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Coordination chemistry of *o*-$Ph_2PNHC_6H_4P(S)Ph_2$ a P,S-donor ligand: synthesis of new Ru, Rh and Ir complexes

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Abstract

The late transition metal complexes [(Ar)$RuCl_2$(PS)] (Ar = C_6H_6, *o*-$MeC_6H_4(^iPr)$ and C_6Me_6), [$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})$(PS)], [RhCl(cod)(PS)] (cod = 1,5-cyclooctadiene) and [(Cp*)MCl_2(PS)] (Cp* = pentamethylcyclopentadienyl, M = Rh or Ir) (where PS = $Ph_2PNHC_6H_4P(S)Ph_2$) have been synthesised by the reaction of $Ph_2PNHC_6H_4P(S)Ph_2$ with the appropriate chloride bridged transition metal dimers. In all of these complexes the ligand is monodentate *P*-bound. Chloride abstraction from representative complexes, using Ag[ClO_4], gave the cationic compounds [(*o*-$MeC_6H_4\{^iPr\}$)RuCl(PS)][ClO_4], [Rh(cod)(PS)][ClO_4] and [(Cp*)RhCl(PS)][ClO_4] in which the ligand is k^2-*P*,*S* bound. All new compounds were characterised by a combination of $^{31}P\{^1H\}$ and ^1H NMR spectroscopy, microanalysis, FAB mass spectrometry and IR spectroscopy. The molecular structures of five complexes have been determined by single-crystal X-ray diffraction—both monodentate and chelate coordination has been characterised. The *P*-monodentate compounds all display intramolecular N–H···S hydrogen bonding.

Keywords: Phosphorus sulfur ligand; Monodentate bidentate; Transition metal complexes; Crystal structures

1. Introduction

The coordination chemistry of unsymmetrical potentially polydentate ligands containing different donor atoms is well documented. Particular attention has been paid to ligands bearing PO [1], PN [2–4] and PS [5] donor sets in part because of the potential hemilability [6] displayed by these type of ligand. The chemistry of phosphorus sulfur ligands is particularly rich due to the large number of sulfur containing functionalities that can be utilised in the preparation of these molecules examples include phosphine-thioethers [7–11], phosphine-thiolate [12–16], phosphine-thioformamide [17], phosphine-thiophene [18–20], phosphine-sulfoxide [21], the methyl [22,23] $Ph_2PCH_2P(S)Ph_2$, ethyl [23,24] $Ph_2PCH_2CH_2P(S)Ph_2$ and the propyl [25] $Ph_2P(CH_2)_3P(S)Ph_2$ backboned bis(phosphine)monosulfides as well as the bis(phosphino)amine monosulfides $Ph_2PNHP(S)Ph_2$ [26] and $Ph_2PNPhP(S)Ph_2$ [27]. We recently reported the synthesis and coordination chemistry of the unsymmetrical diphosphine ligand $Ph_2PNHC_6H_4PPh_2$ [28,29] and also the preparation of the monosulfide $Ph_2PNHC_6H_4P(S)Ph_2$ [30] and its reactivity towards platinum palladium and gold precursors. Here we report on the coordination chemistry of ruthenium, rhodium and iridium with the mixed phosphine-aminophosphinesulfide ligand $Ph_2PNHC_6H_4P(S)Ph_2$

2. Results and discussion

2.1. Monodentate coordination chemistry of $Ph_2PNHC_6H_4P(S)Ph_2$

We have previously demonstrated [30] that the direct reaction of the heterofunctional phosphine $Ph_2PNHC_6H_4P(S)Ph_2$ with dinuclear [Pd(μ-Cl)(η^3-C_3H_5)]$_2$, [{PtCl(μ-Cl)(PMe_2Ph)}$_2$] and tetranuclear systems such as [Pt(μ-Cl)(μ-$\eta^2{:}\eta^1$-C_3H_5)]$_4$ is an excellent preparative technique for the preparation of neutral

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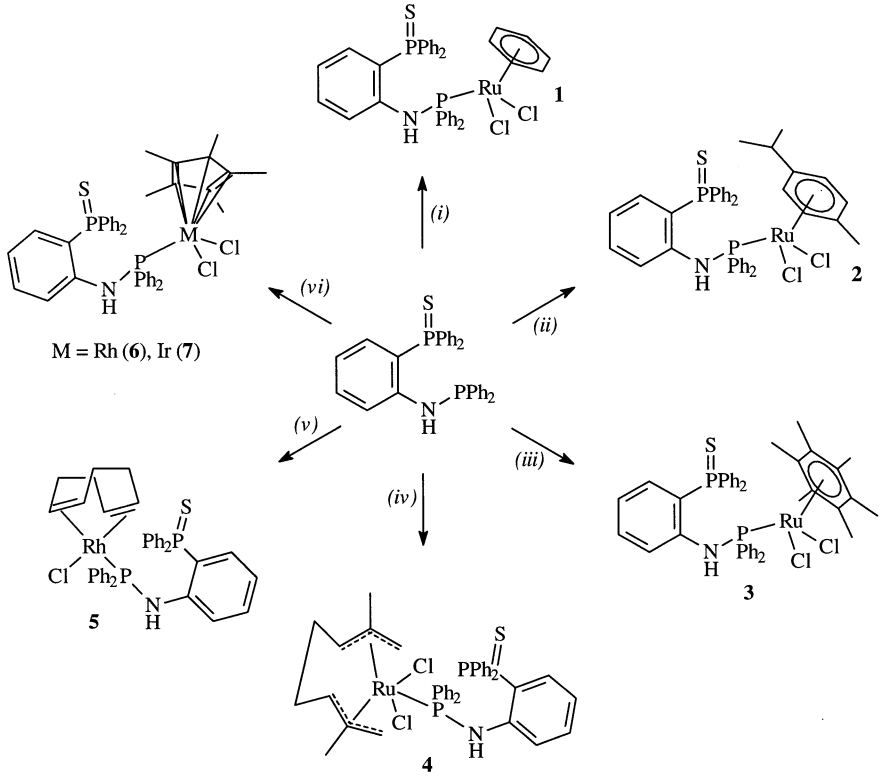
mononuclear complexes bearing a pendent or dangling $-P(S)Ph_2$ group. The same preparative method has been extended successfully to obtain neutral mononuclear complexes of Groups 8 and 9 bearing the $Ph_2PNHC_6H_4P(S)Ph_2$ ligand. Thus the reaction of the dinuclear chloride complexes $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_6)\}_2]$, $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-}MeC_6H_4^iPr)\}_2]$, $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6Me_6)\}_2]$, $[\{RuCl(\mu\text{-}Cl)(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})\}_2]$, $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ and $[\{MCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)\}_2]$ (M = Rh or Ir), with 2 equiv. of $Ph_2PNHC_6H_4P(S)Ph_2$ at room temperature leads to the formation of the mononuclear complexes $[\{(\eta^6\text{-}C_6H_6)RuCl_2\{PS\}\text{-}P\}]$ (**1**), $[\{(\eta^6\text{-}p\text{-}MeC_6H_4^iPr)RuCl_2\{PS\}\text{-}P\}]$ (**2**), $[\{(\eta^6\text{-}C_6Me_6)RhCl_2\{PS\}\text{-}P\}]$ (**3**), $[\{(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})RuCl_2\{PS\}\text{-}P\}]$ (**4**), $[\{(cod)RhCl\{PS\}\text{-}P\}]$ (**5**), $[\{(\eta^5\text{-}C_5Me_5)RhCl_2\{PS\}\text{-}P\}]$ (**6**), $[\{(\eta^5\text{-}C_5Me_5)IrCl_2\{PS\}\text{-}P\}]$ (**7**), in good to excellent yield (76–90%) (Scheme 1). All of the neutral complexes display the anticipated $^{31}P\{^1H\}$ NMR resonances (Table 1). The spectra of compounds **1**–**7** are of the AX type with no observable $^4J(^{31}P_A{-}^{31}P_X)$ coupling between the two phosphorus environments. The pendant thiophosphoryl group typically occurs at around δ_P 40 ppm which is concordant with non-coordinating behaviour and is comparable to that of the 'free' ligand (δ_P 39.6 ppm) [30]. The chemical shift of the phosphorus(III) moiety is dependent on the metal it is coordinated to and can be observed between the values δ_P 27.1 ppm for **7** and δ_P 62.0 ppm for **6**. The bound $-HNPPh_2$ group resonances of the rhodium complexes **5** and **6** appear as doublets with $^1J(^{103}Rh{-}^{31}P^{(III)})$ couplings of 164 and 163 Hz, respectively. In complexes **1**, **3**, **4**, **6**, and **7** the ligand amine proton resonance is displayed as a broad doublet at approximately δ_H 8.1 ppm with an average $^2J(^{31}P{-}^1H)$ coupling constant of 5 Hz. The

Table 1
$^{31}P\{^1H\}$ NMR spectral parameters for compounds **1**–**10** inclusive $\{(P_A) = -P(S)Ph_2$ group and $(P_X) = Ph_2PNH-$ group$\}$

Compound		Chemical shifts (ppm)	
	$\delta(P_A)$	$\delta(P_X)$	
1 [a]	$[\{(\eta^6\text{-}C_6H_6)\{RuCl_2(PS)\text{-}P\}\}]$	39.5	58.2
2 [a]	$[\{(\eta^6\text{-}p\text{-}MeC_6H_4^iPr)RuCl_2\{PS\}\text{-}P\}]$	40.9	57.7
3 [a]	$[\{(\eta^6\text{-}C_6Me_6)RhCl_2\{PS\}\text{-}P\}]$	39.5	55.6
4 [b]	$[\{(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})RuCl_2\{PS\}\text{-}P\}]$	40.6	46.3
5 [b]	$[\{(cod)RhCl\{PS\}\text{-}P\}]$	40.5	59.6(164) [c]
6 [a]	$[\{(\eta^5\text{-}C_5Me_5)RhCl_2\{PS\}\text{-}P\}]$	39.4	62.0(163) [c]
7 [a]	$[\{(\eta^5\text{-}C_5Me_5)IrCl_2\{PS\}\text{-}P\}]$	39.4	27.1
8 [b]	$[\{(\eta^6\text{-}p\text{-}MeC_6H_4^iPr)RuCl\{PS\}\text{-}P,S\}]$	49.6	76.7
9 [b,e]	$[\{(cod)Rh\{PS\}\text{-}P,S\}]$	42.7(2) [d]	67.0(158) [c]
10 [a,f]	$[\{(\eta^5\text{-}C_5Me_5)RhCl\{PS\}\text{-}P,S\}]$	47.4(3) [d]	85.9(155) [c]

[a] Spectra (101.3 MHz) measured in $CDCl_3$.
[b] Spectra (109.4 MHz) measured in CD_2Cl_2.
[c] Values in parentheses denote $^1J(^{103}Rh{-}^{31}P)$/Hz.
[d] Values in parentheses denote $^2J(^{103}Rh{-}^{31}P)$/Hz.
[e] Other $^{31}P\{^1H\}$ spectral parameters for **9** $^3J(^{31}P_A{-}^{31}P_X)$ 7 Hz.
[f] Other $^{31}P\{^1H\}$ spectral parameters for **10** $^3J(^{31}P_A{-}^{31}P_X)$ 5 Hz.



Scheme 1. (i) $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_6)\}_2]$; (ii) $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}MeC_6H_4^iPr)\}_2]$; (iii) $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6Me_6)\}_2]$; (iv) $[\{RuCl(\mu\text{-}Cl)(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})\}_2]$; (v) $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$; (vi) $[\{MCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)\}_2]$.

amine protons of complexes **2** and **5** appear as a broad singlet and a broad pseudo triplet, respectively. The remaining proton data for compounds **1**–**7** is consistent with the structural assignments (see Section 3). Further evidence in support of the monodentate phosphorus-bound coordination mode is provided by the IR spectra of the complexes which all display distinct ν(P=S) bands at 631–635 cm^{-1} which are very similar to those of the free ligand value [ν(P=S) 634 cm^{-1}] and characteristic of no interaction between the $-P(S)Ph_2$ and the metal centre. Additional data for the neutral mononuclear complexes include bands at around 634 cm^{-1} which we have assigned as ν(P–N) and also a band assigned to ν(N–H) at between 3103 and 3293 cm^{-1}. In most cases the observed frequency of the ν(N–H) band of the complexes is significantly lower than that of the 'free' ligand [ν(N–H) = 3223 cm^{-1}] [30]. We have previously observed this phenomenon in $Ph_2PNHC_6H_4P(S)Ph_2$ complexes of platinum, palladium and gold and it is suggestive of intramolecular hydrogen bonding interactions between the amine proton and the sulfur atom of the ligand which we observed in the solid state structure of $[AuClPh_2PNHC_6H_4P(S)Ph_2]$ [30]. Single crystals of compounds $[\{(\eta^6\text{-}C_6H_6)RuCl_2\{PS\}\text{-}P\}]\cdot 0.5C_4H_{10}$ (**1**), $[\{(\eta^6\text{-}p\text{-}MeC_6H_4^iPr)RuCl_2\{PS\}\text{-}P\}]\cdot 1.5CHCl_3$ (**2**), $[\{(\eta^6\text{-}C_6Me_6)RhCl_2\{PS\}\text{-}P\}]\cdot 0.5C_2H_5OH$ (**3**) and $[\{(\eta^5\text{-}C_5Me_5)IrCl_2\{PS\}\text{-}P\}]\cdot CHCl_3$ (**7**) suitable for X-ray diffraction studies were grown by the slow diffusion of petroleum ether **1**, **2** and **7** or ethanol **3** into concentrated chloroform or dichloromethane solutions of the complexes. Those of **3** (Fig. 1) and **7** (Fig. 2) are pictured here (solvent molecules omitted for the sake of clarity) along with selected bond lengths and angles (Table 3) for all four complexes. The predicted intramolecular amine proton sulfur hydrogen-bonding interaction is corroborated by the X-ray crystallographic evidence. The molecules all display very similar bond lengths, angles and geometries. All possess the expected three-legged 'piano stool' structures and the metal in all cases is coordinated to an arene or Cp* group, two chlorine atoms and the phosphorus(III) centre, P(1), of

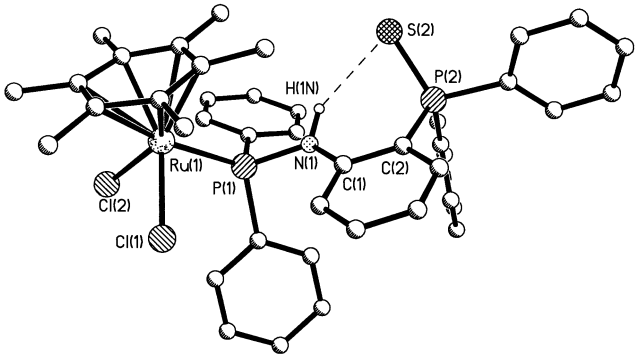


Fig. 1. Crystal structure of $[(\eta^6\text{-}C_6Me_6)RuCl_2\{Ph_2PNHC_6H_4P(S)Ph_2\text{-}P\}]$ (**3**) showing the intra-molecular amine-proton sulfur hydrogen-bonding interaction.

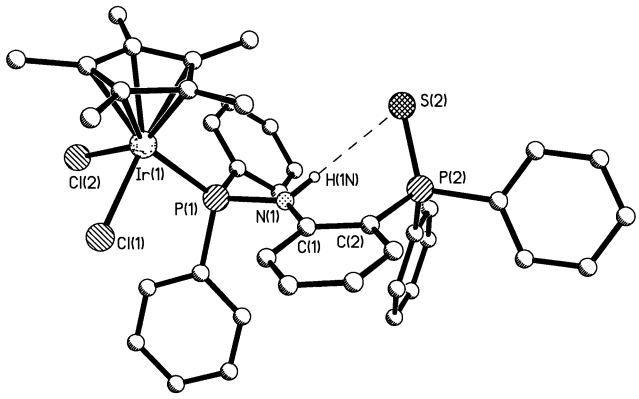


Fig. 2. Crystal structure of $[(\eta^5\text{-}C_5Me_5)IrCl_2\{Ph_2PNHC_6H_4P(S)Ph_2\text{-}P\}]$ (**7**) showing the intra-molecular amine-proton sulfur hydrogen-bonding interaction.

the $Ph_2PNHC_6H_4P(S)Ph_2$ ligand. The P(1)–N(1)–C(1)–C(2)–P(2) ligand backbone of complex **7** is essentially planar whilst the P(1) atoms of **1**, **2** and **3** lie 0.11 Å below, 0.1 Å below and 0.22 Å above their P(1)–N(1)–C(1)–C(2)–P(2) mean planes, respectively. The molecular structures of complexes **1**, **2** and **3** reveal, as suggested by the ν(NH) stretching frequencies in their IR spectra, intramolecular hydrogen-bond between the amine hydrogen H(1n) and the S(2) atom [in **1**–**3** H(1n)···S(2) approximately 2.45 Å, S(2)···N(1) approximately 3.30 Å, N(1)–H(1n)···S(2) approximately 140°] though this is somewhat longer in **7**. In addition a '*syn*' type arrangement of the P(1) and P(2) atoms is common to all four complexes (Table 2 and Figs. 1 and 2).

2.2. Bidentate coordination chemistry of $Ph_2PNHC_6H_4P(S)Ph_2$

We have previously reported that chelation of the potentially bidentate P,N 2-(Ph_2PNH)py [31] and P,P ligands $Ph_2PNHC_6H_4PPh_2$ [28] as well as $Ph_2PNHC_6H_4P(S)Ph_2$ [30] can be induced by the use of halide abstraction using $Ag[BF_4]$ or $Ag[ClO_4]$. Here we have used this preparative technique to bring about the chelation of the monodentate $Ph_2PNHC_6H_4P(S)Ph_2$ ligand in representative complexes of Groups 8 and 9 resulting in the formation of cationic species containing seven-membered P–N–C–C–P–S–M rings. Halide abstraction from the neutral complexes $[\{(\eta^6\text{-}p\text{-}MeC_6H_4^iPr)RuCl_2\{PS\}\text{-}P\}]$ (**2**), $[\{(cod)RhCl\{PS\}\text{-}P\}]$ (**5**) and $[\{(\eta^5\text{-}C_5Me_5)RhCl_2\{PS\}\text{-}P\}]$ (**6**) with 1 equiv. of $Ag[ClO_4]$ in dichloromethane gave the cationic compounds $[\{(\eta^6\text{-}p\text{-}MeC_6H_4^iPr)RuCl\{PS\}\text{-}k^2\text{-}P,S\}][ClO_4]$ (**8**), $[\{(cod)RhCl\{PS\}\text{-}k^2\text{-}P,S\}][ClO_4]$ (**9**) and $[\{(\eta^5\text{-}C_5Me_5)RhCl_2\{PS\}\text{-}k^2\text{-}P,S\}][ClO_4]$ (**10**)

.

The cationic complexes display the anticipated analytic and spectral properties. Their $^{31}P\{^1H\}$ NMR spectra

Table 3
Selected bond lengths (Å) and angles (°) for complexes **1**, **2**, **3**, **7** and **10** (where M = Ru, Rh or Ir)

Complex	**1**	**2**	**3**	**7**	**10**
Bond lengths					
P(2)–S(2)	1.968(2)	1.961(4)	1.966(2)	1.9538(18)	2.008(3)
P(2)–C(2)	1.813(6)	1.816(8)	1.816(5)	1.809(5)	1.808(12)
C(2)–C(1)	1.419(7)	1.429(10)	1.420(7)	1.410(6)	1.375(12)
C(1)–N(1)	1.418(7)	1.402(9)	1.402(7)	1.405(5)	1.441(12)
N(1)–P(1)	1.697(4)	1.688(6)	1.715(4)	1.705(4)	1.684(8)
P(1)–M(1)	2.347(2)	2.338(3)	2.3415(14)	2.3029(12)	2.309(3)
M(1)–Cl(1)	2.408(2)	2.405(3)	2.408(2)	2.3875(12)	2.401(3)
M(1)–Cl(2)	2.410(2)	2.415(3)	2.418(14)	2.422(13)	
M(1)–S(2)					2.402(3)
M(1)–C range	2.153–2.203	2.154–2.248	2.214–2.293	2.168–2.240	2.173–2.241
Bond angles					
S(2)–P(2)–C(2)	112.7(2)	113.0(4)	114.6(2)	113.9(2)	118.1(3)
P(2)–C(2)–C(1)	120.8(4)	121.1(6)	121.2(4)	121.3(3)	120.2(7)
C(2)–C(1)–N(1)	118.8(5)	120.3(8)	120.4(4)	120.2(4)	117.7(8)
C(1)–N(1)–P(1)	126.3(4)	126.3(6)	127.9(4)	129.5(3)	122.9(7)
N(1)–P(1)–M(1)	115.5(2)	114.1(3)	117.6(2)	116.89(14)	116.2(3)
P(1)–M(1)–Cl(1)	90.59(8)	90.31(9)	89.66(5)	91.00(4)	92.71(10)
P(1)–M(1)–Cl(2)	85.06(6)	89.37(8)	88.58(5)	91.72(5)	
P(1)–M(1)–S(2)					89.16(11)
H···S(2)	2.50	2.45	2.48	2.60	
N(1)···S(2)	3.30	3.24	3.33	3.42	
N(1)–H···S	139	138	142	142	

Table 2
Microanalytical data for complexes **1**–**10** inclusive

Complex		C	H	N
1	[{(η^6-C_6H_6)$RuCl_2$(**L**)}]	58.5 (58.1)	4.3 (4.2)	1.9 (1.9)
2	[{(η^6-*p*-Cy)$RuCl_2$(**L**)}]	60.0 (60.1)	4.6 (4.9)	2.2 (1.7)
3	[{(η^6-C_6Me_6)$RuCl_2$(**L**)}]	60.5 (60.9)	4.9 (5.2)	1.6 (1.7)
4	[{(η^3:η^3-$C_{10}H_{16}$)$RuCl_2$(**L**)}]	59.8 (59.9)	5.1 (5.1)	1.7 (1.7)
5	[{(cod)RhCl(**L**)}]	61.4 (61.7)	4.7 (5.0)	1.8 (1.9)
6	[{(η^5-C_5Me_5)$RhCl_2$(**L**)}]	60.0 (59.9)	5.0 (5.0)	1.5 (1.7)
7	[{(η^5-C_5Me_5)$IrCl_2$(**L**)}]	54.1 (53.9)	4.8 (4.5)	1.3 (1.6)
8	[{(η^6-*p*-Cy)RuCl(**L**)}][ClO_4]	55.4 (55.8)	4.3 (4.4)	1.4 (1.6)
9	[{(cod)Rh(**L**)}][ClO_4]	56.0 (56.8)	4.6 (4.6)	1.7 (1.7)
10	[{(η^5-C_5Me_5)$RhCl_2$(**L**)}]	55.4 (55.4)	4.1 (4.6)	1.3 (1.6)

Calculated values in parentheses. **L** = $Ph_2PNHC_6H_4P(S)Ph_2$.

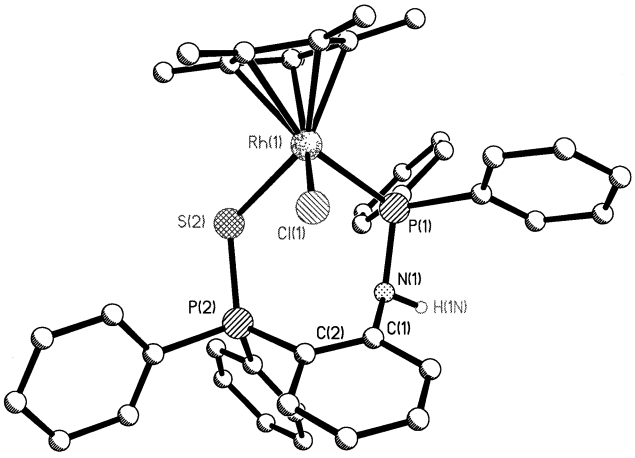
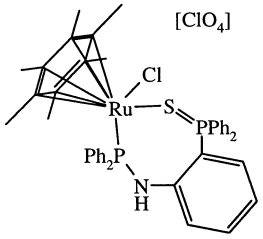


Fig. 3. Crystal structure of [(η^5-C_5Me_5)RhCl{$Ph_2PNHC_6H_4P(S)Ph_2$-k^2-*P*,*S*}][ClO_4] (**10**) ClO_4 (counterion omitted for clarity).

show that upon chelation the chemical shift of both the phosphorus centres occur at significantly higher frequencies than their neutral monodentate P bound parent compounds (Table 1). The shift to higher frequency is a



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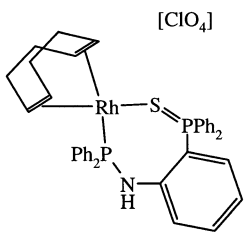

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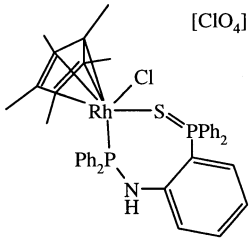

10

consequence of the chelate ring effect [32] and has been previously observed in the cationic allyl complexes $[M(\eta^3\text{-}C_3H_5)(Ph_2PNHC_6H_4P(S)Ph_2\text{-}k^2\text{-}P,S)][ClO_4]$ (where M = Pt and Pd) [30]. Also indicative of chelating ligand behaviour are the small $^2J(^{103}Rh-^{31}P^{(V)})$ 2 and 3 Hz (for **9** and **10**) and $^3J(^{31}P^{(III)}-^{31}P^{(V)})$ 7 and 5 Hz (for **9** and **10**) couplings observed in the rhodium complexes. Proton NMR assignments are consistent with the proposed structures. The X-ray structure of **10** confirms the formation of a seven-membered Rh–P–N–C–C–P–S ring (Fig. 3). Upon chelation the P–S distance is enlarged. The P–Rh–S bite angle is 89.1(1)° whilst the rest of the internal angles in the seven-membered ring are close to trigonal angles—the most distorted being the N(1)–P(1)–Rh [116.1(3)°] with the C(1)–N(1)–P(1) being significantly reduced in **10** compared to the monodentate systems. The N(1)–C(1)–C(2)–P(2) backbone of the ring is planar and the P(2)–S(2)–N(1)–P(1) portion of the ring is distorted planar with the seven-membered ring adopting a boatlike conformation. The Cl(1) atom sits approximately over the C(1)–C(2) bond [Cl(1)···C(1) 3.33, Cl(1)···C(2) 3.19 Å).

This work clearly demonstrates the utility of $Ph_2PNHC_6H_4P(S)Ph_2$ to form monodentate and chelate complexes—the seven-membered ring is readily obtained and appears to be quite stable.

3. Experimental

3.1. General

Unless otherwise stated, manipulations were performed under an oxygen-free nitrogen atmosphere using predried solvents and standard Schlenk techniques. The complexes $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_6)\}_2]$ [33], $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-}MeC_6H_4^iPr)\}_2]$ [34], $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6Me_6)\}_2]$ [34], $[\{RuCl(\mu\text{-}Cl)(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})\}_2]$ [35], $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ [36] and $[\{MCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)\}_2]$ (M = Rh or Ir) [37] were prepared according to literature procedures. $Ag[ClO_4]$ (Aldrich 99% purity) was obtained commercially and used without further purification.

IR spectra were recorded as KBr pellets in the range 4000–220 cm^{-1} on a Perkin–Elmer system 2000 Fourier transform spectrometer, ^1H NMR spectra (250 or 270 MHz) either on a Bruker AC250 FT or a JEOL GSX270 spectrometer with δ referenced to external $SiMe_4$ and $^{31}P\{^1H\}$ NMR spectra (101.3 or 109.4 MHz) either on a JEOL GSX270 or a Bruker AC250 FT spectrometer with δ referenced to external H_3PO_4. Elemental analyses were performed by the St. Andrews University Analytical Service within the School of Chemistry Service. Fast atom bombardment (FAB) mass spectra were run by the EPSRC mass spectrometry service at Swansea.

Precious metal salts were provided on loan by Johnson Matthey plc.

3.2. Preparations

3.2.1. $[(\eta^6\text{-}C_6H_6)RuCl_2\{Ph_2PNHC_6H_4P(S)Ph_2\text{-}P\}]$ (**1**)

To a thf (2.5 cm^3) suspension of $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_6)\}_2]$ (0.133 g, 0.266 mmol) was added as a solid in one portion $o\text{-}Ph_2PNHC_6H_4P(S)Ph_2$ (0.263 g, 0.532 mmol). After stirring for 40 min the red/brown solid was further precipitated by the addition of light petroleum (b.p. 40–60 °C) (15 cm^3) and collected by suction filtration. The crude material was re-dissolved in CH_2Cl_2 (5 cm^3) and filtered through a small Celite plug to remove a small amount of insoluble material. The solution was concentrated under reduced pressure to approximately 1–2 cm^3 and addition of light petroleum (b.p. 40–60 °C) (20 cm^3) gave the product as a dark red/brown solid which was collected by suction filtration, washed with Et_2O (2×10 cm^3) and dried in vacuo. Yield: 0.301 g, 76%. ^1H NMR ($CDCl_3$): δ 8.06 (br d, $^2J(^{31}P-^1H)$ 4 Hz, 1H, NH), 7.85 (m, 4H, aromatics), 7.69–7.52 (m, 12H, aromatics), 7.38–7.20 (m, 6H, aromatics), 6.85–6.76 (m, 2H, aromatics) and 5.39 (s, 6H, C_6H_6). FAB$^+$ MS: m/z 744 $[M]^+$, 709 $[M-Cl]^+$ and 673 $[M-2Cl]^{2+}$. Selected IR data (KBr): 3129m [ν(N–H)], 907s [ν(P–N)], 635s cm^{-1} [ν(P=S)].

3.2.2. $[(\eta^6\text{-}MeC_6H_4^iPr)RuCl_2\{Ph_2PNHC_6H_4P(S)Ph_2\text{-}P\}]$ (**2**)

To a thf (2 cm^3) suspension of $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}MeC_6H_4^iPr)\}_2]$ (0.141 g, 0.230 mmol) was added as a solid in one portion $o\text{-}Ph_2PNHC_6H_4P(S)Ph_2$ (0.230 g, 0.466 mmol). The mixture was stirred for 90 min and the resulting red/brown microcrystalline solid was collected by suction filtration, washed with ice cold thf (2 cm^3) and Et_2O (2×10 cm^3) and dried in vacuo. Yield: 0.309 g, 84%. ^1H NMR ($CDCl_3$): δ 8.11 (br s, 1H, NH), 7.95 (m, 4H, aromatics), 7.75–7.56 (m, 12H, aromatics), 7.41–7.21 (m, 6H, aromatics), 6.87–6.77 (m, 2H, aromatics), 5.19–5.09 (m, 4H, aromatics), 2.41 (hept, $^3J(^1H-^1H)$ 6 Hz, 1H, CH), 1.56 (s, 3H, Me) and 0.87 (d, $^3J(^1H-^1H)$ 7 Hz, 6H, Me). FAB$^+$ MS: m/z 800 $[M]^+$, 764 $[M-Cl]^+$ and 729 $[M-2Cl]^{2+}$. Selected IR data (KBr): 3179m(br) [ν(N–H)], 899s, [ν(P–N)], 633s cm^{-1}[ν(P=S)].

3.2.3. $[(\eta^6\text{-}C_6Me_6)RuCl_2\{Ph_2PNHC_6H_4P(S)Ph_2\text{-}P\}]$ (**3**)

This was prepared in the same way as complex **2** using $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6Me_6)\}_2]$ (0.145 g, 0.217 mmol) in thf (2.5 cm^3) and $o\text{-}Ph_2PNHC_6H_4P(S)Ph_2$ (0.218 g, 0.442 mmol). After stirring for approximately 18 h the dark red microcrystalline solid was collected by suction filtration washed with ice cold thf (2 cm^3) and Et_2O

(2×5 cm^3) and dried in vacuo. Yield: 0.320 g, 89%. ^{1}H NMR ($CDCl_3$): δ 8.05 (br d, $^2J(^{31}P-^1H)$ 6 Hz, 1H, NH), 7.88 (m, 4H, aromatics), 7.73–7.55 (m, 12H, aromatics), 7.27–7.02 (m, 6H, aromatics), 6.80–6.72 (m, 2H, aromatics) and 1.86 (s, 18H, Me). FAB$^+$ MS: *m*/*z* 828 $[M]^+$, 793 $[M-Cl]^+$ and 757 $[M-2Cl]^{2+}$. Selected IR data (KBr): 3103w [ν(N–H)], 910m [ν(P–N)], 634m cm^{-1} [ν(P=S)].

3.2.4. [(η^3:η^3-$C_{10}H_{16}$)$RuCl_2${$Ph_2PNHC_6H_4P(S)Ph_2$-*P*}] (**4**)

This was prepared in a similar manner to complex **2** by adding solid *o*-$Ph_2PNHC_6H_4P(S)Ph_2$ (0.254 g, 0.515 mmol) to a thf (5 cm^3) suspension of [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] (0.158 g, 0.256 mmol). The dark yellow/brown solution deposited a dark yellow solid upon further stirring and to this was added Et_2O (15 cm^3) to further precipitate the product which was collected by suction filtration, washed with Et_2O (2×5 cm^3) and dried in vacuo. Yield: 0.325 g, 79%. ^{1}H NMR (CD_2Cl_2): δ 8.11 (br d, $^2J(^{31}P-^1H)$ 5 Hz, 1H, NH), 7.90–7.31 (m, 20H, aromatics), 6.73–6.51 (m, 3H, aromatics), 6.23 (m, 1H, aromatic), 4.72 (m, 2H, CH), 3.79 (d, $J(^1H-^1H)$ 9 Hz, 4H, CH_2), 2.54 (dd, $J(^1H-^1H)$ 1 and 5 Hz, 4H, CH_2) and 2.03 (s, 6H, Me). FAB$^+$ MS: *m*/*z* 801/2 $[M]^+$, 766 $[M-Cl]^+$ and 730/1 $[M-2Cl]^{2+}$. Selected IR data (KBr): 3293w [ν(N–H)], 900m [ν(P–N)], 637m cm^{-1} [ν(P=S)].

3.2.5. [(cod)$RhCl${$Ph_2PNHC_6H_4P(S)Ph_2$-*P*}] (**5**)

To a CH_2Cl_2 (4 cm^3) solution of [{Rh(μ-Cl)(cod)}$_2$] (0.131 g, 0.266 mmol) was added dropwise a solution (4 cm^3) of *o*-$Ph_2PNHC_6H_4P(S)Ph_2$ (0.263 g, 0.533 mmol) in the same solvent. The deep yellow solution was stirred for 15 min and Et_2O (40 cm^3) was added to give **5** as a yellow powder. The product was collected by suction filtration, washed with Et_2O (2×5 cm^3) and dried in vacuo. Yield: 0.334 g, 85%. ^{1}H NMR ($CDCl_3$): δ 8.19 (br t, $^2J(^{31}P-^1H)$ 7 Hz, 1H, NH), 7.76–7.23 (m, 22H, aromatics), 6.80–6.63 (m, 2H, aromatics), 5.52 (br m, 2H, olefinic CH), 3.12 (br m, 2H, olefinic CH), 2.31 (br m, 4H, CH_2), 2.05 (br m, 2H, CH_2) and 1.91 (br, m, 2H, CH_2). FAB$^+$ MS: *m*/*z* 704/5 $[M-Cl]^+$ and 596/7 $[M-Cl-(C_8H_{12})]^+$. Selected IR data (KBr): 3130w [ν(N–H)], 902m [ν(P–N)], 633m cm^{-1} [ν(P=S)].

3.2.6. [(η^5-C_5Me_5)$RhCl_2${$Ph_2PNHC_6H_4P(S)Ph_2$-*P*}] (**6**)

This was prepared in a similar fashion to complex **2** by adding solid *o*-$Ph_2PNHC_6H_4P(S)Ph_2$ (0.180 g, 0.365 mmol) to a thf (1.5 cm^3) suspension of [{RhCl(μ-Cl)(η^5-C_5Me_5)}$_2$] (0.112 g, 0.181 mmol). The suspension was dissolved and after a few minutes stirring the product **6** precipitated. After stirring for approximately 90 min, the dark red micro-crystalline solid was collected by suction filtration and washed with ice cold thf (3 cm^3) followed by Et_2O (2×5 cm^3) and dried in vacuo. Yield: 0.262 g, 90%. ^{1}H NMR ($CDCl_3$): δ 8.20 (br d, $^2J(^{31}P-^1H)$ 5 Hz, 1H, NH), 7.94–7.12 (m, 22H, aromatics), 6.79–6.71 (m, 2H, aromatics) and 1.40 (d, 15H, $^4J(^{31}P-^1H)$ 4 Hz, C_5Me_5). FAB$^+$ MS: *m*/*z* 803 $[M]^+$, 767 $[M-Cl]^+$ and 732 $[M-2Cl]^{2+}$. Selected IR data (KBr): 3145w [ν(N–H)], 902m [ν(P–N)], 634m cm^{-1} [ν(P=S)].

3.2.7. [(η^5-C_5Me_5)$IrCl_2${$Ph_2PNHC_6H_4P(S)Ph_2$-*P*}] (**7**)

This was prepared in the same way as complex **2** using [{IrCl(μ-Cl)(η^5-C_5Me_5)}$_2$] (0.80 g, 0.100 mmol) in thf (1 cm^3) and solid *o*-$Ph_2PNHC_6H_4P(S)Ph_2$ (0.100 g, 0.203 mmol). The bright orange microcrystalline solid was collected by suction filtration washed with ice cold thf (1 cm^3) and Et_2O (2×5 cm^3) and dried in vacuo. Yield: 0.158 g, 88%. ^{1}H NMR ($CDCl_3$): δ 8.08 (br d, $^2J(^{31}P-^1H)$ 6 Hz, 1H, NH), 7.90–7.54 (m, 16H, aromatics), 7.29–7.15 (m, 6H, aromatics), 6.79–6.70 (m, 2H, aromatics) and 1.41 (d, $^4J(^{31}P-^1H)$ 3 Hz, 15H, C_5Me_5). FAB$^+$ MS: *m*/*z* 892 $[M]^+$, 856 $[M-Cl]^+$ and 821 $[M-2Cl]^{2+}$. Selected IR data (KBr): 3146w [ν(N–H)], 903w [ν(P–N)], 635m cm^{-1} [ν(P=S)].

3.2.8. [(η^6-$MeC_6H_4^iPr$)$RuCl${$Ph_2PNHC_6H_4P(S)Ph_2$-k^2-*P*,*S*}][ClO_4] (**8**)

To a CH_2Cl_2 (10 cm^3) solution of [(η^6-Me-$C_6H_4^iPr$)$RuCl_2${$Ph_2PNHC_6H_4P(S)Ph_2$-*P*}] (**2**) (0.155 g, 0.194 mmol) was added solid Ag[ClO_4] (0.040 g, 0.193 mmol). The reaction mixture was stirred in the dark for approximately 17 h and then filtered through a small plug of Celite to remove precipitated AgCl. The dark red/brown filtrate was concentrated in vacuo to approximately 4 cm^3 to which was added with stirring Et_2O (20 cm^3) to give a dark red micro-crystalline solid. The product was collected by suction filtration, washed with Et_2O (2×10 cm^3) and dried overnight in vacuo. Yield: 0.132 g, 79%. ^{1}H NMR ($CDCl_3$): δ 7.83–7.35 (m, 16H, aromatics), 7.30–7.07 (m, 6H, aromatics), 6.67 (m, 2H, aromatics), 6.32 (br t, $^2J(^{31}P-^1H)$ 8 Hz, 1H, NH), 5.31–5.30 (m, 4H, aromatics), 2.43 (hept, $^3J(^1H-^1H)$ 7 Hz, 1H, CH) and 1.55 (s, 3H, Me) and 0.87 (d, $^3J(^1H-^1H)$ 7 Hz, 6H, Me). FAB$^+$ MS: *m*/*z* 764 $[M-ClO_4]^+$ and 729 $[M-ClO_4-Cl]^+$. Selected IR data (KBr): 3186w [ν(N–H)], 1101 [ν(ClO_4)], 901m [ν(P–N)], 620m cm^{-1} [ν(P=S)].

3.2.9. [(cod)Rh{$Ph_2PNHC_6H_4P(S)Ph_2$-k^2-*P*,*S*}][ClO_4] (**9**)

This was prepared in the same way as complex **8** using [(cod)RhCl{$Ph_2PNHC_6H_4P(S)Ph_2$-*P*}] (**5**) (0.158 g, 0.213 mmol) and Ag[ClO_4] (0.045 g, 0.217 mmol) to give a dark yellow powder. Yield: 0.165 g, 96%. ^{1}H NMR ($CDCl_3$): δ 8.08 (br t, $^2J(^{31}P-^1H)$ 7 Hz, 1H, NH), 7.81–7.25 (m, 22H, aromatics), 6.79 (m, 1H, aromatics),

Table 4
Crystallographic data for the complexes

Complex	1	2 [a]	3	7	10
Empirical formula	$C_{36}H_{31}Cl_2NP_2RuS\cdot 0.5C_4H_{10}$	$C_{40}H_{39}Cl_2NP_2RuS\cdot 1.5CHCl_3$	$C_{42}H_{43}Cl_2NP_2RuS\cdot 0.5C_2H_5OH$	$C_{40}H_{40}Cl_2IrNP_2S\cdot CHCl_3$	$C_{40}H_{40}ClNP_2RhS\{ClO_4\}\cdot 0.25H_2O$
M	772.65	978.74	850.78	1011.20	866.54
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	11.5885(2)	17.2265(3)	9.3675(2)	9.1068(2)	9.3522(2)
b (Å)	18.7922(4)	10.6163(2)	14.5943(2)	15.0037(2)	13.2807(4)
c (Å)	16.7547(4)	25.300(1)	17.2491(1)	30.7196(5)	17.1141(5)
α (°)	90	90	112.920(1)	90	93.420(1)
β (°)	101.143(1)	91.909(1)	91.270(1)	92.4960(10)	96.067(1)
γ (°)	90	90	95.248(1)	90	91.304(1)
U (Å^3)	3580	4624	2159	4193	2109
Z	4	4	2	4	2
μ (mm^{-1})	0.763	0.858	0.640	3.659	0.695
Reflections measured	15 130	19 413	9572	18 072	10 676
Independent reflections	5083	6609	6074	5992	5993
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0514, 0.1045	0.0681, 0.1673	0.0532, 0.1519	0.0284, 0.0617	0.0809, 0.1916

[a] This structure was also determined as $\mathbf{2}\cdot(H_2O)_{0.5}$ to a comparable quality, with no significant differences in the molecular structure, the data has been deposited at the CCDC.

6.50 (m, 1H, aromatics), 5.41 (br m, 2H, olefinic CH), 3.34 (br m, 2H, olefinic CH), 2.13 (br m, 4H, CH_2) and 1.94 (br m, 4H, CH_2). FAB$^+$ MS: m/z 704/5 [$M-ClO_4$]$^+$ and 596/7 [$M-ClO_4-(C_8H_{12})$]$^+$. Selected IR data (KBr): 3237w [ν(N–H)], 1101vs(br) [$\nu(ClO_4)$], 907w [ν(P–N)], 623s cm^{-1} [ν(P=S)].

3.2.10. *[(η^5-C_5Me_5)RhCl{$Ph_2PNHC_6H_4P(S)Ph_2$-k^2-P,S}][ClO_4] (**10**)*

This was prepared in an identical manner to complex **8** using [(η^5-C_5Me_5)$RhCl_2${$Ph_2PNHC_6H_4P(S)Ph_2$-*P*}] (**6**) (0.140 g, 0.174 mmol) and Ag[ClO_4] (0.036 g, 0.174 mmol). The dark red microcrystalline product was collected by suction filtration, washed with Et_2O (2 × 5 cm^3) and dried in vacuo. Yield: 0.138 g, 91%. ^{1}H NMR ($CDCl_3$): δ 7.94 (m, 4H, aromatics), 7.76–7.20 (m, 17H, aromatics), 7.01 (m, 1H, aromatic), 6.61 (m, 1H, aromatic), 6.38 (m, 1H, aromatic), 5.12 (br d, 1H, $^2J(^{31}P-^1H)$ 8 Hz, NH) and 1.33 (d, $^4J(^{31}P-^1H)$ 4 Hz, 15H, C_5Me_5). FAB$^+$ MS: m/z 767 [$M-ClO_4$]$^+$ and 731 [$M-ClO_4-Cl]^{+2}$)]$^+$. Selected IR data (KBr): 3202br [ν(N–H)], 1099vs(br) [$\nu(ClO_4)$], 904w [ν(P–N)], 622s cm^{-1} [ν(P=S)].

3.3. X-ray crystallography

Details of the structure determination are given in Table 4. X-ray diffraction measurements were made with graphite-monochromated Mo Kα X-radiation (λ = 0.71073 Å) using a Siemens SMART diffractometer, intensity data were collected using 0.3 or 0.15° width ω steps accumulating area detector frames spanning a hemisphere of reciprocal space for all structures (data were integrated using the SAINT program). All data were corrected for Lp and long-term intensity fluctuations. Absorption effects were corrected on the basis of multiple equivalent reflections or by semi-empirical methods. Structures were solved by direct methods and refined by full-matrix least-squares against F^2 (SHELXTL). C–H hydrogen atoms were assigned isotropic displacement parameters and were constrained to idealised geometries. The perchlorate counterions in **10** were refined in idealised geometries. All calculations were made with SHELXTL [38].

4. Supplementary material

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 189511–189516. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-

1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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