα, J_{HH} = 16.4 Hz, J_{HP} = 2.7 Hz); 7.32–7.36, 7.52–7.57 (m × 2, 30H, C_6H_5), 12.80 (s(br), 2H, $NHMe_2$) ppm. MS (ES +ve) *m/z* (abundance) = 1000 (95) $[M]^+$; 738 (75) $[M - PPh_3]^+$. Analysis: Calculated for $C_{58}H_{67}F_6N_3O_5P_2RuS_2$ (M_w = 1227.31): C 56.8%, H 5.5%, N 3.4%; Found: C 56.8%, H 5.7%, N 3.3%.

[Ru(=CHCH=CPh$_2$){S$_2$CN(CH$_2$CH$_2$CH$_2$NHMe$_2$)$_2$}(CO)-(PPh$_3$)$_2$](O$_2$CCF$_3$)$_3$ (19)

A solution of $[Ru(CH{=}CHCPh_2OH)\{S_2CN(CH_2CH_2CH_2NMe_2)_2\}(CO)(PPh_3)_2]$ (100 mg, 0.089 mmol) in dichloromethane (30 mL) was treated with excess trifluoroacetic acid (15 drops) in dichloromethane (1 mL) and stirred for 5 min leading to a deep red colour. All solvent was removed (rotary evaporator) and the crude product triturated ultrasonically in petroleum ether (20 mL) to give a dark red product. This was washed with petroleum ether (10 mL) and dried to yield 110 mg of product (85%). IR (solid state): 2721 (ν_{NH}), 1952 (ν_{CO}), 1782, 1739, 1673 ($\nu_{C=O}$), 1600, 1575, 1384, 1309, 1174, 1127, 938, 830, 798 cm^{-1}. ^{31}P NMR ($CDCl_3$): 32.0 (s, PPh_3) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): 310.5 (t, RuC, J_{CP} = 8.6 Hz); 204.8 (s, CS_2); 201.4 (t, CO, J_{CP} = 12.8 Hz); 161.3 (s, CPh_2); 160.9 (q, O_2C, J_{CF} = 37.8 Hz); 147.1 (t, Cβ, J_{CP} = unresolved); 140.0, 138.1 (s × 2, 2 × CC_6H_5); 134.6 (t^v, *o/m*-PC_6H_5, J_{CP} = 4.7 Hz); 133.5, 131.9 (s × 2, 2 × CC_6H_5); 131.4 (s, *p*-PC_6H_5); 131.1 (s, CC_6H_5); 130.3 (t^v, *ipso*-PC_6H_5, J_{CP} = 24.1 Hz); 129.5 (s, CC_6H_5); 128.7 (t^v, *o/m*-PC_6H_5, J_{CP} = 4.5 Hz); 128.6 (s, CC_6H_5); 116.3 (q, CF_3, J_{CF} = 289.1 Hz); 55.2, 55.1 (s × 2, NCH_2); 47.4 (s, NCH_2), 43.5 (s, $NHMe_2$); 22.3, 21.9 (s × 2, CCH_2C) ppm. ^{1}H NMR ($CDCl_3$): 1.41 (m, 2 × 2H, $NCH_2CH_2CH_2N$); 2.80, 2.83 (s × 2, 2 × 6H, NMe_2); 2.98 (m, 4H + 4H, CH_2NMe_2 + CH_2NCS_2); 6.14 (d, 2H, *ortho*-CC_6H_5, J_{HH} = 7.0 Hz); 7.11 (m, 4H, CC_6H_5); 7.29–7.85 (m, 30H + 4H, PC_6H_5 + CC_6H_5); 8.10 (d, 1H, Hβ, J_{HH} = 14.0 Hz); 11.83 (s(br), 2H, $NHMe_2$); 14.68 (d, 1H, Hα, J_{HH} = 14.0 Hz) ppm. MS (FAB +ve) *m/z* (abundance) = 1108 (16) $[M]^+$, 916 (40) $[M - alkenylcarbene]^+$, 846 (100) $[M - PPh_3]^+$. Analysis: Calculated for $C_{69}H_{68}F_9N_3O_7P_2RuS_2{\cdot}3CH_2Cl_2$ (M_w = 1449.43): C 50.7%, H 4.4%, N 2.5%; Found: C 51.2%, H 4.1%, N 2.5%.

Crystallography

Single crystals of complexes **3** and **15** were grown by slow diffusion of ethanol into a dichloromethane solution of each complex.

Crystal data for **3**: $[C_{57}H_{58}NO_2P_4RuS_2](PF_6)$, $M = 1223.08$, monoclinic, $P2_1/c$ (no. 14), $a = 17.3740(3)$, $b = 12.01286(19)$, $c = 26.6409(4)$ Å, $\beta = 95.1247(14)°$, $V = 5538.04(15)$ Å^3, $Z = 4$, $D_c = 1.467$ g cm^{-3}, μ(Mo-Kα) = 0.566 mm^{-1}, $T = 173$ K, pale yellow needles, Oxford Diffraction Xcalibur 3 diffractometer; 12994 independent measured reflections ($R_{int} = 0.0300$), F^2 refinement, R_1(obs) = 0.0316, wR_2(all) = 0.0721, 9490 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 58°$], 705 parameters. CCDC 750274.

Crystal data for **15**: $C_{53}H_{53}NO_3P_2RuS_2{\cdot}0.3CH_2Cl_2$, $M = 1004.57$, triclinic, $P\bar{1}$ (no. 2), $a = 11.9999(3)$, $b = 15.2412(3)$, $c = 15.3608(4)$ Å, $\alpha = 111.203(2)$, $\beta = 106.398(2)$, $\gamma = 95.0213(18)°$, $V = 2455.53(12)$ Å^3, $Z = 2$, $D_c = 1.359$ g cm^{-3}, μ(Cu-Kα) = 4.631 mm^{-1}, $T = 173$ K, pale yellow platy needles, Oxford Diffraction Xcalibur PX Ultra diffractometer; 9694 independent measured reflections ($R_{int} = 0.0248$), F^2 refinement, R_1(obs) = 0.0278, wR_2(all) = 0.0713, 8842 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 145°$], 629 parameters. CCDC 750275.

The structures were refined using the SHELXTL and SHELX-97 program systems.[23] Further details can be found in the Supporting Information.†

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