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Thione complexes of Rh(I): a first comparison with the bonding and catalytic activity of related carbene and imine compounds†

Arno Neveling, Gerrit R. Julius, Stephanie Cronje, Catharine Esterhuysen and Helgard G. Raubenheimer*

Department of Chemistry, University of Stellenbosch, Private Bag X1, Matieland, 7602, Stellenbosch, South Africa. E-mail: hgr@sun.ac.za; Fax: +27 21 808 3849; Tel: +27 21 808 3850

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Heterocyclic mono(thione), *trans*-bis(thione), *cis*-bis(thione), *trans*-(carbene–thione), *cis*-(carbene–thione), *trans*-(phosphine-thione) and mono(imine) complexes of rhodium(I) have been prepared and fully characterised. Chloro(η^4-1,5-cyclooctadiene)(L)rhodium(I) (**1a**, L = 1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-thione; **1b**, L = 1,3,4,5-tetramethyl-2,3-dihydro-1*H*-imidazol-2-thione) appear as isomers at room temperature due to slow coordination exchange on the S-donor atom. In the three structures determined, the substituent on the sulfur appears *syn* to Cl. Hindered rotation about the Rh–carbene bond is revealed in the NMR spectra of seven new complexes with isopropyl substituents on the heterocyclic carbene ligands. The *trans* influence of the thione ligands is smaller than that of carbenes but larger than that shown by imines and chloride. Thione complexes are better catalyst precursors than the carbene complexes for the hydroformylation of 1-hexene under the chosen reaction conditions: 80 °C, 8 MPa CO–H_2 (1 : 1), 16 h, 1 : 1000 catalyst to 1-hexene ratio.

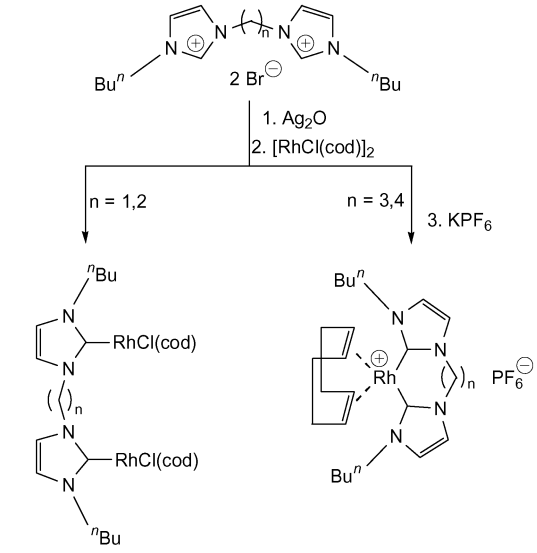
Introduction

Thione complexes of organometallic Rh(I) are rare. Cauzzi and co-workers used rhodium(I)-anchored thiourea-functionalised silica xerogels [1] and later silesquioxanes [2] in the hydroformylation of styrene. Certain carbonyl complexes that contain these ligands are unstable but crystal structures of cyclooctadiene-(cod)-stabilised products have been determined. Later, Breuzard *et al.* employed chiral thioureas in an attempted asymmetric hydroformylation of styrene.[3]

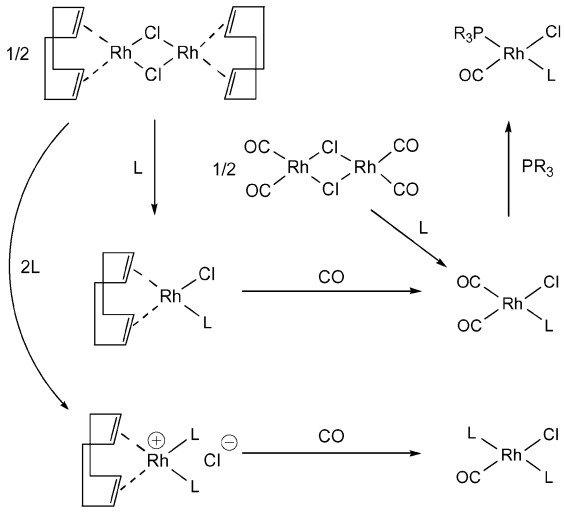
The striking similarities between phosphines and *N*-heterocyclic carbenes both from viewpoints of complex synthetic methodologies and chemical bonding, have been noted by many authors and are probably eventually best described by Herrmann *et al*.[4,5] The advantages of the latter ligand-types in homogeneous catalysis are also well established.[6] However, few complexes with rhodium(I) have been made. Crudden and co-workers prepared and characterised two carbene analogues of Wilkinson's catalyst, and studied their application in the hydroformylation of styrene.[7] Mata *et al.*[8] recently reported that $[RhCl(cod)]_2$ favours bidentate coordination with bis(carbene) ligands that contain long $(CH_2)_n$ linkers, whereas linkers with $n = 1$ or 2 afford dinuclear, monodentately-coordinated compounds (Scheme 1).

Building on the work of Oro *et al*.[9] we reported new rhodium complexes coordinated by anionic and neutral bidentate imine ligands.[10]

Here we describe the synthesis of a series of thione complexes derived from $[RhCl(cod)]_2$ and $[RhCl(CO)_2]_2$. A new group of neutral and cationic heterocyclic carbene complexes as well as neutral imine compounds are also discussed. Finally, the effectivity and activity of the former two series of compounds as precatalysts in the hydroformylation of 1-hexene under mild conditions, are compared.



Scheme 1



Scheme 2

Results and discussion

Synthetic aspects

All compounds were prepared according to the reactions in Scheme 2 *via* the addition of a ligand, L (L = thione,

† Electronic supplementary information (ESI) available: Overlay of complexes **6** and **9**. See http://www.rsc.org/suppdata/dt/b4/b414040k/

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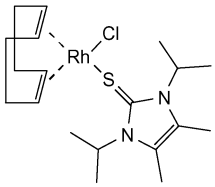
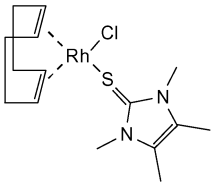
carbene or imine), to Cl-bridged $[RhCl(cod)]_2$. The carbonyl complexes, $RhCl(CO)_2L$, were obtained by substitution of the cyclooctadiene ligand with CO. Replacement of the halide is also possible, leading to the formation of cationic complexes.

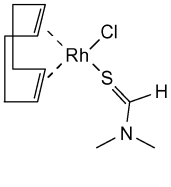
Complexes **1a**, **1b** and **2** formed in high yields while complexes **3a**, **3b** and **4** were only obtained in very low yields. However, the use of $[RhCl(CO)_2]_2$ as starting material with the thione ligands which were added in stoichiometric amounts at room temperature, produced the carbonyl complexes **3** and **4** in almost quantitative yields.



1a



1b



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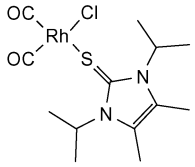
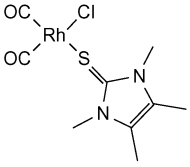
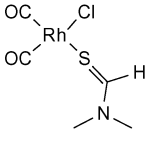


3a

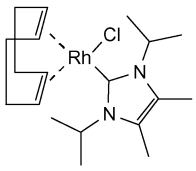


3b



4

A cyclooctadiene rhodium(I) carbene complex (**5**) related to **1a** was isolated and the addition of two mole quantities of carbene ligand per mole of rhodium atom, led to the formation of the cationic species (**6**). Bubbling carbon monoxide through THF solutions of the cyclooctadiene complexes **5** and **6**, yielded the monocarbene complex **7** as well as the *trans*-bis(carbene) complex **8**.



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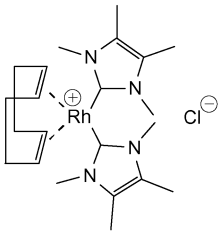
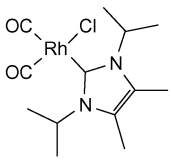
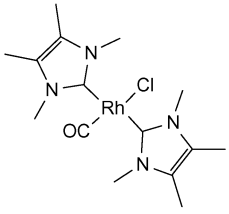


6

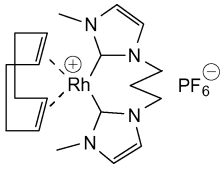


7

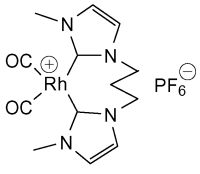


8

A cationic cyclooctadiene rhodium complex with a bidentate carbene ligand (**9**) was prepared according to Scheme 2 (2L replaced by L^L) by deprotonation of the imidazolium salt precursor with KO^{t}Bu. The corresponding cationic carbonyl complex (**10**) formed readily in the presence of CO. Our method differs somewhat from that of Mata *et al.* mentioned before (see Scheme 1).[8]

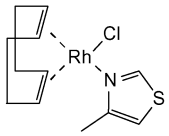


9

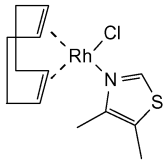


10

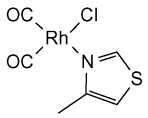
The binuclear rhodium complexes $[RhCl(cod)]_2$ and $[RhCl(CO)_2]_2$ are also readily cleaved by *N*-donor ligands.[11–13] The imines 4-methylthiazole and 4,5-dimethylthiazole afforded the neutral monorhodium complexes **11a** and **11b**, whereas the addition of 4-methylthiazole to $[RhCl(CO)_2]_2$ furnished complex **12** at room temperature.



11a

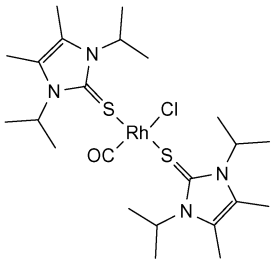


11b



12

Reaction of an excess thione (1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-thione) with complex **3a** gave the *trans*-bis(thione) complex **13**, but only in a low yield. The addition of trimethylamine oxide (to oxidise and remove CO) to the reaction mixture, led to the desired complex **13** in a reasonable yield. Complex **14** was obtained similarly from **7**.



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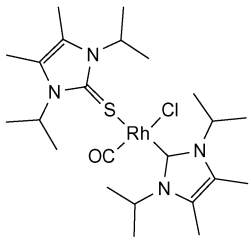


14

The addition of two mole quantities of thione per mole rhodium in $[RhCl(cod)]_2$ only furnished the mononuclear thione complex **1a** again. However, addition of $AgBF_4$ to the reaction mixture precipitated the chloride leading to the formation of the desired ionic complex **15**. Complex **16**, a *cis*-bis(thione) compound, formed in the presence of CO. The assignment of a *cis*-configuration to this complex was based on IR and NMR data. Complexes **17** and **18** that each contain a carbene ligand as well as a thione ligand, were prepared in similar fashion to **15** and **16**.

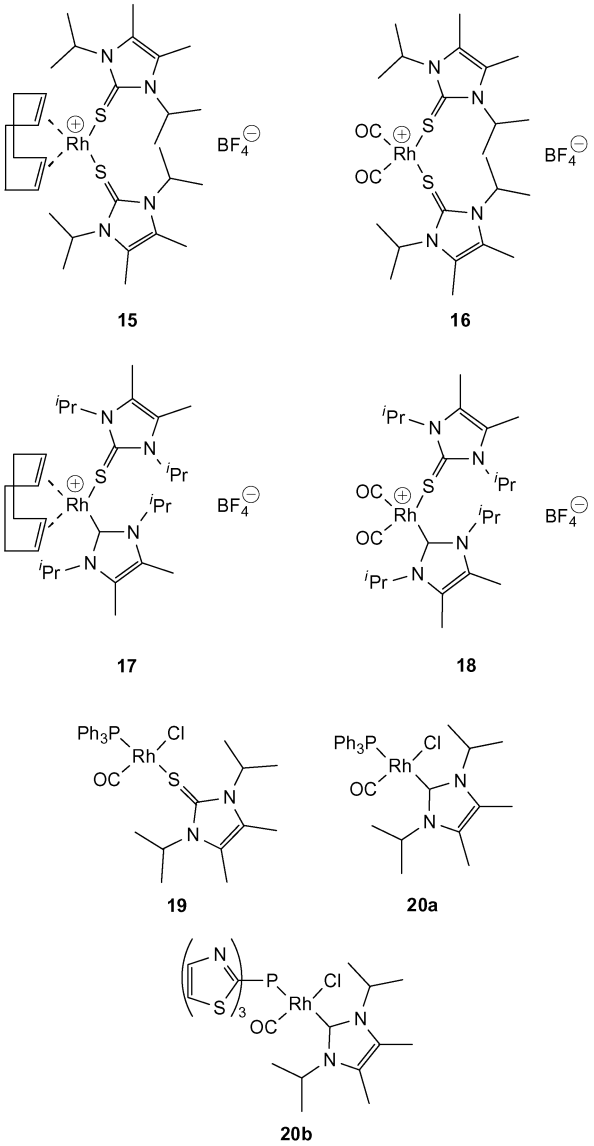
The phosphine-containing compounds **19–20b** resulted from the addition of the chosen phosphine to complexes **3a** or **7**.

Spectroscopic characterisation

The NMR signals of the thione complex **1a** exhibit broadening and coalescence in its ^{1}H NMR spectrum, a phenomenon also observed by Müller and Stock during the characterisation of cyclooctadiene(imine)rhodium(I) complexes.[13]

Interestingly, two broad signals appeared for all the protons of the two methyl groups, on the imidazole ring, in **1a** and **1b**. For the N–C*H*$(CH_3)_2$ protons of the thione ligand in **1a**, however, only one broad peak was observed, similar to the NMR spectrum of the free ligand. Each of the carbon atoms of the thione ligand gave rise to two signals at room temperature, whereas none of the cyclooctadiene carbon atoms exhibited this phenomenon. At higher temperatures, the signals in both the proton and ^{13}C NMR spectra (in toluene-d_8) coalesce but still remain somewhat broad (Fig. 1).

The room-temperature NMR information suggests the presence of isomers (Fig. 2) caused by slow inversion about the rhodium sulfur bond. Abel *et al*. reported the occurrence of a ring-flipping process in rhodium complexes with sulfur-donor ligands due to possible sulfur inversions as indicated by variable-temperature NMR studies.[14]



However, sharp signals were observed in the room temperature NMR spectra of the carbonyl complexes **3a**, **3b**, **16**, **18**, the carbene-containing complex **14**, the triphenylphosphine-containing complex **19** as well as in the cyclooctadiene complexes **15** and **17**. In the cyclooctadiene complexes this is probably due to the presence of only one isomer as a result of steric reasons, whereas the carbonyl complexes most probably undergo very fast sulfur inversions.

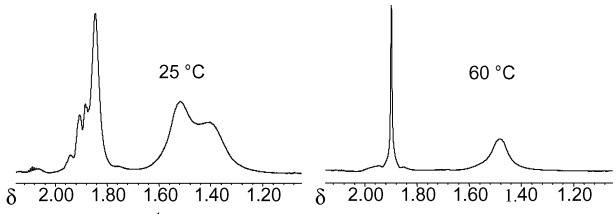


Fig. 1 ^{1}H NMR spectra of complex **1a** in toluene-d_8.

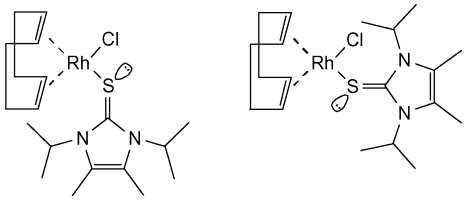


Fig. 2 Two possible isomers of **1a**.

No indication of inversion was found for the thione complexes **2** and **4**. The protons and carbons of both methyl groups of **2** were observed as two separate multiplets in the ^{1}H NMR spectrum due to restricted rotation about the N–C(S) bond. These signals were similar to the corresponding ones in free *N*,*N*-dimethylthioformamide (δ 3.22 and 3.15).

Broadening and coalescence of resonances occurs in both the proton and ^{13}C NMR spectra of the cyclooctadiene(thiazole) complexes **11a** and **11b** during temperature variation but in the dicarbonyl complex **12**, free rotation occurs around the Rh–N bond.

The most significant changes are observed for the signals of the one methyl group of the thiazole ligand upon complexation of the ligand in **11b**. The two methyl groups of the free ligand are observed at δ 2.34 and 2.33 in the ^{1}H NMR spectrum, whereas they occur at δ 2.89 and 2.33 (S–C–CH_3) in the complex.

The appearance of diastereotopic methyl signals for the isopropyl substituents in the carbene complexes **5**, **7**, **14**, **17**, **18**, **20a** and **20b** indicate hindered rotation around the Rh–$C_{carbene}$ bond.[15]

Rh–C and Rh–P coupling constants are used to determine the relative *trans* influences exhibited by ligands.[16] By comparing the Rh–P coupling constants in the ^{31}P NMR spectra of **20a** (116.3Hz), **19** (158.5Hz) as well as in *trans*-[RhCl(CO)(L^{Et})(PPh_3)] (112 Hz) (L^{Et} is 1,3-diethyl-2,3,4,5-tetrahydro-1*H*-imidazol-2-ylidene), *trans*-[RhCl(CO)(PPh_3)$_2$] (129 Hz), *trans*-[Rh(CO)(L^{Et})$_2$(PPh_3)]Cl (117 Hz) and *trans*-[Rh(CO)(L^{Et})(PPh_3)$_2$]Cl (132 Hz),[16] it is clear that the heterocyclic carbenes effect a larger *trans* influence than phosphines and phosphines larger than thiones. This order is substantiated by the data in Table 1. Although some exceptions occur (group a), it can be stated with certainty that the *trans* ligand is statically more influenced by thiones than by imines or chlorides (in that order). An unusual coupling of the phosphorous atom in **20b** to the proton in the 4-position of the thiazole ring *via* the sulfur atom, was confirmed by selective homonuclear proton decoupling as well as selective heteronuclear phosphorus decoupling (Fig. 3).

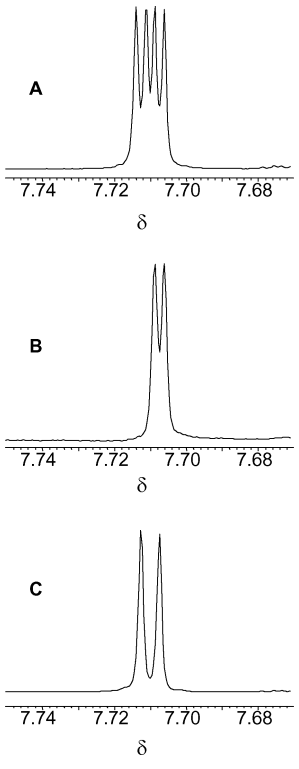


Fig. 3 The signal of the proton in the 4-position of the thiazole ring observed in the ^{1}H NMR spectrum of **20b** (A); after selective homonuclear proton proton decoupling (B), and after selective heteronuclear phosphorus decoupling (C).

Table 1 ^{31}C NMR chemical shifts and coupling constants of selected complexes

Group	Complex	Ligands	Ligand in *trans* position	Chemical shifts and coupling constants *trans* to the ligand	
				δ/ppm	J_{Rh-C}
a	**1a**	thione, Cl	cod	83.7, 74.4	11.6, 14.5
	5	carbene, Cl	cod	97.4, 68.1	7.4, 14.7
	11b	imine, Cl	cod	85.1, 76.3	8.4, 11.1
b	**6**	bis(carbene)	cod	89.3	7.3
	15	bis(thione)	cod	81.2	11.6
	[Rh(cod)(Hbbtm)][BF_4][10,a]	bis(imine)	cod	85.3	12.1
c	**17**	thione, carbene	cod	75.4, 92.7	12.1, 7.4
d	**3b**	thione, Cl	CO	182.9, 182.9	66.9, 66.9
	7	carbene, Cl	CO	187.7, 184.4	54.3, 75.4
	12	imine, Cl	CO	184.1, 180.8	70.1, 72.9
e	**10**	bis(carbene)	CO	189.9	57.6
	16	bis(thione)	CO	184.3	69.8
	[$Rh(CO)_2$(Hbbtm)][BF_4][10,a]	bis(imine)	CO	182.7	70.1
f	**18**	thione, carbene	CO	183.6, 189.2	70.6, 56.7
g	**14**	thione	carbene	175.1	54.8
	20a	PPh_3	carbene	177.2	45.4

[a] Hbbtm = bis{benzothiazol-2-yl}methane.

Table 2 Catalytic hydroformylation of 1-hexene (80 °C, 8 MPa CO–H_2 (1 : 1), reaction time of 16 h and a catalyst : substrate ratio of 1 : 1000)

Catalyst precursor	Conversion (%)	Yield of aldehydes (%)	*l* : *b* Ratio[a]	2-Ethylpentanal[b] (%)
1a	100	100	1 : 1	9
3a	100	100	1 : 1	9
5	100	100	1 : 0.9	6
6	29	21	1 : 0.6	0
7	100	100	1 : 1.1	9
8	20	16	1 : 0.6	0
9	100	100	1 : 1	10
10	64	53	1 : 0.6	0
12	100	100	1 : 1	7
15	100	100	1 : 1.3	11
17	100	100	1 : 1	8
16	100	100	1 : 1.3	11
18	100	100	1 : 1.1	11
19	100	100	1 : 0.7	5
19 + 4PPh_3[c]	100	100	1 : 0.4	0
19 + 4 thione[d]	100	100	1 : 0.7	5
20a	100	100	1 : 0.6	0
20a + 4PPh_3[c]	100	100	1 : 0.9	8
$Rh(PPh_3)_3Cl$	100	100	1 : 0.8	7
[$Rh(CO)_2$(Hbbtm)]BF_4[10]	100	100	1 : 1.2	10

[a] *l* : *b* = *n*-aldehyde: all other aldehydes. [b] Amount of all 2-ethylpentanal/amount of all aldehydes × 100. [c] 4 denotes four mole equivalents; [d] thione = 1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-thione.

From the observed vibrational frequencies of the dicarbonyl complexes **3a**, **3b** and **4** it is clear that the heterocyclic thiones donate more electron density to the metal centre than thioformamide. The carbene complex **7** exhibits ν(CO) vibration frequencies similar to those of the thione complexes **3a** and **3b**. The IR data also suggest that the two thione ligands in the cationic *cis*-bis(thione) complex, **16**, donate only slightly more electron density to the Rh centre than the carbene and thione ligands of the *cis*-carbene(thione) complex, **18**.

The mass spectra of thione complexes other than **3a** and **4**, could not be determined by electron impact probably because of the easy dissociation of the thione ligand. Electron spray ionisation mass spectrometry (in acetonitrile) was used for all the other thione complexes. In many such instances acetonitrile remained coordinated to the complexes, often after thione dissociation had occurred.

Hydroformylation results

In a series of preliminary experiments to probe and compare the use of thione, carbene and imine ligands in hydroformylation, a number of the new rhodium compounds were used as catalyst precursors for the conversion of 1-hexene into aldehydes in toluene. First experiments were carried out under a set of conditions (8 MPa, 80 °C, CO–H_2 (1 : 1)), chosen to comply with the safety features of the reactor system used. The results are summarised in Table 2. Conversion of the alkene to aldehydes is quantitative in almost all the experiments. No measurable hydrogenation occurs.

Incomplete reactions (after 16 h) are only found for three of the precursor catalysts, the *cis*-bis(carbene) compounds **6** and **10**, and the *trans*-bis(carbene) complex **8**. This is in contrast to the quantitative conversion by the chelated bis(carbene)cyclooctadiene **9**. Unreacted 1-hexene as well as 2-hexene and 3-hexene (8, 4 and 11%, respectively, for complexes **6**, **8** and **10**) are present in the three incompletely hydrofomylated reaction mixtures.

All the thione and imine complexes afford all three possible aldehydes, whereas the carbene complexes **6**, **8**, **10** (mentioned above) and **20a** yield only 1-heptanal and 2-methylhexanal, with **20a** giving a 100% conversion. With added phosphine the thione complex **19** also affords no formation of 2-ethylpentanal. A product *l* : *b* ratio of close to 1 : 1 is found for most of the complexes. The two complexes with two thione ligands (**15** and

Table 3 Catalytic hydroformylation of 1-hexene under varied conditions

Catalyst precursor	Conditions[a]	Conversion (%)	Yield of aldehydes (%)	Isomerised hexene present (%)	*l* : *b* Ratio	2-Ethylpentanal (%)
3a	*A*	0	—	—	—	—
7	*A*	0	—	—	—	—
19	*A*	100	100	0	1 : 0.5	0
20a	*A*	100	100	0	1 : 0.4	0
3a	*B*	100	100	0	1 : 1	8
7	*B*	91	74	17	1 : 0.6	0
19	*B*	100	100	0	1 : 1	8
20a	*B*	100	100	0	1 : 0.5	2
$Rh(PPh_3)_3Cl$	*B*	0	—	—	—	—
3a	*C*	100	100	0	1 : 1.6	12
7	*C*	100	62	38	1 : 0.5	2
19	*C*	100	100	0	1 : 0.5	3
20a	*C*	100	56	44	1 : 0.4	0
3a	*D*	31	22	9	1 : 0.6	0
7	*D*	3	3	0	1 : 0.5	0
19	*D*	0	—	—	—	—
20a	*D*	0	—	—	—	—
3a	*E*	100	100	0	1 : 1	9
7	*E*	71	62	9	1 : 0.6	0
19	*E*	14	14	0	1 : 0.4	0
20a	*E*	30	30	0	1 : 0.4	0

[a] *Conditions*: *A*: 80 °C, 8 MPa, 16h, catalyst : substrate 1 : 1000, $[BMIM]BF_4$ as solvent; *B*: 80 °C, 8 MPa, 16h, catalyst : substrate 1 : 1000, dodecane as solvent; *C*: 80 °C, 4 MPa, 16h, catalyst : substrate 1 : 1000, toluene as solvent; *D*: 80 °C, 8 MPa, 3h, catalyst : substrate 1 : 1000, toluene as solvent; *E*: 80 °C, 8 MPa, 6h, catalyst : substrate 1 : 1000, toluene as solvent. [b] TOF = (mol aldehydes formed/mol catalyst) h^{-1}.

16) effect the worst *l* : *b* ratios (1 : 1.3), whereas the phosphine-containing complexes **19** and **20a**, and the three complexes that give incomplete reactions, exhibit *l* : *b* ratios much better than 1 : 1. The addition of phosphine to the carbene complex **20a** (Table 2) leads to a worse *l* : *b* ratio and the formation of 2-ethylpentanal, while the opposite effect occurs with the thione complex **19**. Added free thione has no measureable effect.

Hydroformylation reactions were carried out in the ionic liquid $[BMIM]BF_4$ (BMIM = 1-butyl-3-methyl-1*H*-imidazol-3-ium) followed by extraction with ether after 16 h, (Table 3, *A*). The carbonyl(thione) complex, **3a**, and the carbene(carbonyl) complex, **7**, are inactive in the ionic liquid, while the *trans*-phosphine(thione) complex, **19**, and the *trans*-carbene(phosphine) complex, **20a**, unfortunately leach into the organic phase.

Reactions in dodecane (Table 3, *B*) indicate that the catalyst activity is solvent dependent. Wilkinson's catalyst is completely inactive in dodecane and complex **7** is less active than in toluene.

At a lower pressure of 4 MPa (Table 3, *C*) the catalytic activity of the carbene complexes, **7** and **20a**, are less than at 8 MPa, whereas the thione complexes, **3a** and **19**, still yield a 100% conversion to aldehydes. At the lower pressure, the *l* : *b* ratio for **19** improves somewhat while this ratio is lowered with **3a**. A large amount of isomerised hexene is present in the reaction mixtures of **7** and **20a**.

Variation of the total reaction time (Table 3, *D* and *E*) indicates that the active catalytic species forms only after a period of time under hydroformylation conditions. With a reaction time of 3 h only **3a** and **7** are active, whereas all four chosen complexes, as well as Wilkinson's catalyst, are active after 6 h. The *l* : *b* ratio of the aldehydes formed is higher for the incomplete hydroformylation reactions than for the completed reactions. In addition, the amount of isomerised hexene observed after a certain time differs for the four complexes used, indicating that the rate of isomerisation of the substrate again depends on the nature of the catalyst. Complex **3a** is by far the most active catalyst (TOF > 167 h^{-1} after 6 h) allthough the *l* : *b* ratio is low. Complex **20a** produces a 100% conversion to aldehydes after a reaction time of 9 h (TOF > 111 h^{-1}). The hydroformylation of styrene carried out by Tiripicchio *et al.* using a thiourea complex of rhodium, also yields a 100% conversion to aldehyde, but only after reaction times of 10–12 h.[1]

X-Ray structure determinations

The molecular structures of the three thione complexes (**1b**, **2** and **19**) are shown in Figs. 4–6 and selected bond lengths (Å) and angles (°) are given in Table 4 while the two carbene complexes (**6** and **9**) are shown in Figs. 7 and 8 with selected bond lengths and angles given in Table 5. The molecular structures of these complexes exhibit square planar configurations around the central Rh atoms. These configurations are distorted in all examples except **19** since two of the coordination points are at the centers of the double bonds in the cod ligands. In **1b**, **2** and **19** the substituent on the sulfur is *syn* to the Cl.

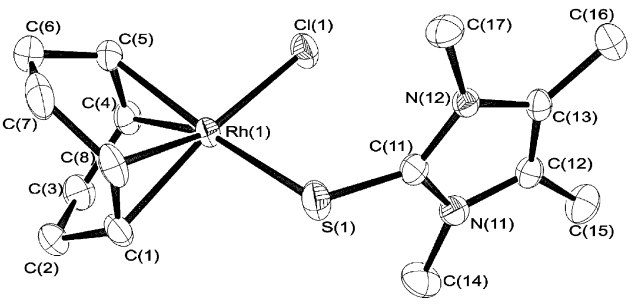


Fig. 4 The molecular structure of **1b** showing the numbering scheme. Hydrogen atoms have been omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.

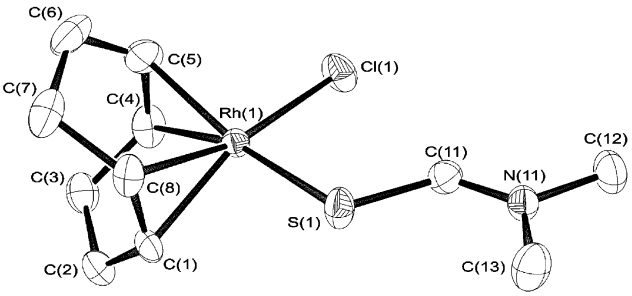


Fig. 5 The molecular structure of **2** showing the numbering scheme. Hydrogen atoms have been omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.

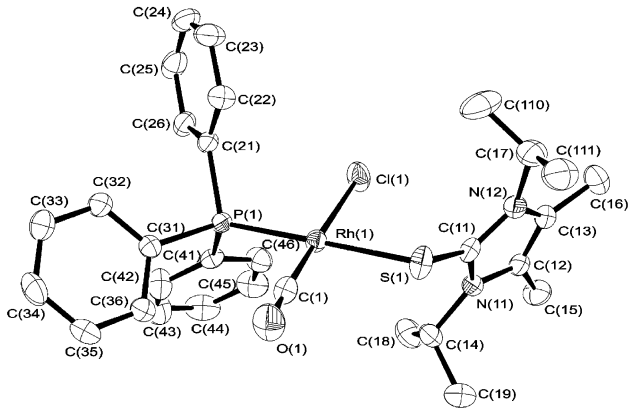


Fig. 6 The molecular structure of **19** showing the numbering scheme. Hydrogen atoms have been omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.

Table 4 Selected bond lengths (Å) and angles (°) for the thione complexes **1b**, **2** and **19**

	1b	**2**	**19**
Rh(1)–Cl(1)	2.3783(9)	2.3808(9)	2.3700(6)
Rh(1)–S(1)	2.3602(7)	2.3665(8)	2.4067(6)
S(1)–C(11)	1.725(2)	1.688(3)	1.723(2)
Cl(1)–Rh(1)–S(1)	92.95(2)	95.05(3)	90.25(2)
C(11)–S(1)–Rh(1)	108.81(7)	110.87(12)	106.85(7)

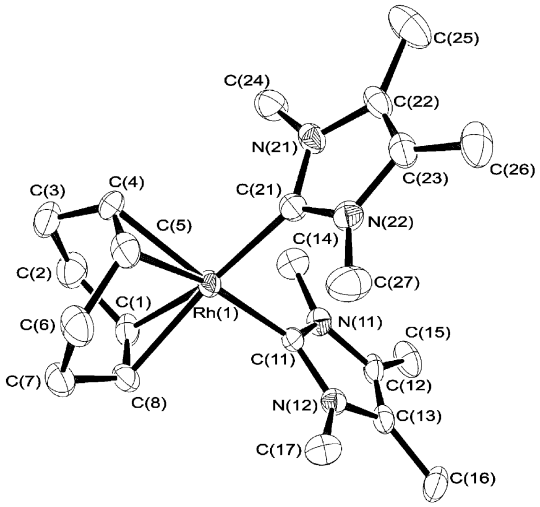


Fig. 7 The molecular structure of the cation of **6** showing the numbering scheme. Hydrogen atoms, solvent molecules and counter ion have been omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.

The relatively long Rh–S bond distance (2.4067(6) Å) in **19** can be attributed to the *trans* influence of phosphine, as discussed above. The C–S distance in **2** is somewhat shorter than in the other thiones **1b** and **19** indicating that the C–S bond is also strengthend by the high neighbouring double bond character.

The imidazole rings in molecular structures **1b**, **6**, **9** and **19** are oriented approximately perpendicular to the molecular square plane (89.24(7)°; 83.9(1) and 82.5(1)°; 82.6(2), 81.6(2), 83.7(2) and 80.3(2)°; 77.51(5)° respectively), with the greatest deviation from 90° seen for **19** due to the presence of the sulfur. A view along S(1)–Rh(1)–P(1) (thus also along one of the axes of the molecular plane) shows that the thione ligand is staggered with respect to the triphenylphosphine ligand (torsion angle C(11)–S(1)–P(1)–C(31) 166.7(1)°). The isopropyl groups also have different orientations leading to the imidazole ring being twisted asymmetrically away from the molecular plane. In **2** however, the plane through the *N*,*N*-dimethylthioformamide ligand is almost co-planar with the molecular plane.

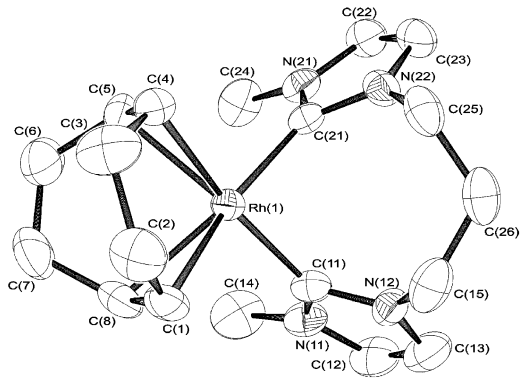


Fig. 8 The molecular structure of the cation of **9** showing the numbering scheme. Hydrogen atoms, solvent molecules, counter ions and one of the independent molecules in the asymmetric unit have been omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.

Table 5 Selected bond lengths (Å) and angles (°) for carbene complexes **6** and **9**. Values for both independent molecules in the asymmetric unit of **9** are listed

	6	**9**
Rh(1)–C(11)	2.059(4)	2.038(4)
Rh(1)–C(21)	2.051(4)	2.020(4)
Rh(2)–C(41)		2.028(4)
Rh(2)–C(51)		2.023(4)
C(11)–Rh(1)–C(21)	88.43(13)	83.77(15)
C(41)–Rh(2)–C(51)		83.79(15)

The presence of a bridge between the two imidazole rings in **9**, surprisingly, does not play as large a role in the orientation of the imidazole rings as might be expected, and an overlay of **6** and **9** indicates that there is very little difference in their structures despite the two imidazole rings being linked in **9** and not in **6** (see ESI†). The greatest difference is in the C–Rh–C bond angles, which are 88.43(13) and 83.73(15)°, respectively.

The molecular structures of **1b**, **2**, **6**, **9** and **19** show that complex **2**, followed by **1b** and **19**, exhibits the least steric hindrance around the central Rh atom.

Only complex **19** exhibits any intermolecular interactions, where phenyl face-to-edge interactions between triphenylphosphine groups on neighbouring molecules result in alternating layers of triphenylphosphine and thione ligands. A similar packing arrangement is observed for **1b**, but since there are no intermolecular interactions driving the packing, the cod and thione layers are more loosely defined. Layered structures are also observed for **6** and **9**, where the anions and solvents form layers between the complexes. In **6** the disordered water and dichloromethane solvent molecules form hydrogen bonded chains within the layer structure.

Concluding remarks

Our results demonstrate that thione and imine complexes of Rh(I) are as readily prepared and characterised as comparable carbene (or phosphine) complexes. Thione ligands may also be combined with carbene ligands in forming stable complexes. More spesifically, mono(thione), *trans*-bis(thione), *cis*-bis-(thione), *trans*-(carbene–thione), *cis*-(carbene–thione), *trans*-(phosphine–thione) and mono(imine) complex-types of rhodium(I) are now known. The thione complexes under selected conditions are more active catalyst precursors than the carbenes for hydroformylation of 1-hexene although their selectivity is low.

Questions to be answered are whether the role played by the thione (or carbene or imine) ligand(s) is kinetically or thermodynamically important and, furthermore, whether thiones might

become more useful in hydroformylation or other processes as catalyst-ligands by effective design and tailoring.

Experimental

General procedures and analytical equipment

All reactions and manipulations were carried out under a dry argon atmosphere using standard Schlenk and vacuum-line techniques. All solvents were dried and purified by conventional methods and freshly distilled under nitrogen shortly before use. Flash column chromatography was performed with "flash grade" SiO_2 (SDS 230–400 mesh). All the common reagents, including *N*,*N*-dimethylthioformamide and KO^{t}Bu, were used as obtained from commercial suppliers without further purification. The two easily accessible starting materials, $[RhCl(cod)]_2$ and $[RhCl(CO)_2]_2$, were prepared by literature procedures[17] as were 1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-thione, 1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-ylidene, 1,3,4,5-tetramethyl-2,3-dihydro-1*H*-imidazol-2-thione and 1,3,4,5-tetramethyl-2,3-dihydro-1*H*-imidazol-2-ylidene.[18] All compounds prepared are stable in air and in solution unless otherwise stated. The rhodium complexes are soluble in polar organic solvents and insoluble in non-polar organic solvents in general while some are also insoluble in diethyl ether.

Melting points were determined on an Electrothermal 9100 apparatus and are uncorrected. Mass spectra were recorded on an AMD 604 (EI, 70 eV), VG Quattro (ESI, 70 eV, solvent acetonitrile) or VGA 70-70E (FAB, 70 eV, Xe gas as bombardment gas and 3-nitrobenzyl alcohol as matrix) instrument, the IR spectra on a Perkin-Elmer 1600 Series FTIR spectrometer and NMR spectra on a Varian 300 FT or INOVA 600MHz spectrometer (^{1}H NMR at 300/600 MHz, $^{13}C\{^1H\}$ NMR at 75/150 MHz and $^{31}P\{^1H\}$ NMR at 121/243 MHz, δ reported relative to the solvent resonance or external reference 85% H_3PO_4). Elemental analyses were carried out by the Department of Chemistry, University of Cape Town, South Africa.

Chloro(η^4-1,5-cyclooctadiene)(1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-thione)rhodium(I) (1a). 1,3-Diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-thione (0.18 g, 0.84 mmol) and $[RhCl(cod)]_2$ (0.21 g, 0.42 mmol) were mixed together in THF (25 cm^3). A precipitate formed within seconds of combining the starting materials. Stirring was continued for 90 min and then the solvent was stripped *in vacuo*. Complex **1a** was purified by flash chromatography on a short column (2 cm diameter) of silica (2 cm). The excess $[RhCl(cod)]_2$ that remained after the reaction was removed from the column with CH_2Cl_2, after which yellow complex **1a** (0.34 g, 88% after drying *in vacuo*) was obtained upon washing with ether. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 5.63 (broad signal, 2H, N–CH), 4.33 (m, 2H, cod olefinic *trans* to thione ligand), 3.82 (m, 2H, cod olefinic *cis* to thione ligand), 2.35 (m, 4H, cod aliphatic equatorial), 2.20 (m, 3H, N–C–CH$_3$), 2.14 (m, 3H, N–C–CH$_3$), 1.75 (m, 4H, cod aliphatic axial), 1.53 (m, 3H, N–CH–(CH_3)$_2$), 1.40 (m, 3H, N–CH–(CH_3)$_2$); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 155.6 (s, C=S), 155.4 (s, C=S), 125.3 (s, N–*C*=*C*–N), 122.3 (s, N–*C*=*C*–N), 83.7 (d, ^1J(C,Rh) = 11.6 Hz, cod olefinic *trans* to thione ligand), 74.4 (d, ^1J(C,Rh) = 14.5 Hz, cod olefinic *cis* to thione ligand), 51.9 (s, N–CH), 49.9 (s, N–CH), 32.5 (s, cod aliphatic *trans* to thione ligand), 31.4 (s, cod aliphatic *cis* to thione ligand), 21.4 (s, N–CH–*C*H$_3$), 21.1 (s, N–CH–*C*H$_3$), 11.0 (s, N–C–*C*H$_3$), 10.8 (s, N–C–*C*H$_3$); MS (ESI): *m*/*z* 635 ([M$^+$ − Cl + thione ligand], 100), 458 ([M$^+$], 1), 423 ([M$^+$ − Cl], 100), 212 ([thione ligand$^+$], 14), 180 ([carbene ligand$^+$], 20%); mp 140–141 °C. Anal. Calc. for $C_{19}H_{32}ClN_2SRh$: C, 49.73; H, 7.03; N, 6.10. Found: C, 49.58; H, 6.81; N, 6.26%.

Chloro(η^4-1,5-cyclooctadiene)(1,3,4,5-tetramethyl-2,3-dihydro-1*H*-imidazol-2-thione)rhodium(I) (1b). Complex **1b** was prepared in the same way as **1a**, using $[RhCl(cod)]_2$ (0.18 g, 0.49 mmol) and 1,3,4,5-tetramethyl-2,3-dihydro-1*H*-imidazol-2-thione (0.11 g, 0.72 mmol). A yellow microcrystalline solid (0.36 g, 90%) was obtained. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 4.28 (m, 2H, cod olefinic *trans* to thione ligand), 3.87 (m, 2H, cod olefinic *cis* to thione ligand), 3.62 (m, 6H, N–CH$_3$), 2.35 (m, 4H, cod aliphatic equatorial), 2.09 (m, 6H, N–C–CH$_3$), 1.72 (m, 4H, cod aliphatic axial); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 156.3 (s, C=S), 124.4 (s, N–*C*=*C*–N), 83.6 (d, ^1J(C,Rh) = 11.9 Hz, cod olefinic *trans* to thione ligand), 74.8 (d, ^1J(C,Rh) = 13.8 Hz, cod olefinic *cis* to thione ligand), 33.6 (s, N–CH$_3$), 32.4 (s, cod aliphatic *trans* to thione ligand), 31.3 (s, cod aliphatic *cis* to thione ligand), 9.7 (s, N–C–*C*H$_3$); MS (ESI): *m*/*z* 523 ([M$^+$ − Cl + thione ligand], 87), 408 ([M$^+$ − Cl + CH$_3$CN], 100), 402 ([M$^+$], 3), 367 ([M$^+$ − Cl], 82), 212 ([thione ligand$^+$], 30), 180 ([carbene ligand$^+$], 16%); mp 199–200 °C. Anal. Calc. for $C_{15}H_{24}ClN_2SRh$: C, 44.73; H, 6.01; N, 6.95. Found: C, 44.62; H, 6.03; N, 7.13%.

Chloro(η^4-1,5-cyclooctadiene)(N,N-dimethylthioformamide)-rhodium(I) (2). *N*,*N*-dimethylthioformamide (0.07 cm^3, 0.75 mmol) was added to a solution of $[RhCl(cod)]_2$ (0.19 g, 0.38 mmol) in THF (30 cm^3). A yellow suspension formed within 2 min. Stirring was continued for another hour after which the solvent was removed. The microcrystalline yellow solid was washed three times with ether (50 cm^3) and dried *in vacuo* (0.25 g, 97%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 9.75 (s, 1H, S=CH), 4.61 (m, 2H, cod olefinic *trans* to thione ligand), 3.85 (m, 2H, cod olefinic *cis* to thione ligand), 3.33 (m, 3H, N–CH$_3$), 3.23 (m, 3H, N–CH$_3$), 2.38 (m, 4H, cod aliphatic equatorial), 1.83 (m, 4H, cod aliphatic axial); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 191.6 (s, C=S), 87.1 (m, cod olefinic *trans* to thione ligand), 75.5 (m, cod olefinic *cis* to thione ligand), 47.5 (s, N–CH$_3$), 40.1 (s, N–CH$_3$), 32.2 (s, cod aliphatic *trans* to thione ligand), 31.2 (s, cod aliphatic *cis* to thione ligand); MS (ESI): *m*/*z* 389 ([M$^+$ + thione ligand], 58), 341 ([M$^+$ − Cl + CH$_3$CN], 9), 335 ([M$^+$], 1), 300 ([M$^+$ − Cl], 100%); mp 209 °C (decomp.). Anal. Calc. for $C_{11}H_{19}ClNSRh$: C, 39.36; H, 5.70; N, 4.17. Found: C, 40.01; H, 5.64; N,4.24%.

Chloro(dicarbonyl)(1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-thione)rhodium(I) (3a). A solution of $[RhCl(CO)_2]_2$ (0.18 g, 0.46 mmol) in THF (10 cm^3) was treated with 1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-thione (0.20 g, 0.92 mmol). The orange solution turned light yellow. After stirring the reaction mixture for 1 h the solvent was removed *in vacuo*. The remaining solid was washed three times with pentane (10 cm^3) to yield **3a** as a pale yellow microcrystalline solid (0.15 g, 85%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 5.52 (broad signal, 2H, N–CH), 2.23 (m, 6H, N–C–CH$_3$), 1.49 (d, ^3J(H,H) = 7.2 Hz, 12H, N–CH–(CH_3)$_2$); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 184.2, 183.2 (two doublets, ^1J(C,Rh) = 67.5 Hz, CO-ligands), 151.6 (s, C=S), 126.4 (s, N–*C*=*C*–N), 52.4 (s, N–CH), 21.2 (s, N–CH–*C*H$_3$), 10.9 (s, N–C–*C*H$_3$); MS (EI): *m*/*z* 406 ([M$^+$], 3), 378 ([M$^+$ − CO], 2), 314 ([M$^+$ − 2CO − Cl], 5), 212 ([thione ligand$^+$], 87%); IR (CH_2Cl_2): ν(CO) 2069, 1994 cm^{-1}; mp 88–90 °C. Anal. Calc. for $C_{13}H_{20}ClN_2O_2SRh$: C, 38.39; H, 4.96; N, 6.89. Found: C, 38.10; H, 5.05; N, 6.98%.

Chloro(dicarbonyl)(1,3,4,5-tetramethyl-2,3-dihydro-1*H*-imidazol-2-thione)rhodium(I) (3b). The same procedure as for **3a** was followed for the preparation of **3b** from $[RhCl(CO)_2]_2$ (0.10 g, 0.24 mmol) and 1,3,4,5-tetramethyl-2,3-dihydro-1*H*-imidazol-2-thione (0.07 g, 0.47 mmol). Complex **3b** is a yellow–brown microcrystalline solid (0.15 g, 85%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 3.65 (s, 6H, N–CH$_3$), 2.23 (s, 6H, N–C–CH$_3$); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 182.9 (d, ^1J(C, Rh) = 66.9 Hz, CO-ligands), 152.3 (s, C=S), 125.6 (s, N–*C*=*C*–N), 34.0 (s, N–CH$_3$), 9.8 (s, N–C–*C*H$_3$); MS (ESI): *m*/*z* 471 ([M$^+$ − Cl + thione ligand], 100), 443 ([M$^+$ − CO–Cl + thione ligand], 30), 415 ([M$^+$ − 2CO − Cl + thione ligand],

35), 156 ([thione ligand$^+$], 43), 156 ([thione ligand$^+$ − S], 26%); IR (CH_2Cl_2): ν(CO) 2071, 1998 cm^{-1}; mp 88–89 °C (decomp.). Anal. Calc. for $C_9H_{12}ClN_2O_2SRh$: C, 30.83; H, 3.45; N, 7.99. Found: C, 31.08; H, 3.28; N, 7.83%.

Chloro(dicarbonyl)(*N*,*N*-dimethylthioformamide)rhodium(I) (4). Complex **4** was prepared in the same way as **3a** from $[RhCl(CO)_2]_2$ (0.22 g, 0.58 mmol) and *N*,*N*-dimethylthioformamide (0.10 cm^3, 1.17 mmol). The product was washed with pentane (20 cm^3) and with two portions of ether (20 cm^3). Complex **4** is a slightly hygroscopic brown–yellow microcrystalline solid (0.27 g, 83%) and cannot be stored indefinitely. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 9.66 (m, 1H, S=CH), 3.43 (m, 3H, N–CH_3), 3.35 (d, J(H,H) = 0.08 Hz, N–CH_3); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 189.1 (s, S=C), 182.5 (d, ^1J(C, Rh) = 70.4 Hz, CO-ligands), 48.4 (s, N–CH_3), 40.7 (s, N–CH_3); MS (EI): m/z 283 ([M$^+$], 1), 103 ([Rh$^+$], 14), 89 ([thione ligand$^+$], 100%); IR (CH_2Cl_2): ν(CO) 2081, 2009 cm^{-1}; mp 52 °C. Anal. Calc. for $C_5H_7ClNO_2SRh$: C, 21.18; H, 2.49; N, 4.94. Found: C, 21.33; H, 2.51; N, 4.82%.

Chloro(η^4-1,5-cyclooctadiene)(1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-ylidene)rhodium(I) (5). The reaction of 0.84 g (4.68 mmol) 1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-ylidene with 1.21 g (2.45 mmol) $[RhCl(cod)]_2$ in THF (40 cm^3) yielded the monocarbene complex **5** as a yellow solid. An excess of $[RhCl(cod)]_2$ was used to prevent the formation of a biscarbene complex. Complex **5** was purified by flash chromatography on a short column. The excess $[RhCl(cod)]_2$ that remained after the reaction was removed from the column with CH_2Cl_2. Complex **5** was isolated from the column with ether and dried *in vacuo* to yield a yellow microcrystalline solid (1.74 g, 85%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 6.10 (septet, ^3J(H,H) = 7.2 Hz, 2H, N–CH), 4.81 (m, 2H, cod olefinic *trans* to carbene ligand), 3.31 (m, 2H, cod olefinic *cis* to carbene ligand), 2.32 (m, 4H, cod aliphatic equatorial), 2.10 (s, 6H, N–C–CH_3), 1.87 (m, 4H, cod aliphatic axial), 1.55 (d, ^3J(H,H) = 7.2 Hz, 6H, N–CH–(CH_3)$_2$); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 180.7 (d, ^1J(C,Rh) = 51.5 Hz, N–C–N), 126.1 (s, N–*C*=*C*–N), 97.4 (d, ^1J(C,Rh) = 7.4 Hz, cod olefinic *trans* to carbene ligand), 68.1 (d, ^1J(C,Rh) = 14.7 Hz, cod olefinic *cis* to carbene ligand), 54.4 (s, N–CH), 33.5 (s, cod aliphatic *trans* to carbene ligand), 29.5 (s, cod aliphatic *cis* to carbene ligand), 22.6 (s, N–CH–*C*H_3), 22.3 (s, N–CH–*C*H_3), 10.7 (s, N–C–*C*H_3); MS (EI): m/z 426 ([M$^+$], 26), 282 ([M$^+$–cod–Cl], 24), 180 ([carbene ligand$^+$], 86); mp 193 °C (decomp.). Anal. Calc. for $C_{19}H_{32}ClN_2Rh$: C, 53.47; H, 7.56; N, 6.56. Found: C, 53.31; H, 7.62; N, 6.66%.

***Cis*-[(η^4-1,5-cyclooctadiene)bis(1,3,4,5-tetramethyl-2,3-dihydro-1*H*-imidazol-2-ylidene)rhodium(I)]chloride (6).** $[RhCl(cod)]_2$ (0.22 g, 0.44 mmol) dissolved in 5 cm^3 of THF was treated with a freshly prepared solution of the carbene ligand in THF (10 cm^3, 9.0 mmol). A yellow precipitate formed immediately. Stirring was continued for 2 h. The suspension was filtered and the light yellow precipitate was then washed with ether (20 cm^3). Complex **6** (0.12 g, 56%) was recrystallised from CH_2Cl_2 and pentane. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 4.19 (m, 4H, cod olefinic), 3.84 (s, 12H, N–CH_3), 2.39 (m, 4H, cod aliphatic equatorial), 2.13 (m, 4H, cod aliphatic axial), 2.00 (m, 12H, C–CH_3); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 178.7 (d, ^1J(C,Rh) = 53.2 Hz, N–C–N), 126.7 (s, N–*C*=*C*–N), 89.3 (d, ^1J(C,Rh) = 7.3 Hz, cod olefinic), 36.7 (s, N–CH_3), 31.6 (s, cod aliphatic), 9.6 (s, C–CH_3); MS (ESI): m/z 459 ([M$^+$], 100%); mp 159 °C (decomp.). Anal. Calc. for $C_{22}H_{36}ClN_4Rh$: C, 53.39; H, 7.33; N, 11.32. Found: C, 53.02; H, 7.69; N, 11.08%.

Chloro(dicarbonyl)(1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-ylidene)rhodium(I) (7). Carbon monoxide was bubbled through a yellow solution of **5** (0.27 g, 0.63 mmol) in 20 cm^3 of CH_2Cl_2. The reaction mixture turned orange within moments. After 5 min the reaction mixture was dried *in vacuo* and washed with pentane (10 cm^3). The remaining yellow powder was again dissolved in CH_2Cl_2 (20 cm^3) after which carbon monoxide was bubbled through the solution for 10 min. The mixture was again reduced to dryness and washed with pentane. Complex **7** is a light yellow microcrystalline solid (0.20 g, 93%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 5.32 (septet, ^3J(H,H) = 7.1 Hz, 2H, N–CH), 2.16 (s, 6H, N–C–CH_3), 1.51 (d, ^3J(H,H) = 7.1 Hz, 6H, N–CH–(CH_3)$_2$), 1.49 (d, ^3J(H,H) = 7.1 Hz, 6H, N–CH–(CH_3)$_2$); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 187.7 (d, ^1J(C,Rh) = 54.3 Hz, CO *trans* to the carbene ligand), 184.4 (d, ^1J(C,Rh) = 75.4 Hz, CO *cis* to the carbene ligand), 170.7 (d, ^1J(C,Rh) = 43.0 Hz, N–C–N), 127.2 (s, N–*C*=*C*–N), 54.7 (s, N–CH), 22.7 (s, N–CH–*C*H_3), 22.2 (s, N–CH–*C*H_3), 10.6 (s, N–C–*C*H_3); MS (EI): m/z 374 ([M$^+$], 6), 346 ([M$^+$ − CO], 14), 282 ([M$^+$ − 2CO − Cl], 100%); IR (CH_2Cl_2): ν(CO) 2076, 1996 cm^{-1}; mp 150 °C (decomp.). Anal. Calc. for $C_{13}H_{20}ClN_2O_2Rh$: C, 41.67; H, 5.38; N, 7.48. Found: C, 42.03; H, 5.22; N, 7.31%.

Chloro(carbonyl)-*trans*-bis(1,3,4,5-tetramethyl-2,3-dihydro-1*H*-imidazol-2-ylidene)rhodium(I) (8). Carbon monoxide was bubbled through a yellow solution of **6** (0.16 g, 0.32 mmol) in 25 cm^3 of CH_2Cl_2 for 30 min. The reaction mixture was dried *in vacuo* and washed twice with pentane (50 cm^3) and twice with ether (50 cm^3). The yellow microcrystalline solid (0.12 g, 90%) was dried *in vacuo*. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 3.91 (s, 12H, N–CH_3), 2.11 (s, 12H, C–CH_3); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 188.4 (d, ^1J(C,Rh) = 82.8 Hz, CO ligand), 182.9 (d, ^1J(C,Rh) = 40.6 Hz, N–C–N), 125.3 (s, N–*C*=*C*–N), 36.0 (s, N–CH_3), 9.7 (s, C–CH_3); MS (EI): m/z 414 ([M$^+$], 6), 386 ([M$^+$ − CO], 41), 351 ([M$^+$ − CO − Cl], 2), 124 [carbene ligand$^+$]; IR (CH_2Cl_2): ν(CO) 1934 cm^{-1}; mp 219 °C (decomp.). Anal. Calc. for $C_{15}H_{24}ClN_4ORh$: C, 43.44; H, 5.83; N, 13.51. Found: C, 43.72; H, 5.77; N, 13.36%.

[(η^4-1,5-Cyclooctadiene)-*cis*-(1,1′-propylene-3,3′-dimethyl-2,3,2′,3′-tetrahydro-1,1′*H*-diimidazol-2,2′-diylidene)rhodium(I)] hexafluorophosphate (9). $[RhCl(cod)]_2$ (0.17 g, 0.35 mmol) was added to a suspension of [1,1′-propylene-3,3′-dimethyl-1,1′*H*-diimidazole][dihexafluorophosphate][19] (0.16 g, 0.38 mmol) in 15 cm^3 THF. The addition of KO^{t}Bu (0.130 g, 1.14 mmol) yielded a dark yellow solution. This solution was stirred for 4 h before the solvent was removed *in vacuo*. The remaining yellow powder was washed with 5 portions of 30 cm^3 of ether. Complex **9** was extracted with THF (five portions, 30 cm^3) and filtered through anhydrous $MgSO_4$. Complex **9** was isolated using THF from a short column after removal of the last traces of $[RhCl(cod)]_2$ with CH_2Cl_2. Complex **9** is a yellow microcrystalline solid (0.12 g, 56%). ^{1}H NMR (300 MHz, acetone-d_6): δ 7.21 (d, ^2J(H,H) = 1.8 Hz, 2H, N–C*H*=CH), 7.11 (d, ^2J(H,H) = 1.8 Hz, 2H, N–C*H*=CH), 5.09 (dd, ^3J(H,H) = 11.3 Hz, ^2J(H,H) = 14.4 Hz, 2H, N–CH_2 equatorial), 4.63 (m, 2H, cod olefinic), 4.08 (m, 2H, cod olefinic), 4.45 (dd, ^3J(H,H) = 6.4 Hz, ^2J(H,H) = 14.4 Hz, 2H, N–CH_2 axial), 4.06 (s, 6H, N–CH_3), 2.81 (m, 2H, N–CH_2–CH_2–CH_2–N), 2.55 (m, 4H, cod aliphatic equatorial), 2.26 (m, 4H, cod aliphatic axial); ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6): δ 183.8 (d, ^1J(C,Rh) = 52.5 Hz, N–C–N), 124.6 (s, N–*C*=*C*–N), 91.2 (d, ^1J(C,Rh) = 7.9 Hz, cod olefinic), 90.1 (d, ^1J(C,Rh) = 7.9 Hz, cod olefinic), 54.2 (s, N–CH_3), 39.3 (s, N–CH_2), 34.8 (s, N–CH_2–*C*H_2–CH_2–N), 32.3 (s, cod aliphatic), 32.1 (s, cod aliphatic); MS (FAB): m/z 415 ([M$^+$], 55), 307 ([M$^+$ − cod], 32%); mp 215–217 °C. Anal. Calc. for $C_{19}H_{28}F_6N_4PRh$: C, 40.73; H, 5.04; N, 10.00. Found: C, 40.88; H, 5.33; N, 9.86%.

[Dicarbonyl(*cis*-(1,1′-propylene-3,3′-dimethyl-2,3,2′,3′-tetrahydro-1,1′*H*-diimidazol-2,2′-diylidene)rhodium(I)] hexafluorophosphate (10). Complex **10**, a light yellow microcrystalline solid (0.05 g, 88%), was prepared in the same way as **7**, using **9** (0.07 g, 0.12 mmol). ^{1}H NMR (300 MHz, acetone-d_6):

δ 7.38 (d, ^2J(H,H) = 1.9 Hz, 2H, N–C*H*=CH), 7.31 (d, ^2J(H,H) = 1.9 Hz, 2H, N–C*H*=CH), 4.78 (dd, ^3J(H,H) = 11.6 Hz, ^2J(H,H) = 14.4 Hz, 2H, N–CH_2 equatorial), 4.50 (dd, ^3J(H,H) = 5.9 Hz, ^2J(H,H) = 14.4 Hz, 2H, N–CH_2 axial), 3.98 (s, 6H, N–CH_3), 2.82 (m, 2H, N–CH_2–CH_2–CH_2–N); $^{13}C\{^1H\}$ NMR (75 MHz, acetone-d_6): δ 189.9 (d, ^1J(C,Rh) = 57.6 Hz, CO ligands), 173.9 (d, ^1J(C,Rh) = 44.6 Hz, N–C–N), 125.9 (s, N–*C*=*C*–N), 125.7 (s, N–*C*=*C*–N), 54.5 (s, N–CH_3), 39.7 (s, N–CH_2), 33.6 (s, N–CH_2–CH_2–CH_2–N); MS (FAB): *m*/*z* 363 ([M$^+$], 100), 335 ([M$^+$ − CO], 12), 307 ([M$^+$ − 2CO], 52); IR (CH_2Cl_2): ν(CO) 2085, 2028 cm^{-1}; mp 174 °C (decomp.). Anal. Calc. for $C_{13}H_{16}F_6N_4O_2PRh$: C, 30.73; H, 3.17; N, 11.03. Found: C, 30.90; H, 3.08; N, 11.17%.

Chloro(η^4-1,5-cyclooctadiene)(4-methylthiazole)rhodium(I) (11a). 4-Methylthiazole (0.09 cm^3, 0.77 mmol) was added to a solution of $[RhCl(cod)]_2$ (0.20 g, 0.40 mmol) in THF (10 cm^3). A yellow suspension was observed after 30 min. Stirring was continued for another 3 days. Complex **11a** was isolated from a short SiO_2 flash chromatography column with CH_2Cl_2 as eluant and dried *in vacuo* as a yellow microcrystalline solid (0.20 g, 72%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.85 (s, 1H, N=CH–S), 7.06 (s, 1H, S–CH_2), 4.57 (m, 2H, cod olefinic *trans* to thiazole ligand), 3.49 (m, 2H, cod olefinic *cis* to thiazole ligand), 2.93 (s, 3H, N–CH–C*H*$_3$), 2.46 (m, 4H, cod aliphatic equatorial), 1.78 (m, 4H, cod aliphatic axial); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 154.3 (s, N=C–S), 153.4 (s, N–*C*=C), 115.5 (s, S–*C*=C), 85.3 (m, cod olefinic *trans* to thiazole ligand), 76.4 (m, cod olefinic *cis* to thiazole ligand), 32.0 (m, cod aliphatic *trans* to thiazole ligand), 31.3 (m, cod aliphatic *cis* to thiazole ligand), 18.5 (m, N–C–*C*H$_3$); MS (FAB): *m*/*z* 346 ([M$^+$], 7), 310 ([M$^+$ − Cl], 10), 211 ([M$^+$ − Cl − thiazole ligand], 16%); mp 232–233 °C (decomp.). Anal. Calc. for $C_{12}H_{17}ClNSRh$: C, 41.69; H, 4.96; N, 4.05. Found: C, 41.81; H, 4.88; N, 4.16%.

Chloro(η^4-1,5-cyclooctadiene)(4,5-dimethylthiazole)rhodium(I) (11b). The procedure followed for **11a** was used to prepare **11b** from $[RhCl(cod)]_2$ (0.19 g, 0.39 mmol) and 4,5-dimethylthiazole (0.09 cm^3, 0.80 mmol). Complex **11b** is a yellow microcrystalline solid (0.19 g, 67%) with the same solubility properties as **11a**. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.63 (s, 1H, N=CH–S), 4.56 (m, 2H, cod olefinic *trans* to thiazole ligand), 3.49 (m, 2H, cod olefinic *cis* to thiazole ligand), 2.89 (s, 3H, N–CH–C*H*$_3$), 2.46 (m, 4H, cod aliphatic equatorial), 2.33 (d, *J*(H,H) = 0.8 Hz, 3H, S–CH–C*H*$_3$), 1.79 (m, 4H, cod aliphatic axial); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 150.0 (s, N=C–S), 149.7 (s, N–*C*=C), 128.5 (s, S–*C*=C), 85.1 (d, ^1J(C,Rh) = 8.4 Hz, cod olefinic *trans* to thiazole ligand), 76.3 (d, ^1J(C,Rh) = 11.1 Hz, cod olefinic *cis* to thiazole ligand), 32.2 (s, cod aliphatic *trans* to thiazole ligand), 31.1 (s, cod aliphatic *cis* to thiazole ligand), 16.9 (m, N–C–*C*H$_3$), 12.1 (m, S–C–*C*H$_3$); MS (FAB): *m*/*z* 359 ([M$^+$], 11), 323 ([M$^+$ − Cl − H], 53), 211 ([M$^+$ − Cl − thiazole ligand], 38%); mp 226 °C (decomp.). Anal. Calc. for $C_{12}H_{19}ClNSRh$: C, 43.41; H, 5.32; N, 3.89. Found: C, 43.23; H, 5.44; N, 3.80%.

Chloro(dicarbonyl)(4-methylthiazole)rhodium(I) (12). Following the same procedure as for **3a**, **12** was prepared from $[RhCl(CO)_2]_2$ (0.10 g, 0.24 mmol) and 4-methylthiazole (0.04 cm^3, 0.44 mmol) in THF (5 cm^3) as a yellow–brown microcrystalline solid (0.08 g, 64%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 9.05 (d, ^4J(H,H) = 2.5 Hz, 1H, N=CH–S), 7.21 (dq, ^4J(H,H) = 1.0 Hz, ^4J(H,H) = 2.5 Hz, 1H, S–CH_2), 2.69 (s, 3H, N–CH–C*H*$_3$); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 184.1 (d, ^1J(Rh,C) = 70.1 Hz, CO ligand *trans* to the thiazole ligand), 180.8 (d, ^1J(Rh,C) = 72.9 Hz, CO ligand *cis* to the thiazole ligand), 157.8 (s, N=C–S), 153.8 (s, N–*C*=C), 116.3 (s, S–*C*=C), 19.0 (m, N–C–*C*H$_3$); MS (FAB): *m*/*z* 293 ([M$^+$], 1), 99 ([thiazole ligand$^+$], 100%); IR (CH_2Cl_2): ν(CO) 2088, 2014 cm^{-1}; mp 57–58 °C (decomp.). Anal. Calc. for $C_6H_5ClNO_2SRh$: C, 24.55; H, 1.72; N, 4.77. Found: C, 24.49; H, 1.81; N, 4.64%.

Chloro(carbonyl)-*trans*-bis(1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-thione)rhodium(I) (13). Complex **3a** (0.16 g, 0.40 mmol) was added to a suspension of trimethylamine oxide (0.03 g, 0.40 mmol) in 30 cm^3 of THF. After stirring for 30 min, 1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-thione (0.08 g, 0.40 mmol) was added to the orange solution. The reaction mixture was stirred for two weeks and then dried *in vacuo*. The solid was washed five times with pentane (20 cm^3), dissolved in ether (100 cm^3), filtered over anhydrous $MgSO_4$ (2 cm) and dried *in vacuo* as an orange microcrystalline solid (0.10 g, 43%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 5.91 (broad signal, 4H, N–CH), 2.18 (m, 12H, N–C–CH_3), 1.49 (m, 24H, N–CH–(C*H*$_3$)$_2$); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 187.1 (d, ^1J(C,Rh) = 75.3 Hz, CO), 153.5 (m, C=S), 125.9 (m, N–*C*=*C*–N), 51.9 (m, N–CH), 21.7 (m, N–CH–*C*H$_3$), 11.1 (m, N–C–*C*H$_3$); MS (ESI): *m*/*z* 808 ([M$^+$ − Cl + thione ligand + CH_3CN], 53), 596 ([M$^+$ − Cl + CH_3CN], 10), 212 ([thione ligand$^+$], 22), 156 ([thione ligand$^+$ − S], 100%); IR (CH_2Cl_2): ν(CO) 1931 cm^{-1}; mp 131–132 °C. Anal. Calc. for $C_{23}H_{40}ClN_4OS_2Rh$: C, 46.74; H, 6.82; N, 9.48. Found: C, 46.53; H, 6.79; N, 9.55%.

Chloro(carbonyl)-*trans*-(1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-thione)(1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-ylidene)rhodium(I) (14). Complex **14** was prepared in a similar fashion than **13** using complex **7** (0.16 g, 0.44 mmol), trimethylamine oxide (0.03 g, 0.44 mmol) and 1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-thione (0.09 g, 0.43 mmol). Complex **14** was purified by flash chromatography on a short column. Excess **7** was separated from **14** by elution with ether, and **14** was then isolated from the column with THF. The yellow solution was dried *in vacuo* to yield a yellow microcrystalline solid (0.14 g, 56%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 6.21 (septet, ^3J(H,H) = 7.2 Hz, 2H, N–CH carbene ligand), 5.96 (broad signal, 2H, N–CH thione ligand), 2.21 (s, 6H, N–C–CH_3), 2.16 (s, 6H, N–C–CH_3), 1.53 (d, ^3J(H,H) = 7.2 Hz, 12H, N–CH–(C*H*$_3$)$_2$ thione ligand), 1.48 (d, ^3J(H,H) = 7.2 Hz, 6H, N–CH–(C*H*$_3$)$_2$ carbene ligand), 1.45 (d, ^3J(H,H) = 7.2 Hz, 6H, N–CH–(C*H*$_3$)$_2$ carbene ligand); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 187.5 (d, ^1J(C,Rh) = 80.8 Hz, CO), 175.1 (d, ^1J(C,Rh) = 54.8 Hz, N–C–N carbene ligand), 157.2 (s, C=S), 125.6 (s, N–*C*=*C*–N), 124.5 (s, N–*C*=*C*–N), 54.3 (s, N–CH carbene ligand), 51.5 (s, N–CH thione ligand), 22.1 (s, N–CH–*C*H$_3$ carbene ligand), 22.0 (s, N–CH–*C*H$_3$ carbene ligand), 21.2 (s, N–CH–*C*H$_3$ thione ligand), 10.9 (s, N–C–*C*H$_3$), 10.9 (s, N–C–*C*H$_3$); MS (ESI): *m*/*z* 735 ([M$^+$ − Cl + thione ligand, 4), 564 ([M$^+$ − Cl + CH_3CN], 4), 523 ([M$^+$ − Cl], 62), 495 ([M$^+$ − Cl − CO], 15), 352 ([M$^+$ − Cl − thione ligand + CH_3CN], 14), 324 ([M$^+$ − Cl − thione ligand − CO + CH_3CN], 100), 311 ([M$^+$ − Cl − thione ligand], 7), 283 ([M$^+$ − Cl − thione ligand − CO], 41%); IR (CH_2Cl_2): ν(CO) 1934 cm^{-1}; mp 172–173 °C. Anal. Calc. for $C_{23}H_{40}ClN_4OSRh$: C, 49.42; H, 7.21; N, 10.02. Found: C, 49.11; H, 7.13; N, 10.33%.

[(η^4-1,5-Cyclooctadiene)bis(1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-thione)rhodium(I) tetrafluoroborate (15). A solution of $[RhCl(cod)]_2$ (0.19 g, 0.39 mmol) and 1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-imidazole-2(3*H*)-thione (0.33 g, 1.56 mmol) in THF (5 cm^3) was added to a suspension of $AgBF_4$ (0.16 g, 0.79 mmol) in THF (5 cm^3). The precipitation of AgCl was observed almost immediately. Stirring was continued for 2 h. The reaction mixture was filtered over Celite (2 cm) and the filtrate dried *in vacuo*. The yellow microcrystalline solid (0.46 g, 83%) was washed three times with ether (20 cm^3) and dried *in vacuo*. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 5.44 (broad signal, 4H, N–CH), 3.76 (m, 4H, cod olefinic), 2.30 (m, 4H, cod aliphatic equatorial), 2.21 (s, 12H, N–C–CH_3), 1.80 (m, 4H, cod aliphatic axial), 1.49

(d, ^3J(H,H) = 7.2 Hz, 24H, N–CH–(CH_3)$_2$); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 152.2 (s, C=S), 126.8 (s, N–*C*=*C*–N), 81.2 (d, ^1J(C,Rh) = 11.6 Hz, cod olefinic), 52.1 (s, N–CH), 31.7 (s, cod aliphatic), 21.5 (s, N–CH–*C*H$_3$), 11.0 (s, N–C–*C*H$_3$); MS (ESI): *m*/*z* 635 ([M$^+$], 74), 464 ([M$^+$ − thione ligand + CH_3CN], 81), 423 ([M$^+$ − thione ligand], 100), 212 ([thione ligand$^+$], 17), 180 ([thione ligand$^+$ − S], 21%); mp 182 °C. Anal. Calc. for $C_{30}H_{52}BF_4N_4S_2Rh$: C, 49.87; H, 7.25; N, 7.75. Found: C, 49.71; H, 7.24; N, 7.85%.

[(Dicarbonyl)-*cis*-bis(1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-thione)rhodium(I)] tetrafluoroborate (16). The same procedure as used to prepare **7** was employed to prepare complex **16** from **15** (0.24 g, 0.33 mmol). Complex **16** is a slightly hygroscopic yellow–orange microcrystalline product (0.21 g, 95%) and cannot be stored indefinitely. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 5.45 (broad signal, 4H, N–CH), 2.27 (s, 12H, N–C–CH$_3$), 1.52 (d, ^3J(H,H) = 7.2 Hz, 24H, N–CH–(CH_3)$_2$); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 184.3 (d, ^1J(C,Rh) = 69.8 Hz, CO ligands), 149.9 (s, C=S), 127.5 (s, N–*C*=*C*–N), 52.6 (s, N–CH), 21.2 (s, N–CH–*C*H$_3$), 10.9 (s, N–C–*C*H$_3$); MS (ESI): *m*/*z* 767 ([M$^+$ − CO + thione ligand], 6), 596 ([M$^+$ − CO + CH_3CN], 4), 583 ([M$^+$], 100), 555 ([M$^+$ − CO], 39), 527 ([M$^+$ − 2CO], 18), 212 ([thione ligand$^+$], 63%); IR (CH_2Cl_2): *ν*(CO) 2066, 2001 cm^{-1}; mp 65 °C. Anal. Calc. for $C_{24}H_{40}BF_4N_4O_2S_2Rh$: C, 43.00; H, 6.01; N, 8.36. Found: C, 42.89; H, 6.14; N, 8.29%.

[(η^4-1,5-Cyclooctadiene)(1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-thione)(1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-ylidene)rhodium(I)] tetrafluoroborate (17). A solution of **5** (0.19 g, 0.44 mmol) and 1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-thione (0.09 g, 0.44 mmol) in 5 cm^3 of THF was added to a suspension of $AgBF_4$ (0.10 g, 0.51 mmol) in THF (5 cm^3). A white precipitate, AgCl, was observed almost immediately. Stirring was continued for 1 h. Yellow microcrystalline complex **17** (0.28 g, 91%) was isolated in the same manner as **15**. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 5.97 (septet, ^3J(H,H) = 7.2 Hz, 2H, N–CH carbene ligand), 5.32 (broad signal, 2H, N–CH thione ligand), 3.92 (m, 2H, cod olefinic *trans* to carbene ligand), 3.75 (m, 2H, cod olefinic *trans* to thione ligand), 2.33 (m, 4H, cod aliphatic equatorial), 2.24 (s, 6H, N–C–CH$_3$), 2.17 (s, 6H, N–C–CH$_3$), 1.95 (m, 4H, cod aliphatic axial), 1.61 (d, ^3J(H,H) = 7.2 Hz, 6H, N–CH–(CH_3)$_2$ carbene ligand), 1.56 (d, ^3J(H,H) = 7.2 Hz, 6H, N–CH–(CH_3)$_2$ carbene ligand), 1.51 (d, ^3J(H,H) = 7.2 Hz, 12H, N–CH–(CH_3)$_2$ thione ligand); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 176.5 (d, ^1J(C,Rh) = 50.2 Hz, N–C–N carbene ligand), 152.9 (s, C=S), 127.2 (s, N–*C*=*C*–N), 126.8 (s, N–*C*=*C*–N), 92.7 (d, ^1J(C,Rh) = 7.4 Hz, cod olefinic *trans* to carbene ligand), 75.4 (d, ^1J(C,Rh) = 12.1 Hz, cod olefinic *trans* to thione ligand), 54.8 (s, N–CH carbene ligand), 52.2 (s, N–CH thione ligand), 32.8 (s, cod aliphatic *trans* to carbene ligand), 30.0 (s, cod aliphatic *trans* to thione ligand), 22.5 (s, N–CH–*C*H$_3$ carbene ligand), 22.1 (s, N–CH–*C*H$_3$ carbene ligand), 21.6 (s, N–CH–*C*H$_3$ thione ligand), 11.1 (s, N–C–*C*H$_3$), 10.8 (s, N–C–*C*H$_3$); MS (ESI): *m*/*z* 603 ([M$^+$], 45), 432 ([M$^+$ − thione ligand + CH_3CN], 15), 391 ([M$^+$ − thione ligand], 100), 349 ([M$^+$ − thione ligand − ^{i}Pr], 93), 212 ([thione ligand$^+$], 46), 180 ([carbene ligand$^+$], 40%); mp 141 °C (decomp.). Anal. Calc. for $C_{30}H_{52}BF_4N_4SRh$: C, 52.18; H, 7.59; N, 8.11. Found: C, 52.39; H, 7.64; N, 7.98%.

[(Dicarbonyl)-*cis*-(1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-thione)(1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-ylidene)rhodium(I)] tetrafluoroborate (18). Carbon monoxide was bubbled through a solution of **17** (0.10 g, 0.15 mmol) in CH_2Cl_2, (30 cm^3) for 30 min. The reaction mixture was dried *in vacuo* to yield a green microcrystalline solid. The product was dissolved in CH_2Cl_2 (15 cm^3) and filtered over Celite, dried *in vacuo* and washed with pentane (20 cm^3). Complex **18** was purified using short column chromatography. It was isolated with THF after removal of all the other products from the column with CH_2Cl_2. Complex **18** was dried *in vacuo* and washed with pentane (10 cm^3) and ether (10 cm^3) leaving a yellow microcrystalline solid (0.07 g, 74%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 5.36 (broad signal, 2H, N–CH thione ligand), 5.30 (septet, ^3J(H,H) = 7.2 Hz, 2H, N–CH carbene ligand), 2.29 (s, 6H, N–C–CH$_3$), 2.22 (s, 6H, N–C–CH$_3$), 1.58 (d, ^3J(H,H) = 7.2 Hz, 6H, N–CH–(CH_3)$_2$ carbene ligand), 1.56 (d, ^3J(H,H) = 7.2 Hz, 6H, N–CH–(CH_3)$_2$ carbene ligand), 1.57 (d, ^3J(H,H) = 7.2 Hz, 12H, N–CH–(CH_3)$_2$ thione ligand); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 189.2 (d, ^1J(C,Rh) = 56.7 Hz, CO *trans* to carbene ligand), 183.6 (d, ^1J(C,Rh) = 70.6 Hz, CO *trans* to thione ligand), 164.9 (d, ^1J(C,Rh) = 40.9 Hz, N–C–N carbene ligand), 152.2 (s, C=S), 128.6 (s, N–*C*=*C*–N), 127.1 (s, N–*C*=*C*–N), 55.3 (s, N–CH carbene ligand), 52.4 (s, N–CH thione ligand), 22.6 (s, N–CH–*C*H$_3$ carbene ligand), 22.1 (s, N–CH–*C*H$_3$ carbene ligand), 21.1 (s, N–CH–*C*H$_3$ thione ligand), 10.9 (s, N–C–*C*H$_3$), 10.8 (s, N–C–*C*H$_3$); MS (ESI): *m*/*z* 551 ([M$^+$], 81), 523 ([M$^+$ − CO], 67), 495 ([M$^+$ − 2CO], 17), 352 ([M$^+$ − CO − thione ligand + CH_3CN], 10), 324 ([M$^+$ − 2CO − thione ligand + CH_3CN], 100), 311 ([M$^+$ − CO − thione ligand], 7), 283 ([M$^+$ − 2CO − thione ligand], 53), 212 ([thione ligand$^+$], 11), 180 ([carbene ligand$^+$], 22%); IR (CH_2Cl_2): *ν*(CO) 2071, 2009 cm^{-1}; mp 123–124 °C. Anal. Calc. for $C_{24}H_{40}BF_4N_4O_2SRh$: C, 45.15; H, 6.32; N, 8.78. Found: C, 45.27; H, 6.28; N, 8.81%.

Chloro(carbonyl)-*trans*-(triphenylphosphine)(1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-thione)rhodium(I) (19). Triphenylphosphine (0.26 g, 1.00 mmol) was added to a solution of **3a** (0.41 g, 1.00 mmol) in THF (10 cm^3). Carbon monoxide evolution was observed as the mixture was stirred at room temperature. After 30 min, the reaction mixture was dried *in vacuo* and washed four times with 20 cm^3 of ether. Complex **19** is a yellow microcrystalline solid (0.52 g, 82%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.68 (m, 6H, aromatic protons), 7.37 (m, 9H, aromatic protons), 5.87 (broad signal, 2H, N–CH), 2.19 (s, 6H, N–C–CH$_3$), 1.52 (d, ^3J(H,H) = 7.2 Hz, 6H, N–CH–(CH_3)$_2$); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 188.5 (dd, ^1J(C,Rh) = 75.5 Hz, ^2J(C,P) = 16.2 Hz, CO), 155.3 (s, C=S), 135.6 (d, ^1J(C,P) = 46.5 Hz, Ph–C *ipso*), 135.5 (d, ^2J(C,P) = 11.6 Hz, Ph–C *ortho*), 130.8 (d, ^3J(C,P) = 1.8 Hz, Ph–C *meta*), 128.8 (d, ^4J(C,P) = 9.8 Hz, Ph–C *para*), 125.4 (s, N–*C*=*C*–N), 51.9 (s, N–CH), 21.2 (s, N–CH–*C*H$_3$), 10.9 (s, N–C–*C*H$_3$); ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2): δ 32.5 (d, ^1J(C,P) = 158.5 Hz); MS (ESI): *m*/*z* 817 ([M$^+$ − Cl + thione ligand], 100), 605 ([M$^+$ − Cl], 17), 180 ([thione ligand$^+$], 7); IR (CH_2Cl_2): *ν*(CO) 1959 cm^{-1}; mp 177–180 °C. Anal. Calc. for $C_{30}H_{35}ClN_2OPSRh$: C, 56.21; H, 5.50; N, 4.37. Found: C, 56.41; H, 5.43; N, 4.44%.

Chloro(carbonyl)-*trans*-(triphenylphosphine)(1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-ylidene)rhodium(I) (20a). Complex **20a** was preapared in the same manner as **19** using triphenylphosphine (0.09 g, 0.34 mmol) and **7** (0.13 g, 0.34 mmol). Complex **20a** is a light yellow microcrystalline solid (0.20 g, 97%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.55 (m, 15H, aromatic protons), 5.84 (septet, ^3J(H,H) = 7.2 Hz, 2H, N–CH), 2.19 (s, 6H, N–C–CH$_3$), 1.57 (d, ^3J(H,H) = 7.2 Hz, 6H, N–CH–(CH_3)$_2$), 1.55 (d, ^3J(H,H) = 7.2 Hz, 6H, N–CH–(CH_3)$_2$); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 188.4 (dd, ^1J(C,Rh) = 78.7 Hz, ^2J(C,P) = 15.6 Hz, CO), 177.2 (dd, ^1J(C,Rh) = 45.4 Hz, ^2J(C,P) = 123.2 Hz, N–C–N), 135.7 (d, ^1J(C,P) = 39.1 Hz, Ph–C ipso), 135.6 (d, ^2J(C,P) = 11.9 Hz, Ph–C *ortho*), 130.7 (d, ^3J(C,P) = 1.8 Hz, Ph–C *meta*), 128.9 (d, ^4J(C,P) = 9.5 Hz, Ph–C *para*), 126.3 (d, ^4J(C,P) = 3.1 Hz, N–*C*=*C*–N), 54.4 (s, N–CH), 22.7 (s, N–CH–*C*H$_3$), 22.3 (s, N–CH–*C*H$_3$), 10.7 (s, N–C–*C*H$_3$); ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2): δ 32.8 (d, ^1J(C,P) = 116.3 Hz); MS (ESI): *m*/*z* 614 ([M$^+$], 100), 573 ([M$^+$ − Cl], 57%); IR (CH_2Cl_2): *ν*(CO)

Table 6 Crystallographic data for thione complexes **1a**, **2** and **19**, and complexes **6** and **9**

	1a	**2**	**19**		
Chemical formula	$C_{15}H_{24}N_2SRhCl$	$C_{11}H_{19}NSRhCl$	$C_{30}H_{35}N_2OPSRhCl$	$2(C_{19}H_{28}N_4Rh^+)\cdot 2(PF_6^-)\cdot CH_2Cl_2$	$C_{22}H_{36}N_4Rh^+Cl^-\cdot CH_2Cl_2\cdot 0.5H_2O$
M_r/g mol^{-1}	402.78	335.69	640.99	1205.59	588.84
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_12_12_1$	$C2/c$
a/Å	14.389(3)	7.2603(1)	9.0467(1)	15.8475(2)	26.8149(4)
b/Å	7.7020(15)	15.2871(2)	10.5875(1)	17.4778 (2)	13.2815(3)
c/Å	14.993(3)	11.6752(1)	30.4334(3)	17.5446(2)	18.8678(5)
β/°	100.79 (3)	90.018(1)	94.147(1)	90	126.851(1)
V/Å^3	1632.2(6)	1295.82(3)	2907.34(5)	4859.5(1)	5377.0(2)
Z	4	4	4	4	8
D_c/g cm^{-3}	1.639	1.721	1.464	1.648	1.455
T/K	173(2)	193(2)	193(2)	203(2)	173 (2)
μ/cm^{-1}	1.330	1.654	0.832	0.940	0.953
θ/°	1.4–27.5	1.02–29.58	1.02–28.7	1.02–27.48	1.02–27.48
Crystal size/mm	0.19 × 0.12 × 0.10	0.11 × 0.09 × 0.08	0.22 × 0.21 × 0.17	0.23 × 0.12 × 0.1	0.22 × 0.21 × 0.17
Index ranges, hkl	−18 to 18, −9 to 10, −19 to 19	−9 to 9, −19 to 19, −14 to 14	−11 to 11 −13 to 13 −38 to 38	−19 to 19 −21 to 21 −21 to 19	−31 to 33 −16 to −15 −20 to 23
No. of reflections collected	11509	9994	12308	35432	11822
No. of reflections used	3740	5983	7915	22001	5231
Parameters	197	141	340	641	311
R_1 ($F_o > 2\sigma F_o$)	0.0247	0.0267	0.0271	0.0325	0.0419
wR_2 (all data)	0.0514	0.0788	0.0670	0.0632	0.1053

1958 cm^{-1}; mp 168 °C. Anal. Calc. for $C_{30}H_{35}ClN_2OPRh$: C, 59.17; H, 5.79; N, 4.60. Found: C, 59.31; H, 5.73; N, 4.48%.

Chloro(carbonyl)-*trans*-(tri{2′*H*-thiazol}phosphine)(1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazol-2-ylidene)rhodium(I) (20b). Complex **20b** was prepared in the same way as **20a**, starting from **7** (0.08 g, 0.21 mmol) and tri{2′*H*-thiazol}phosphine (0.06 g, 0.20 mmol). Complex **20b** was isolated as a cream microcrystalline solid (0.11 g, 82%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.10 (d, ^3J(H,H) = 3.1 Hz, 3H, N–C*H*–CH), 7.71 (dd, ^3J(H,H) = 3.1 Hz, ^4J(H,H) = 1.7 Hz, 3H, S–C*H*–CH), 5.77 (septet, ^3J(H,H) = 7.2 Hz, 2H, N–CH), 2.22 (s, 6H, N–C–CH$_3$), 1.60 (d, ^3J(H,H) = 7.2 Hz, 6H, N–CH–(C*H*$_3$)$_2$), 1.57 (d, ^3J(H,H) = 7.2 Hz, 6H, N–CH–(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 186.5 (dd, ^1J(C,Rh) = 77.1 Hz, ^2J(C,P) = 15.6 Hz, CO), 173.6 (dd, ^1J(C,Rh) = 46.1 Hz, ^2J(C,P) = 137.4 Hz, N–C–N), 163.7 (d, ^1J(C,P) = 60.0 Hz, P–C), 145.9 (d, ^3J(C,P) = 17.7 Hz, P–C–N–*C*), 126.5 (d, ^3J(C,P) = 3.8 Hz, P–C–S–*C*), 126.4 (s, N–*C*=*C*–N), 54.8 (s, N–CH), 22.9 (s, N–CH–*C*H$_3$), 22.5 (s, N–CH–*C*H$_3$), 10.9 (s, N–C–*C*H$_3$); ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2): δ 15.6 (d, ^1J(C,P) = 122.5 Hz); MS (EI): m/z 602 ([M$^+$ − CO], 2), 421 ([M$^+$ − CO − carbene ligand], 17), 283 ([M$^+$ − CO − Cl − phosphine ligand], 19%); IR (CH_2Cl_2): ν(CO) 1981 cm^{-1}; mp 168–171 °C. Anal. Calc. for $C_{21}H_{26}ClN_5OPS_3Rh$: C, 40.08; H, 4.27; N, 11.41. Found: C, 40.32; H, 4.11; N, 11.24%.

General procedure for hydroformylation reactions

The catalyst precursor and a magnetic stirrer bar were placed inside a 300 cm^3 stainless steel autoclave. The apparatus was sealed, all the air was removed by vacuum and the autoclave filled with argon. The solvent and substrate were then added and the autoclave charged with a 1 : 1 hydrogen–carbon monoxide mixture. The vessel was placed in an oil bath set at a certain temperature. After the chosen reaction time the apparatus was cooled, opened and the solution removed. A sample was taken to determine the conversion and n : l ratio using gas chromatography on a non-polar column (PS 255, FS 66, 1.2 mm × 40 m × 0.32 mm). For the standard set of conditions 0.016 mmol precursor catalyst, 2 cm^3 substrate (1-hexene) and 10 cm^3 solvent (toluene) was used. When the ionic liquids were used instead of toluene, the solvent was added before sealing the autoclave. Isolation of the product was done by extraction of the organic product with ether.

Crystallography

The crystal data collection and refinement details for complexes **1b**, **2**, **6**, **9** and **19** are summarised in Table 6. X-Ray quality single crystals of the complexes were obtained by crystallisation from concentrated CH_2Cl_2 solutions layered with pentane. Data were collected on an Enraf-Nonius KappaCCD diffractometer[20] using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and scaled and reduced using DENZO-SMN[21] the structures were solved by the heavy atom method and refined anisotropically for all the non-hydrogen atoms by full-matrix least squares calculations on F^2 using SHELXL-97[22] within the X-Seed environment.[23] In **6** a difference Fourier map showed the presence of disorder in the water and CH_2Cl_2 solvent molecules, as well as the chloride anion. The positions of the disordered atoms (only one Cl of the CH_2Cl_2 was disordered over two sites, in the ratio 0.8:0.2) could be identified from the difference Fourier map and refined anisotropically. The Cl$^-$ and H_2O were both disordered over two sites with 50% occupancy each. Four of the F atoms in one of the PF_6 ions in **9** were also found to be disordered over a number of sites. Nine different disorder positions were identified from the difference Fourier map, and refined anisotropically, with the sum of the site occupancies being 4. Elongated anisotropic displacement parameters suggest that more disorder sites are possible, but these were not further modelled. ORTEP-III for Windows[24]as used to generate the various figures of the five complexes at the 50% probability level.

CCDC reference numbers 250303–250307.

See http://www.rsc.org/suppdata/dt/b4/b414040k/ for crystallographic data in CIF or other electronic format.

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