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Spectroscopic, Structural and Theoretical Investigation of Alkenyl Ruthenium Complexes Supported by Sulfur–Nitrogen Mixed-Donor Ligands

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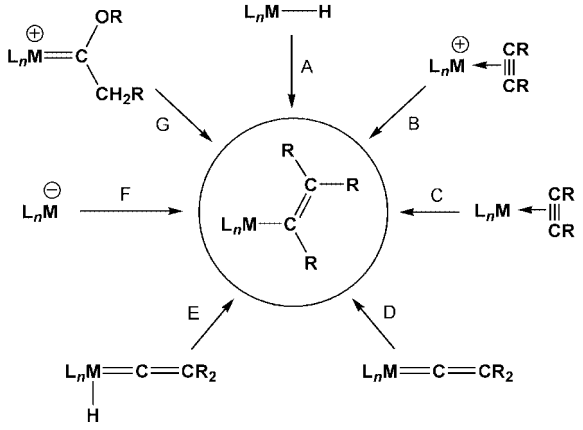
A series of molecules bearing both sulfur and nitrogen donors has been investigated as ligands for σ-alkenyl ruthenium complexes. On deprotonation, the ligands, 4-amino-2-mercaptopyrimidine (HL_1), 2-amino-5-mercapto-1,3,4-thiadiazole (HL_2), 2-mercaptothiazoline (HL_3), 4-hydroxy-2-mercaptopyrimidine (HL_4) and 2-mercaptoquinoline (HL_5) all react with alkenyl complexes of the form [RuRCl(CO)(BTD)-$(PPh_3)_2$] [R = $CH{=}CHC_6H_5$, $CH{=}CHC_6H_4Me$-4, $C(C{\equiv}CPh){=}CHPh$; BTD = 2,1,3-benzothiadiazole] through loss of chloride and BTD ligands to yield [RuR(L)(CO)$(PPh_3)_2$]. Four of these ligands have alternative potential coordination modes and donor groups. In all cases complexation occurs to form four-membered nitrogen–sulfur chelates with the pendant amino or hydroxy functionality playing no role in coordination. In the case of the 4-aminopyrimidine-2-thiolate (L_1) ligand, this was confirmed by a single-crystal X-ray study. 2-Mercaptothiazoline (L_3) has the ability to coordinate through two sulfur donors, however, chelation to nitrogen and sulfur donors is preferred as demonstrated by a structural study. This observation is supported by theoretical calculations, which show that a complex displaying the nitrogen–sulfur chelate is of significantly lower energy than one bonded to the ligand through two sulfur donors, despite lone pairs being available in both cases.

Introduction

The alkenyl ligand is an important member of the σ-organyl ligand family due to its presence as an intermediate in many catalytic reactions, and has attracted substantial interest over the last 40 years. Alkenyl complexes are known for many metals. This is largely due to well-established synthetic routes such as hydrometallation and the reaction of coordinated alkynes with electrophiles or nucleophiles (Scheme 1).[1]

Since the discovery of hydrometallation of alkynes by the compounds [RuHCl(CO)$L_{2/3}$] (L = P*i*Pr_3,[2] PPh_3[3]), the resulting alkenyl complexes have been the subject of much pioneering work by the groups of Werner,[10] Esteruelas[11] Santos,[12] and Caulton and Eisenstein[13] covering functional-group transformation, ligand exchange and theoretical calculations. The hydride complexes themselves are known for their ability to catalyse hydrogenation,[14,15] hydrocarbonylation[16] and hydrosilylation[15,17] reactions as well as the formation of diynes.[18]

Previous work from members of this group has concentrated on alkenyl complexes supported by bidentate and tridentate nitrogen and sulfur donor ligands and the reactions of these complexes.[19] This complemented work by other groups exploring the effect of polydentate donors on the structure and reactivity of alkenyl complexes. The majority of this research has concentrated on the use of symmetrical, bidentate phosphorus,[20] nitrogen[21] or chalcogen donors.[22] The investigation of mixed-donor ligands has been largely confined to simple, often homoleptic, coordination compounds. In particular, very few organometallic compounds bearing these ligands have been reported. The work reported here is part of a programme[23] to synthesise σ-



Scheme 1. Common routes to alkenyl complexes: (A) RC≡CR;[2,3] (B) Nu^-, nucleophile is β to metal;[4] (C) E^+, electrophile is β to metal;[5] (D) Nu^-, nucleophile is α to metal;[6] (E) rearrangement yields alkenyl;[7] (F) $H_2C{=}C(X)R$, X = halide;[8] (G) loss of H^+ to produce α-alkoxyalkenyls.[9]

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alkenyl complexes bearing mixed-donor bidentate ligands and to investigate their effect on migratory insertion reactions and hemilabile behaviour in these complexes.

Although the coordination chemistry of sulfur derivatives of nucleic bases has received sporadic attention due to the interest in metal-based drugs,[24] the potential of thionucleobases and related molecules as sulfur–nitrogen mixed-donor ligands for organotransition-metal compounds has been overlooked. The reactions of five such molecules with coordinatively-saturated σ-alkenyl ruthenium complexes bearing the labile 2,1,3-benzothiadiazole ligand are discussed below. Four of the ligands have alternative possible coordination modes to those adopted and this aspect is explored in one case using a combination of structural and computational methods.

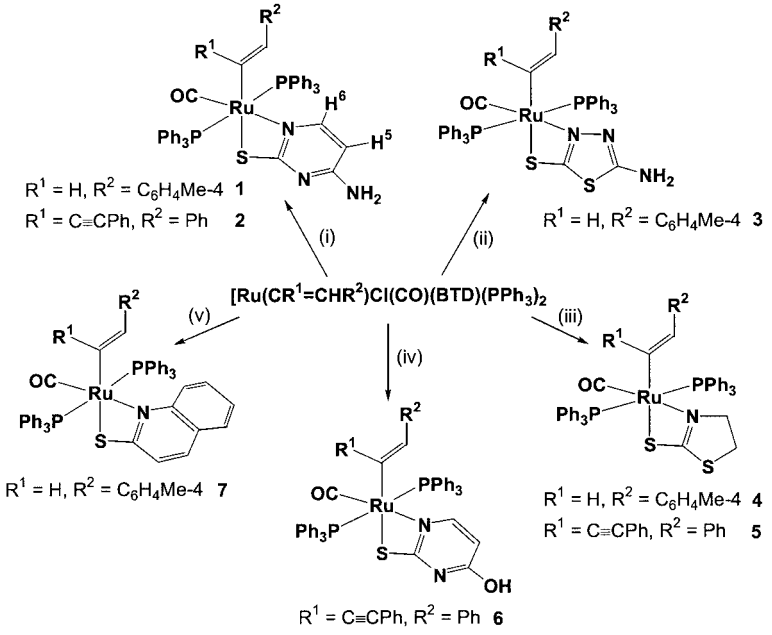
Results and Discussion

The organometallic starting materials used in this work are the 2,1,3-benzothiadiazole (BTD) complexes [Ru(alkenyl)Cl(CO)(BTD)(PPh_3)$_2$],[25] which provide a useful alternative to the 16-electron starting materials, [Ru(alkenyl)Cl(CO)(PPh_3)$_2$]. The BTD compounds do not suffer contamination by free triphenylphosphane and yield microcrystalline starting complexes of excellent purity, which can be easily (re)crystallized from dichloromethane/ethanol mixtures.

4-Amino-2-mercaptopyrimidine (2-thiocytosine) has been shown to play a role in *E. coli* transfer-RNA,[26] and its coordination chemistry has been explored with a number of metals.[27] Of the coinage metals, copper[28] and silver[29] coordination complexes have been reported, and work by members of our group has investigated its use in supramolecular networks of gold(I) based on hydrogen and aurophilic bonding.[30] In all these reports, the thionucleobase is bonded through sulfur, in many cases as a monodentate ligand. In one study,[31] the cisplatin analogue, [$PtCl_2(L_1)_2$], was prepared, in which 2-thiocytosine is bonded through the amino group, demonstrating the range of coordination options available. Only one organometallic complex (of tin) has been reported very recently.[32]

Treatment of a suspension of [Ru(CH=CHC$_6$H$_4$Me-4)Cl(CO)(BTD)(PPh_3)$_2$] and 4-amino-2-mercaptopyrimidine in dichloromethane with an ethanolic solution of sodium methoxide led to an immediate colour change from red to yellow. A yellow microcrystalline solid was isolated. This gave rise to a singlet resonance in the $^{31}P\{^1H\}$ NMR spectrum at δ = 42.1 ppm, indicating a *trans* disposition of the two phosphane ligands; a feature common to all the complexes reported here. The retention of the alkenyl ligand was confirmed by a doublet at 5.84 (J_{HH} = 16.4 Hz) for the β proton and a doublet of triplets to lower field for the α proton at δ = 7.77 ppm (J_{HH} = 16.4 Hz, J_{HP} = 4.3 Hz) in the ^{1}H NMR spectrum. The tolyl substituent was observed as an $(AB)_2$ system at 6.46, 6.87 ppm (J_{AB} = 7.9 Hz) and a methyl resonance at δ = 2.22 ppm. The mixed-donor ligand itself was identified by a singlet at 4.37 (NH_2) and doublet resonances at 4.98 and 6.65 ppm, showing a coupling of 6.3 Hz between the pyrimidine protons. These values are shifted to higher field compared to those at δ = 5.96 and 7.47 ppm (J_{HH} = 7.15 Hz) in the free ligand.[33] A molecular ion at *m*/*z* = 897 in the Fast Atom Bombardment (FAB) mass spectrum and elemental analysis of the dichloromethane solvate confirmed the overall composition as [Ru(CH=CHC$_6$H$_4$Me-4)(L_1)(CO)(PPh_3)$_2$] (**1**) (Scheme 2).

Reaction of [Ru{C(C≡CPh)=CHPh}Cl(CO)(BTD)(PPh_3)$_2$] with HL_1 in a similar manner yielded the disubstituted alkynyl derivative [Ru{C(C≡CPh)=CHPh}(L_1)-



Scheme 2. Alkenyl complexes bearing the mixed-donor ligands, L_1–L_5. (i) $C_4H_5N_3S$ (HL_1), NaOMe; (ii) $C_2H_3N_3S_2$ (HL_2), NaOMe; (iii) $C_3H_5NS_2$ (HL_3), NaOMe; (iv) $C_4H_4N_2OS$ (HL_4), NaOMe; (v) C_9H_7NS (HL_5), NaOMe.

$(CO)(PPh_3)_2]$ (**2**), which gave rise to a ν(C≡C) absorption of low intensity at 2147 cm^{-1} for the enynyl ligand. A broadened singlet at 4.5 ppm was observed in the ^1H NMR spectrum for the NH_2 group. In addition to a singlet for the vinylic proton (δ = 6.13 ppm) and resonances due to the aromatic protons of the alkenyl substituents, two doublets were observed at δ = 5.12 and 7.69 ppm (J_{HH} = 6.3 Hz) in the ^1H NMR spectrum of **2**. The chemical shift of the latter resonance was shifted by approximately 1 ppm downfield with respect to the same feature in complex **1**. A possible explanation for this observation is provided by the crystal structure obtained from single crystals of **2**, grown by slow diffusion of ethanol into a dichloromethane solution of the complex (Figure 1).

An interaction of around 2.6 Å was observed between the triple bond of the enynyl ligand (C10–C11) and the closest proton of the pyrimidine ring (C19–H). The presence of this interaction in solution could explain the apparent deshielding of the proton and hence its shift to lower field. Such CH–π interactions are often found in terminal alkynes,[34] such as in (±)-3-phenylbut-l-ynol, where the distance to the midpoint of the triple bond is 2.62 Å.[34c] On the basis of this evidence, the proton resonances at δ = 5.12 and 7.69 ppm were assigned to the H^5 and H^6 protons, respectively.

Recent reports have shown 2-amino-5-mercapto-1,3,4-thiadiazole (HL_2) to be an effective corrosion inhibitor for copper[35] and bronze.[36] The properties of its metal complexes have been examined in the inhibition of carbonic anhydrase.[37] $[Ru(CH=CHPh)Cl(CO)(BTD)(PPh_3)_2]$ reacts with HL_2 in the presence of base to provide $[Ru(CH=CHPh)(L_2)(CO)(PPh_3)_2]$ (**3**) in good yield. The presence of the mixed-donor ligand was indicated in the ^1H NMR spectrum by a singlet at δ = 5.22 ppm for the NH_2 group, along with typical spectroscopic features for the alkenyl ligand. The formulation of the structure (Scheme 2) was based on these data, a molecular ion at m/z = 889 and elemental analysis.

Thiazoline-2-thiolate (L_3) has been used as a bridging ligand for palladium centres[38] and to generate polymeric clusters of Cu^I and Ag^I.[39] It has also been employed as a ligand in precursor complexes for the deposition of cadmium selenide.[40] However, the potential of the ligand as a bidentate donor has not been widely explored.[41]

The yellow compound $[Ru(CH=CHC_6H_4Me\text{-}4)(L_3)(CO)(PPh_3)_2]$ (**4**) was isolated from the reaction of HL_3 with $[Ru(CH=CHC_6H_4Me\text{-}4)Cl(CO)(BTD)(PPh_3)_2]$ and base (Scheme 2). Similar spectroscopic features for the alkenyl ligand were observed in the ^1H NMR spectrum as for **1**. Two triplets were also present in the spectrum at δ = 2.13 and 2.36 ppm, and these were assigned to the thiazoline ring protons showing mutual coupling of 8.2 Hz. The corresponding enynyl derivative, $[Ru\{C(C\equiv CPh)=CHPh\}(L_3)(CO)(PPh_3)_2]$ (**5**), was prepared in an identical manner. Co-

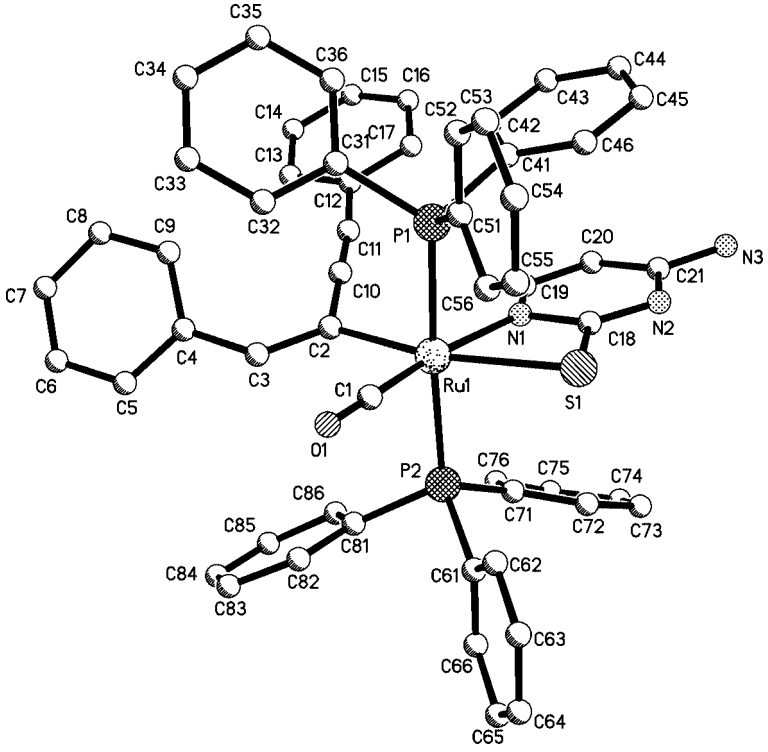


Figure 1. Structure of $[Ru\{C(C\equiv CPh)=CHPh\}(L_1)(CO)(PPh_3)_2]$ (**2**). Selected bond lengths [Å] and angles [°]: Ru1–C1 1.827(4), Ru1–C2 2.111(4), Ru1–N1 2.176(3), Ru1–P2 2.3755(11), Ru1–P1 2.3918(11), Ru1–S1 2.5131(11), S1–C18 1.730(4), N1–C18 1.346(5), C2–C3 1.340(5), C10–C11 1.205(6), C1–Ru1–C2 89.55(16), C2–Ru1–N1 99.97(13), C1–Ru1–P2 89.98(13), C2–Ru1–P2 94.28(11), N1–Ru1–P2 89.80(9), C1–Ru1–P1 89.93(13), C2–Ru1–P1 90.23(11), N1–Ru1–P1 89.55(9), P2–Ru1–P1 175.48(3), C1–Ru1–S1 104.98(13), N1–Ru1–S1 65.49(9), P2–Ru1–S1 89.14(4), P1–Ru1–S1 86.52(4), C18–S1–Ru1 80.18(13), C18–N1–Ru1 102.6(2), C3–C2–Ru1 126.1(3), N1–C18–S1 111.5(3).

ordination of the ligand through a thiolate linkage was expected in view of the basic conditions employed and this assumption was reinforced by the observation of NaCl precipitation during the reactions. However, it was not clear whether a bidentate chelate would be achieved through the sulfur or the nitrogen donor on the thiazoline ring. A theoretical study was undertaken in order to examine the mode of coordination of L_3. This showed that the chelate should form through sulfur and nitrogen donors rather than both sulfur donors and revealed that there is a significant energy difference between the S,S and S,N coordination modes, favouring the latter (Computational Section). These calculations were found to be in good agreement with a later structural determination using single crystals of the enynyl derivative, [Ru{C(C≡CPh)=CHPh}(L_3)(CO)(PPh_3)$_2$] (**5**), which were grown by slow diffusion of ethanol into a dichloromethane solution of the complex (Figure 2).

The thionucleobase, 4-hydroxy-2-mercaptopyrimidine (HL_4), also known as 2-thiouracil, has been used to prepare coordination compounds with a number of metals.[42,27a,27k,31] Recent work has investigated the redox properties of complexes using 2-thiouracil as a bridging ligand between ruthenium centres.[27m] However, no organoruthenium species stabilized by this ligand have been reported as far as we are aware.

[Ru{C(C≡CPh)=CHPh}Cl(CO)(BTD)(PPh_3)$_2$] reacted readily with HL_4 and base to yield [Ru{C(C≡CPh)=CHPh}(L_4)(CO)(PPh_3)$_2$] (**6**), the hydroxy analogue of the 4-aminopyrimidine-2-thiolate complex, **2**, in excellent yield (Scheme 2). The coordination of the ligand was assumed to be through the N1 and sulfur donors in order to minimize steric interaction between the hydroxy group and the carbonyl and enynyl ligands. Coordination of L_4 is also possible as an oxygen–nitrogen mixed-donor. This seemed unlikely, given the thiophilicity of ruthenium(II) and was ruled out by the observation of a broadened singlet at δ = 1.75 ppm for the hydroxy proton. A doublet for one of the pyrimidine protons was noted at δ = 5.22 ppm (J_{HH} = 7.3 Hz) which was assigned to H^5 on the basis of HMQC and HMBC experiments. The H^6 resonance (δ = 7.43 ppm, J_{HH} = 7.7 Hz in the free ligand[33]) was obscured by the aromatic resonances.

Walton and co-workers have investigated the coordination properties of quinoline-2-thiolate (L_5) with rhenium complexes[43] and a few examples have been isolated for molybdenum,[44] cobalt[45] and gold.[46] HL_5 has also been used as an analytical reagent for the determination of nickel, copper and palladium.[47] Reaction of a suspension of [Ru(CH=CHC_6H_4Me-4)Cl(CO)(BTD)(PPh_3)$_2$] with HL_5 and sodium methoxide resulted in the formation of the yellow complex [Ru(CH=CHC_6H_4Me-4)(L_5)(CO)(PPh_3)$_2$] (**7**). The peaks observed in the ^{1}H NMR spectrum for the alkenyl ligand are similar to those seen in the spectra of **1**, **3** and **4**. The protons of the quinoline rings are all obscured

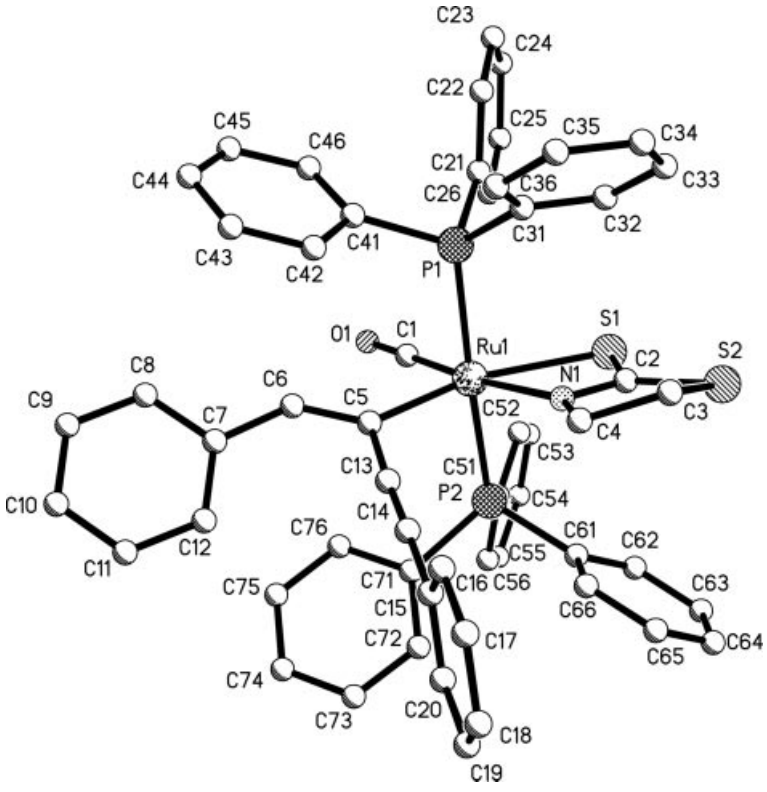


Figure 2. Structure of [Ru{C(C≡CPh)=CHPh}(L_3)(CO)(PPh_3)$_2$] (**5**). Selected bond lengths [Å] and angles [°]: Ru1–C1 1.827(2), Ru1–C5 2.102(2), Ru1–N1 2.1766(19), Ru1–P1 2.3667(6), Ru1–P2 2.3746(6), Ru1–S1 2.5521(6), S1–C2 1.720(2), N1–C2 1.283(3), C5–C6 1.361(3), C13–C14 1.205(3), C1–Ru1–C5 88.28(9), C5–Ru1–N1 98.55(8), C1–Ru1–P1 88.62(7), C5–Ru1–P1 94.82(6), N1–Ru1–P1 88.95(5), C1–Ru1–P2 87.87(7), C5–Ru1–P2 90.58(6), N1–Ru1–P2 93.88(5), P1–Ru1–P2 173.46(2), C1–Ru1–S1 108.27(7), N1–Ru1–S1 65.13(5), P1–Ru1–S1 91.26(2), P2–Ru1–S1 84.61(2), C2–S1–Ru1 76.93(8), C2–N1–Ru1 101.39(15), N1–C2–S1 116.55(17), C6–C5–Ru1 126.48(17).

by the resonances of the PPh_3 ligands with the exception of one proton, which gives rise to a doublet at δ = 7.92 ppm (J_{HH} = 8.3 Hz). The overall formulation is based on these data, a molecular ion in the FAB mass spectrum at m/z = 931 and elemental analysis.

Structural Discussion

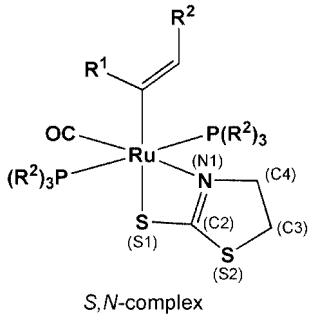
The structure of [Ru{C(C≡CPh)=CHPh}(L_1)(CO)(PPh_3)$_2$] (**2**) (Figure 1) has a distorted octahedral geometry with *cis*-interligand angles in the range 65.49(9)–104.98(13)°. The smallest of these angles corresponds to the bite angle, N1–Ru1–S1, of the 4-aminopyrimidine-2-thiolate ligand (L_1). The structure of 4-amino-5-methylmercaptopyrimidine has been determined[48] and can be assumed to be a direct analogue of the free ligand, HL_1. This report revealed that the molecule exists essentially in the thione form, however, on coordination to divalent ruthenium in our system, the bond lengths of L_1 were observed to be shifted towards the thiolate form. This is seen in the lengthening of the C–S distance from 1.710(4) to 1.730(4) Å in **2**, while the N1–C18 distance shortens from 1.371(5) to 1.346(5) Å on coordination. A complex with the related ligand, 4-methylpyrimidine-2-thiolate (mpymt), [Ru(mpymt)(bpy)$_2$]$^+$ (bpy = 2,2′-bipyridine) has been reported,[42e] in which the C–S distance [1.711(8) Å] is shorter, and the bond length corresponding to N1–C18 [1.367(9) Å] is approximately the same as that found in **2**. This indicates that complexation of L_1 in **2** represents a greater shift from the thione to thiolate form than observed in the literature complex. The Ru–S and Ru–N distances for the chelate in [Ru(mpymt)(bpy)$_2$]$^+$ [2.408(2) and 2.103(6) Å, respectively] are considerably shorter than the corresponding distances in **2** of 2.513(11) and 2.176(3) Å. This is likely to be due to the stronger *trans*-influence of the carbonyl and alkenyl donors in [Ru{C(C≡CPh)=CHPh}(L_1)(CO)(PPh_3)$_2$] (**2**) compared to 2,2′-bipyridine in the literature complex. The bite angle of L_1 in **2** [65.49(9)°] is also smaller than that of 68.2(2)° found in [Ru(mpymt)(bpy)$_2$]$^+$. The bond lengths associated with the alkenyl ligand were found to be unremarkable and fall within the typical range for these ligands.[49] As mentioned above (Results and Discussion), the close proximity of the H^6 proton of L_1 and the triple bond C10–C11 of the enynyl ligand appears to indicate an interaction that is also present in solution, as suggested by ^{1}H NMR evidence.

The structure of 2-mercaptothiazoline (HL_3) was only reported very recently and revealed that the molecule adopts the expected thione form in the solid state with the C–S bond [1.6745(16) Å] displaying clear double bond character.[50] As was found for HL_1, coordination in the deprotonated form results in a shift of double bond character from the C–S bond to the N–C bond involved in the chelate. The C2–S1 distance of 1.720(2) Å found in the structure of [Ru{C(C≡CPh)=CHPh}(L_3)(CO)(PPh_3)$_2$] (**5**) (Figure 2) is considerably longer than that in the free ligand and the N1–C2 distance of 1.283(3) Å is shorter than the corresponding bond length in HL_3, 1.319(2) Å. These variations between bonding in the ligand in free and coordinated states are greater than those discussed for HL_1 above. The bond lengths between the donors and the ruthenium centre are essentially the same in both **2** and **5** with the exception of the Ru1–S1 bond length, which is around 0.03 Å longer in complex **5**. Unlike the 4-aminopyrimidine-2-thiolate (L_1) ligand, the thiazoline-2-thiolate (L_3) moiety is not planar due to the saturated C3–C4 linkage. The overall geometry of the structure of **5** is distorted octahedral with *cis*-interligand angles in the range 65.13(5) – 108.27(7)°, the smallest being due to the bite angle of the bidentate ligand. The bond lengths and distances of the enynyl ligand are similar to those found in [Ru{C(C≡CPh)=CHPh}(L_1)(CO)(PPh_3)$_2$] (**2**).

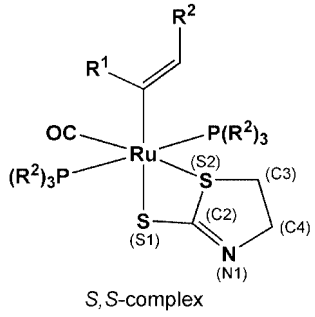
Computational Study

In order to assess the relative stability of the S,N- and S,S-bonding modes available to the complex, [Ru{C(C≡CPh)=CHPh}(L_3)(CO)(PPh_3)$_2$] (**5**), it was decided to use ab initio and density functional theory calculations to compute the optimized geometry of two model complexes derived from structure **5**. The calculations were performed using the NWChem4.6 ab initio package[51] running on a dual processor Apple Xserve. Each optimization was performed using analytic gradients and the default convergence criteria of NWChem.

The simplest model for our computational study is obtained by substituting all phenyl groups and R^2 by hydrogen atoms, thus reducing the enynyl ligand to the parent alkenyl (Scheme 3).



S,N-complex



S,S-complex

Scheme 3. Computational model. Model A corresponds to R^1 = R^2 = H. Model B is for R^1 = C≡CCH_3 and R^2 = CH_3. Numbering scheme is the same as that used in the structural study.

The modest size of model A, along with the use of relativistic pseudo-potentials for each atom developed by Stevens, Basch and Krauss,[52] allowed us to perform fast exploratory calculations using both the Hartree–Fock (HF) method and the local density approximation (LDA) of density functional theory.

The results of our calculations are shown in Table 1, where we report a selection of metal–ligand distances. We observe that the HF distances are much larger than those measured in the experimental X-ray structure, in particular for the two phosphanes and the Ru–S bond. This is to be expected since this method does not take electronic correlation into account. The LDA results for the *S,N*-bonded structure on the other hand are in good agreement with the X-ray values, showing the importance of correlation in describing the electronic structure of transition metal complexes. Moreover, the good agreement with experiment suggests that the computed values for the S,S complex, which was not isolated experimentally, are a plausible representation of the geometrical environment around the ruthenium atom in the S,S system.

In particular, we note that for both levels of theory the S,S complex exhibits a strong degree of ring bending which is absent in the S,N complex. Indeed, Table 1 shows that, while the out-of-plane angle Ru1–S1–C2–C4 remains very low for the S,N complex (about 3° to 5°), the S,S complex has out-of-plane angles between –128° and –110° which indicate that the hybridization of the second sulfur atom (S2) is close to tetrahedral. This, in turn, forces the rest of the thiazoline ring to bend out of the equatorial plane to accommodate the bonding mode of both sulfur donors. The out-of-plane angle computed for the S,N complex on the other hand is in good agreement with that measured in the X-ray structure of –4.5°.

In Table 2, we observe that, for model A, the computed difference of total energy is in favour of the S,N complex in both types of calculations (HF and LDA), which is in line with the experimental observation. The HF method predicts a relatively large energy difference of about 92 kJ·mol^{-1} which is likely to be an overestimation compared to the true value owing to the lack of an appropriate treatment of the electronic correlation. The correlated result computed using LDA brings the energy difference down to about 66 kJ·mol^{-1} which still indicates a very strong preference of the ruthenium for S,N coordination over S,S complex formation.

Table 2. Total energy differences for the *S,N*- and *S,S*-bonded ruthenium structures computed at various levels of ab initio theory.

	Level of theory	E(S,N complex) – E(S,S complex)
Model A	HF	– 92.35 kJ·mol^{-1}
	LDA	– 65.93 kJ·mol^{-1}
Model B	LDA	– 65.41 kJ·mol^{-1}
	BP86	– 64.91 kJ·mol^{-1}

It has been shown that steric effects can have a great influence on the energetics of ruthenium complexes[53] and, to assess the influence of bulkier phosphane and alkenyl ligands, we replaced the hydrogen atoms of our simple model by methyl and propynyl groups to generate Model B (Scheme 3). The influence of these groups on the stability of the bent ring in the S,S complex can result in an increase of the total energy difference between the S,N and S,S complexes. While these groups cannot account for the overall steric bulk of the phenyl groups used experimentally, we expect that any important steric effects would become apparent with this more limited substitution.

The model B compounds were optimized using local density functional theory and then further refined using a gradient-corrected exchange and correlation functional BP86, which has been developed by Becke and Perdew.[54] It has been shown that this exchange and correlation functional gives good results for transition-metal complexes[55] and ruthenium complexes containing carbonyl ligands in particular.[56]

Our results for these calculations are shown in Table 1 and Table 2. First, we see that the change from model A to model B has a small influence on the computed bond lengths and improves their agreement with the X-ray measurements. We note a slight elongation of the Ru–P bonds for both S,N and S,S complexes and a small contraction of the Ru–S distance for the structure with the S,N coordina-

Table 1. Selected metal–ligand distances for the *S,N*- and *S,S*-bonded ruthenium complex computed at various levels of ab initio theory. The atomic numbering scheme is identical to that in Figure 2.

		S,N Complex				**S,S Complex**			
		Model A		Model B		Model A		Model B	
Distance [Å]	X-ray	HF	LDA	LDA	BP86	HF	LDA	LDA	BP86
Ru1–C1	1.827(2)	1.997	1.854	1.842	1.856	1.983	1.843	1.830	1.847
Ru1–C5	2.102(2)	2.116	2.035	2.074	2.121	2.120	2.060	2.078	2.134
Ru1–N1	2.1766(19)	2.203	2.107	2.132	2.208	4.165	3.859	3.823	4.122
Ru1–P1	2.3667(6)	2.529	2.351	2.378	2.445	2.534	2.366	2.409	2.466
Ru1–P2	2.3746(6)	2.525	2.355	2.379	2.446	2.534	2.361	2.384	2.457
Ru1–S1	2.5521(6)	2.730	2.638	2.613	2.681	2.663	2.579	2.581	2.644
Ru1–C2	2.736	2.803	2.744	2.744	2.804	3.063	2.830	2.804	3.010
Ru1–S2	4.471	4.597	4.547	4.560	4.641	2.727	2.528	2.542	2.627
Out-of-plane angle									
Ru1–S1–C2–C4	–4.50°	3.3°	5.0°	2.5°	2.8°	–127.9°	–108.6°	–114.8°	–123.5°

tion mode. The values for the out-of-plane angle are also mildly affected and we see both types of complexes becoming slightly flatter. These observations suggest that the steric effects are small and indicate that our initial model (Model A) already provided a good description of both complexes. Second, we note that the energetics of both complexes are not perturbed by the increase in steric bulk of the substituents since the total energy differences between the S,N and S,S complexes remains at about 65 kJ·mol^{-1}, again in favour of the S,N complex.

To further investigate the effects of electron correlation on the structure and energetics of both types of complexes, the structures obtained from the LDA calculations on model B were re-optimized using BP86. The resulting geometries for both complexes are shown in Figure 3. As expected, since gradient-corrected functionals such as BP86 tends to elongate bonds in transition metal complexes,[55] we observe a lengthening of most bonds in both complexes. In the S,N complex, BP86 overestimates the Ru–P and the Ru–S distances compared with the experimental values, while the other distances and the out-of-plane angle are relatively unaffected (see Table 1). In the case of the S,S complex, the out-of-plane angle increases and the Ru–P, Ru–S bonds are longer than calculated previously using LDA.

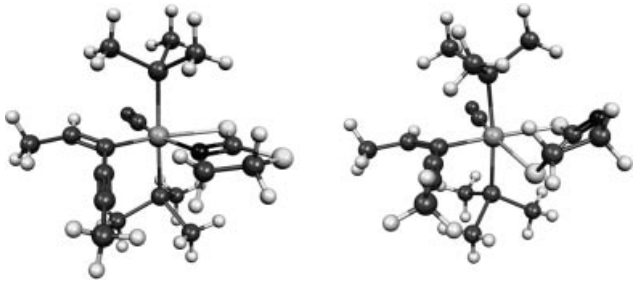


Figure 3. Optimised structures of the S,N complex (left) and S,S complex (right) for model B computed at the BP86/SBK level of theory. Note the large out-of-plane angle in the S,S structure.

Gradient-corrected functionals, such as BP86, provide a more reliable estimation of the binding energy of transition-metal complexes than the local density approximation.[55] Therefore, despite the lengthening of the metal–ligand bonds with BP86, it is interesting to note that the total energy difference between the S,N and the S,S complexes computed with this method remains similar to the value computed using LDA (about 65 kJ·mol^{-1}, see Table 2), again pointing to a marked preference for S,N coordination.

Both models and all levels of theory used in this study indicate that the S,N complex is thermodynamically favoured over the S,S complex. There are several possible reasons for the greater stability of a sulfur–nitrogen combination. First, the S,N configuration of the 2-mercaptothiazoline ligand is able to approach the metal centre more closely than the ligand in the S,S arrangement. Indeed, approach of an S,S donor combination is unfavourable due to the constraining bonding mode of the second sulfur atom (S2), which causes out-of-plane ring bending of the rest of the ligand. Second, the HOMO of the 2-mercaptothiazoline ligand is composed mainly of the p_x orbital of the terminal sulfur atom but has a non-negligible contribution from the nitrogen atom, which allows a degree of π bonding with the ruthenium centre. The presence of π ligands in the complex already (e.g., the carbonyl group) means that an additional ligand that can act as a π donor will participate more efficiently in the bonding at the metal centre. Analysis of the molecular orbitals of the S,S complex shows that such π bonding is not possible when the metal centre is bonded to the ligand using the S,S-configuration.

In order to shed some light on a possible kinetic preference at the ligand-binding stage for the formation of the S,N complex over the S,S complex, we computed the charge distribution of the 2-mercaptothiazoline anionic ligand. This calculation was performed using the GAMESS-US suite of programs[57] at the Møllet-Plesset (MP2) level of theory with a TZV(d,p)++ basis set,[58] since it has been recognized that DFT can have problems describing anions.[59] It should be noted that there is a large negative region around the sulfur atom that protrudes out of the thiazoline ring (S1) and around the N atom (N1), while the sulfur atom within the thiazoline ring (S2) is mainly positively charged. This charge distribution could be responsible for a preferential formation of a S,N complex since the orientation of this anionic ligand with respect to a positively charged centre such as Ru^{II} will naturally lead to a closer contact between the metal centre and the atoms S1 and N1.

Conclusions

This report details the investigation of the coordination properties of five nitrogen–sulfur mixed-donor ligands with alkenyl complexes of ruthenium. We believe that these are the first organoruthenium examples to be reported. Although a number of alternative coordination modes are possible, all ligands adopt a four-membered nitrogen–sulfur chelate, a fact confirmed crystallographically for two examples. In the case of the thiazoline-2-thiolate ligand, the alternative sulfur–sulfur coordination mode was investigated computationally and found to be of much higher energy than the observed S,N coordination, which was confirmed by a structural determination. The excellent correlation of structural and computational data indicates the utility of this theoretical approach in the rationalization of such complexation behaviour.

Experimental Section

All manipulations were carried out under aerobic conditions with commercially available solvents and reagents, which were used as received. Infrared and NMR spectroscopy was carried out at 25 °C using Shimadzu FTIR 8700 (KBr plates and nujol mulls) and Bruker AMX-300 (^{1}H: 299.87 MHz, ^{31}P: 121.39 MHz) spectrometers respectively. Infrared spectroscopic features due to the triphenylphosphane ligands have been omitted to aid clarity. FAB-MS spectra (nitrobenzyl alcohol matrices) were measured using a VG 70-SB magnetic sector mass spectrometer. Elemental analysis

was performed at University College, London. Solvates were determined by integration of the ^{1}H NMR spectra. The complexes [Ru(CH=CHC$_6$H$_4$CH$_3$-4)Cl(CO)(BTD)(PPh$_3$)$_2$],[25] [Ru(CH=CHPh)Cl(CO)(BTD)(PPh$_3$)$_2$],[25] [Ru{C(C≡CPh)=CHPh}Cl(CO)(PPh$_3$)$_2$],[60] were prepared according to published procedures. All other regents were obtained commercially.

Preparation of [Ru(CH=CHC$_6$H$_4$Me-4)(L$_1$)(CO)(PPh$_3$)$_2$] (1): [Ru(CH=CHC$_6$H$_4$Me-4)Cl(CO)(BTD)(PPh$_3$)$_2$] (100 mg, 0.106 mmol) and 4-amino-2-mercaptopyrimidine (HL$_1$) (15 mg, 0.118 mmol) were suspended in dichloromethane (20 mL) and ethanol (10 mL) and treated with sodium methoxide (11 mg, 0.204 mmol) in ethanol (10 mL). The reaction was stirred for 1 h, after which the solvent volume was concentrated under reduced pressure until precipitation of a pale yellow product was complete. This was washed with water (5 mL), ethanol (5 mL) and hexane (10 mL). Yield: 68 mg (72%). IR (KBr/nujol): $\tilde{\nu}$ = 1923 [ν(CO)], 1614, 1572, 1545, 1313, 1256, 1186 cm^{-1}. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 42.1 ppm. ^{1}H NMR (CDCl$_3$): δ = 2.22 (s, 3 H, CH$_3$), 4.37 (s, 2 H, NH$_2$), 4.98, 6.65 [d×2, J_{HH} = 6.3 Hz, 2×1 H, C$_4$*H*$_2$(NH$_2$)N$_2$S], 5.84 (d, J_{HH} = 16.4 Hz, 1 H, Hβ), 6.46, 6.87 [(AB)$_2$, J_{AB} = 7.9 Hz, 4 H, C$_6$H$_4$], 7.25, 7.58 (m×2, 30 H, C$_6$H$_5$), 7.77 (dt, J_{HH} = 16.4 Hz, J_{HP} = 4.3 Hz, 1 H, Hα) ppm. FAB-MS: *m*/*z* (%) = 897 (1) [M]$^+$, 780 (1) [M – alkenyl]$^+$, 635 (2) [M – PPh$_3$]$^+$. C$_{50}$H$_{43}$N$_3$OP$_2$RuS·CH$_2$Cl$_2$ (981.93): calcd. C 62.4, H 4.6, N 4.3; found C 62.8, H 4.8, N 4.3.

Preparation of [Ru{C(C≡CPh)=CHPh}(L$_1$)(CO)(PPh$_3$)$_2$] (2): Synthesis as for **1** using [Ru{C(C≡CPh)=CHPh}Cl(CO)(BTD)(PPh$_3$)$_2$] (100 mg, 0.097 mmol) and 4-amino-2-mercaptopyrimidine (HL$_1$) (14 mg, 0.110 mmol) to provide a yellow product. Yield: 72 mg (76%). IR (KBr/nujol): $\tilde{\nu}$ = 2147 [ν(C≡C)], 1913 [ν(CO)], 1611, 1580, 1537, 1312, 1186, 972, 914 cm^{-1}. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 40.1 ppm. ^{1}H NMR (CDCl$_3$): δ = 4.5 (br. s, 2 H, NH$_2$), 5.12, 7.69 [d×2, J_{HH} = 6.3 Hz, 2×1 H, C$_4$*H*$_2$(NH$_2$)N$_2$S], 6.13 (s, 1 H, RuC=CH), 6.78 (d, J_{HH} = 7.4 Hz, 2 H, *ortho*-C$_6$H$_5$), 6.95 (t, J_{HH} = 7.4 Hz, 1 H, *para*-C$_6$H$_5$), 7.27, 7.61 (m×2, 30 H + 7 H, PC$_6$H$_5$ + C$_6$H$_5$) ppm. FAB-MS: *m*/*z* (%) = 982 (9) [M]$^+$, 856 (3) [M – L$_1$]$^+$, 779 (3) [M – alkenyl]$^+$, 720 (5) [M – PPh$_3$]$^+$, 692 (16) [M–CO–PPh$_3$]$^+$. C$_{57}$H$_{45}$N$_3$OP$_2$RuS (983.09): calcd. C 69.6, H 4.6, N 4.3; found C 69.6, H 4.5, N 4.3.

Preparation of [Ru(CH=CHPh)(L$_2$)(CO)(PPh$_3$)$_2$] (3): Synthesis as for **1** using [Ru(CH=CHPh)Cl(CO)(BTD)(PPh$_3$)$_2$] (100 mg, 0.108 mmol) and 2-amino-5-mercapto-1,3,4-thiadiazole (HL$_2$) (16 mg, 0.121 mmol) to provide a pale yellow-green product. Yield: 79 mg (82%). IR (KBr/nujol): $\tilde{\nu}$ = 1921 [ν(CO)], 1595, 1580, 1553, 1310, 1184, 972, 847 cm^{-1}. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 43.7 ppm. ^{1}H NMR (CDCl$_3$): δ = 5.22 (s, 2 H, NH$_2$), 5.89 (d, J_{HH} = 15.7 Hz, 1 H, Hβ), 6.34 (d, J_{HH} = 7.5 Hz, 2 H, *ortho*-C$_6$H$_5$), 6.82 (t, J_{HH} = 7.5 Hz, 1 H, *para*-C$_6$H$_5$), 6.90 (t, J_{HH} = 7.4 Hz, 2 H, *meta*-C$_6$H$_5$), 7.30–7.53 (m, 30 H, PC$_6$H$_5$), 7.94 (dt, J_{HH} = 15.7 Hz, J_{HP} = 3.2 Hz, 1 H, Hα) ppm. FAB-MS: *m*/*z* (%) = 889 (45) [M]$^+$, 786 (20) [M – alkenyl]$^+$, 627 (12) [M – PPh$_3$]$^+$. C$_{48}$H$_{41}$N$_3$OP$_2$RuS$_2$·1.5CH$_2$Cl$_2$ (1030.42): calcd. C 57.7, H 4.3, N 4.1; found C 57.5, H 4.0, N 4.3.

Preparation of [Ru(CH=CHC$_6$H$_4$Me-4)(L$_3$)(CO)(PPh$_3$)$_2$] (4): Synthesis as for **1** using [Ru(CH=CHC$_6$H$_4$Me-4)Cl(CO)(BTD)(PPh$_3$)$_2$] (100 mg, 0.106 mmol) and 2-mercaptothiazoline (HL$_3$) (14 mg, 0.117 mmol) to provide a yellow product. Yield: 77 mg (82%). IR (KBr/nujol): $\tilde{\nu}$ = 1906 [ν(CO)], 1573, 1304, 1188, 1045, 941, 831 cm^{-1}. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 40.4 ppm. ^{1}H NMR (CDCl$_3$): δ = 2.13, 2.36 (t×2, J_{HH} = 8.2 Hz, 2×2 H, C$_3$H$_4$NS$_2$), 2.26 (s, 3 H, CH$_3$), 5.84 (d, J_{HH} = 16.5 Hz, 1 H, Hβ), 6.60, 6.92 [(AB)$_2$, J_{AB} = 7.93 Hz, 4 H, C$_6$H$_4$], 7.33, 7.69 (m×2, 30 H, C$_6$H$_5$), 7.84 (dt, J_{HH} = 16.5 Hz, J_{HP} = 3.5 Hz, 1 H, Hα) ppm. FAB-MS: *m*/*z* (%) = 906 (3) [M + H$_2$O]$^+$, 888 (3) [M]$^+$, 771 (1) [M – L$_3$]$^+$, 626 (6) [M – PPh$_3$]$^+$, 598 (2) [M–CO–PPh$_3$]$^+$. C$_{49}$H$_{43}$NOP$_2$RuS$_2$·CH$_2$Cl$_2$ (973.97): calcd. C 61.7, H 4.7, N 1.4; found C 61.3, H 4.6, N 1.5.

Preparation of [Ru{C(C≡CPh)=CHPh}(L$_3$)(CO)(PPh$_3$)$_2$] (5): Synthesis as for **1** using [Ru{C(C≡CPh)=CHPh}Cl(CO)(BTD)(PPh$_3$)$_2$] (100 mg, 0.097 mmol) and 2-mercaptothiazoline (HL$_3$) (13 mg, 0.109 mmol) to provide a yellow microcrystalline product. Yield: 72 mg (76%). IR (KBr/nujol): $\tilde{\nu}$ = 2152 [ν(C≡C)], 1917 [ν(CO)], 1591, 1574, 1302, 1049, 941, 914 cm^{-1}. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 39.6 ppm. ^{1}H NMR (CDCl$_3$): δ = 2.08, 2.88 (t×2, J_{HH} = 8.0 Hz, 2×2 H, C$_3$H$_4$NS$_2$), 6.08 (s, 1 H, RuC=CH), 6.98–7.81 (m, 30 H + 10 H, PC$_6$H$_5$ + C$_6$H$_5$) ppm. FAB-MS: *m*/*z* (%) = 973 (2) [M]$^+$, 856 (3) [M – L$_3$]$^+$, 771 (2) [M – alkenyl]$^+$, 711 (1) [M – PPh$_3$]$^+$, 684 (8) [M–CO–PPh$_3$]$^+$. C$_{56}$H$_{45}$NOP$_2$RuS$_2$ (975.13): calcd. C 69.0, H 4.7, N 1.4; found C 69.0, H 4.6, N 1.2.

Preparation of [Ru{C(C≡CPh)=CHPh}(L$_4$)(CO)(PPh$_3$)$_2$] (6): [Ru{C(C≡CPh)=CHPh}Cl(CO)(BTD)(PPh$_3$)$_2$] (100 mg, 0.097 mmol) and 4-hydroxy-2-mercaptopyrimidine (HL$_4$) (14 mg, 0.109 mmol) were suspended in dichloromethane (20 mL) and ethanol (10 mL) and treated with sodium methoxide (10 mg, 0.185 mmol) in ethanol (10 mL). The reaction was stirred for 1 h, after which all solvent was removed. The residue was dissolved in dichloromethane (10 mL) and filtered through diatomaceous earth to remove NaCl. Diethyl ether (40 mL) was slowly added to precipitate the pale yellow product. This was washed with diethyl ether (10 mL) and hexane (10 mL). Yield: 85 mg (89%). IR (KBr/nujol): $\tilde{\nu}$ = 2151 [ν(C≡C)], 1927 [ν(CO)], 1650, 1595, 1275, 1184, 976, 914 cm^{-1}. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 40.3 ppm. ^{1}H NMR (CDCl$_3$): δ = 1.75 (br. s, 1 H, OH), 5.22 [d, J_{HH} = 7.3 Hz, 1 H, C$_5$*H*$_2$(OH)N$_2$S], 6.08 (s, 1 H, RuC=CH), 6.76 (d, J_{HH} = 7.7 Hz, 2 H, *ortho*-C$_6$H$_5$), 6.98–7.72 [m, 30 H + 8 H + 1 H, PC$_6$H$_5$ + C$_6$H$_5$ + C$_5$*H*$_2$(OH)N$_2$S] ppm. FAB-MS: *m*/*z* (%) = 984 (1) [M]$^+$, 857 (0.2) [M – L$_4$]$^+$, 781 (0.6) [M – alkenyl]$^+$, 722 (0.2) [M – PPh$_3$]$^+$, 694 (1.5) [M–CO–PPh$_3$]$^+$, 491 (0.6) [M – alkenyl–CO–PPh$_3$]$^+$. C$_{57}$H$_{44}$N$_2$O$_2$P$_2$RuS·0.75CH$_2$Cl$_2$ (1047.77): calcd. C 66.2, H 4.4, N 2.7; found C 66.2, H 4.4, N 3.0.

Preparation of [Ru(CH=CHC$_6$H$_4$Me-4)(L$_5$)(CO)(PPh$_3$)$_2$] (7): [Ru(CH=CHC$_6$H$_4$Me-4)Cl(CO)(BTD)(PPh$_3$)$_2$] (100 mg, 0.106 mmol) and 2-mercaptoquinoline (HL$_5$) (19 mg, 0.118 mmol) were suspended in dichloromethane (20 mL) and ethanol (10 mL) and treated with sodium methoxide (11 mg, 0.204 mmol) in ethanol (10 mL). The reaction was stirred for 1 h, after which the solvent was concentrated under reduced pressure until precipitation of a yellow product had begun. The flask was then kept at –20 °C for 4 hours. The resulting precipitate was washed with water (5 mL), cold ethanol (5 mL) and hexane (10 mL). Yield: 76 mg (77%). Although the product is partially soluble in ethanol, it can be recrystallised from dichloromethane/ethanol mixtures. IR (NaCl/nujol): $\tilde{\nu}$ = 1913 [ν(CO)], 1591, 1545, 1504, 1296, 1184, 1163, 1109, 974, 874, 845, 814 cm^{-1}. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ = 35.6 ppm. ^{1}H NMR (C$_6$D$_6$): δ = 2.16 (s, 3 H, CH$_3$), 6.09, 6.59 [(AB)$_2$, J_{AB} = 8.7 Hz, 4 H, C$_6$H$_4$], 6.64 (dt, J_{HH} = 16.7 Hz, J_{HP} = 2.0 Hz, 1 H, Hβ), 6.81–7.16, 7.36–7.78 (m×2, 30 H + 5 H, C$_6$H$_5$ + C$_9$H$_6$NS), 7.92 (d, J_{HH} = 8.3 Hz, 1 H, C$_9$H$_6$NS), 8.65 (dt, J_{HH} = 16.7 Hz, J_{HP} = 3.5 Hz, 1 H, Hα) ppm. FAB-MS: *m*/*z* (%) = 931 (4) [M]$^+$, 669 (7) [M – PPh$_3$]$^+$, 641 (8) [M–CO–PPh$_3$]$^+$, 524 (7) [M – alkenyl–CO–PPh$_3$]$^+$. C$_{55}$H$_{45}$NOP$_2$RuS·0.25CH$_2$Cl$_2$ (952.28): calcd. C 69.7, H 4.8, N 1.5; found C 69.9, H 4.8, N 1.5.

X-ray Crystallography: Crystals of complexes **2** and **5** were grown by slow diffusion of ethanol into dichloromethane solutions of the complexes. A single crystal of each compound was mounted on a

glass fibre and all geometric and intensity data were taken from this sample with a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data reduction and integration was carried out with SAINT+ and absorption corrections applied using the program SADABS. The structures were solved by direct methods and developed using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and their thermal parameters linked to those of the atoms to which they were attached (riding model). Structure solution and refinement used the SHELXTL PLUS V6.10 program package.[61] See Table 3 for selected crystal data.

Table 3. Crystal data for compounds **2** and **5**.

	2	**5**·1.5(CH_2Cl_2)
Chemical formula	$C_{57}H_{45}N_3OP_2RuS$	$C_{57.5}H_{48}Cl_3NOP_2RuS_2$
Fw	983.03	1102.45
Crystal system	monoclinic	monoclinic
Crystal colour	yellow	yellow
Crystal size [mm]	0.48×0.12×0.10	0.24×0.22×0.12
Space group	*C*2/*c*	$P2_1/n$
a [Å]	28.321(3)	13.0473(8)
b [Å]	19.249(2)	22.7831(14)
c [Å]	21.145(3)	17.5285(11)
α [°]	90	90
β [°]	119.139(2)	104.5250(10)
γ [°]	90	90
V [Å^3]	10068(2)	5043.9(5)
Z	8	4
Calculated density [g/cm^3]	1.297	1.452
T [K]	293(2)	150(2)
μ(Mo-K_α) [mm^{-1}]	0.458	0.658
F(000)	4048	2260
Reflections collected	43639	44202
Unique reflections (R_{int})	12004 (0.0563)	12093 (0.0304)
R_1 [$I>2\sigma(I)$]	0.0617	0.0405
wR'_2 (all data)	0.1832	0.0952
Residual e·Å^{-3} (max., min.)	1.540, –1.20	1.084, –1.214

CCDC-263406 and -263407 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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