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A novel cis-push–pull effect in cycloruthenated azobenzene thiocarbonyl-containing complexes: crystal and molecular structures of $[RuX(CS)(\eta^2\text{-}C,N\text{-}C_6H_4N{=}NPh)(PPh_3)_2](X = Cl, I)$

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Abstract

Treatment of $[RuHCl(CS)(PPh_3)_3]$ with $Hg(o\text{-}C_6H_4N{=}NC_6H_5)_2$ affords $[RuCl(CS)(\eta^2C,N\text{-}o\text{-}C_6H_4N{=}NC_6H_5)(PPh_3)_2]$ (**1**) in good yield, where the cyclometallated azobenzene ligand coordinates through an ortho-C and one azo-N to give a five-membered chelate ring. Reaction of **1** with $AgNO_3$ followed by NaBr or NaI affords the chloride-exchanged products $[RuX(CO)(\eta^2C,N\text{-}o\text{-}C_6H_4N{=}NC_6H_5)(PPh_3)_2]$ (**2**, **3**), whereas reaction of **1** with AgOC(O)Me or $NaS_2CNEt_2\cdot 2H_2O$ gives the halide mono-phosphine-substituted complexes $[Ru(CS)(LL)(\eta^2C,N\text{-o-}C_6H_4NNC_6H_5)(PPh_3)]$ (**4**, **5**). In the solid-state structures of **1** and **3** there are significant changes in the bond lengths for the cyclometallated azobenzene ligand are observed relative to free azobenzene. These are discussed, with the aid of spectroscopic and crystallographic data, in terms of a cis-push–pull effect. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Azobenzene; Crystal structure; Ruthenium; Thiocarbonyl

1. Introduction

Roper and Wright first reported the transfer of organic groups to ruthenium or osmium using organomercurials in 1977 [1], and since then Roper and coworkers have developed extensive chemistry based upon this methodology [2]. For example, compounds that contain chelating C,N systems such as $[MCl(CO)(\eta^2\text{-}C,N\text{-}2\text{-}C_6H_4\text{-}Py)(PPh_3)_2]$ (M = Ru, Os) and $[OsCl(CO)(\eta^2\text{-}C,N\text{-}Qn)(PPh_3)_2]$ (Qn = 8-quinolyl) have been reported and their chemistry investigated [2e–h]. Transition metal complexes that contain an azobenzene ligand or derivatives of it are well known, and there are several coordination modes documented [3]. One particularly noteworthy structural characteristic of complexes containing a cyclometallated azobenzene ligand is the perturbation of the C–N and N=N bond lengths around the azo-group as well as the C–C bonds in the metallated phenyl ring [4]. We recently reported the preparation of some azo-containing phosphines and explored the well-known [5] azo/hydrazone tautomeric process and this alerted us to the structural changes observed on going from the azo to hydrazone tautomeric form [6]. In a recent paper we drew attention to the similarity in the structural changes that occur on cyclometallation of azobenzene and the tautomeric process and suggested the presence of a cis-push–pull effect [7]. Caulton and coworkers have published a series of papers concerning π-stabilised unsaturation in transition metal complexes [8], and during the course of this work they have shown that the π-acid CO is able to stabilise π-donation in 18 valence electron species, because of its special acceptor capabilities, through a push–pull effect [8b]. In this paper we show that the thiocarbonyl ligand is equally capable of stabilising π-donation in 18 valence electron organometallics, in this instance through a novel cis-push–pull process.

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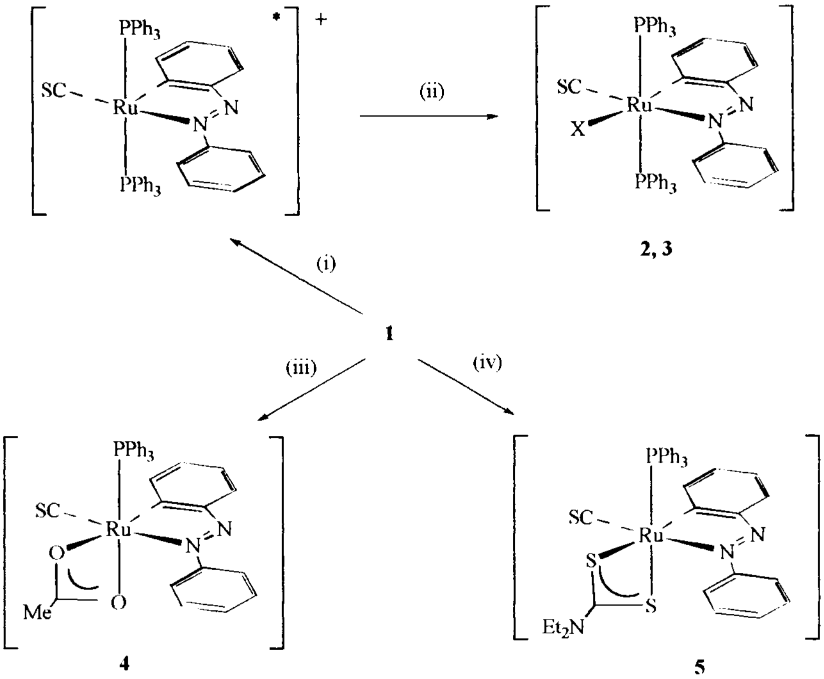
2. Results and discussion

Treatment of $[RuHCl(CS)(PPh_3)_3]$ with $Hg(o\text{-}C_6H_4N{=}NC_6H_5)_2$ in refluxing toluene afforded $[RuCl(CS)(\eta^2\text{-}C,N\text{-}o\text{-}C_6H_4N{=}NC_6H_5)(PPh_3)_2]$ (**1**) in good yield according to Eq. (1).

$$[RuHCl(CS)(PPh_3)_3] + Hg(o\text{-}C_6H_4N{=}NPh)_2 \longrightarrow [RuCl(CS)(\eta^2\text{-}C,N\text{-}C_6H_4N{=}NPh)(PPh_3)_2] + Hg + PPh_3 + PhN{=}NPh \qquad (1)$$

After removal of elemental mercury by filtration and removal of the solvent under reduced pressure, extraction of the crude reaction mixture with hot hexane removed the azobenzene and PPh_3; subsequent recrystallisation of the remaining the material from CH_2Cl_2–Et_2OH afforded **1**. The reactivity of **1** has been investigated and is summarised in Scheme 1.

All of the new compounds **1**–**5** have been characterised by elemental analysis (C, H, N, S), infrared spec-



Scheme 1. (i) $AgNO_3$, CH_2Cl_2, EtOH, H_2O; (ii) NaX (X = Br, I); (iii) AgOC(O)Me, CH_2Cl_2; (iv) $NaS_2CNEt_2{\cdot}2H_2O$, CH_2Cl_2, EtOH, H_2O.

Table 1
Physical[a] and analytical data[b] and infrared data[c] for complexes **1**–**5**

Complex	Colour	Yield (%)	M.p. (°C)	Microanalytical data (%)				ν(CS) (cm^{-1})	Others (cm^{-1})
				C	H	N	S		
1	Purple	85	211	66.1 (66.4)	4.0 (4.4)	3.0 (3.2)	3.2 (3.6)	1267s	
2·$0.5CH_2Cl_2$	Purple	87	202	61.0 (61.1)	4.2 (4.2)	2.9 (2.9)	3.0 (3.3)	1268s	
3	Purple	92	195	59.8 (60.2)	4.0 (4.0)	2.9 (2.9)	3.0 (3.3)	1276s	
4	Red	72	190	61.0 (61.2)	4.1 (4.2)	4.5 (4.3)	5.3 (4.9)	1271s	1524m,1389m
5	Red	66	195	58.4 (58.7)	4.5 (4.7)	5.3 (5.7)	12.5 (13.0)	1275s	1485msh

[a] All compounds soften before melting.

[b] Calculated values in parentheses.

[c] Spectra recorded as KBr discs; s, strong, m, medium, sh, shoulder, br, broad.

Table 2
$^{31}P\{^1H\}$-NMR[a] and proton[b] data for complexes **1**–**5**

Complex	^{31}P (δ, ppm)	^1H (δ, ppm)
1	25.8	7.9 (bd, J_{HH} 8.0, 1H, aryl H); 7.5–6.8 (bm 37H, aryl H); 6.2 (bt, 1H, J_{HH} 7.0, aryl H)
2	24.7	7.9 (bd, J_{HH} 8.0, 2.0, 1H, aryl H); 7.5–7.0 (bm 37H, aryl H); 6.2 (bt, 1H, J_{HH} 8.0, aryl H); 5.29 (s, 0.5H, CH_2Cl_2)
3	23.0	7.9 (bd, J_{HH} 8.0, 1H, aryl H); 7.5–6.5 (bm 37H, arylH); 6.7 (m, 1H, arylH); 6.2 (bt, 1H, J_{HH} 8.0, arylH)
4	50.2	8.2 (bd, J_{HH} 8.0, 1H, aryl H); 7.7–6.8 (bm, 23H, aryl H); 0.9 (s, 3H, CH_3)
5	40.5	8.2 (dd, J_{HH} 8.0, 2.0, 1H, aryl H); 7.9 (bd, J_{HH} 8.0, 1H, aryl H); 7.5–6.8 (bm 22H, aryl H); 3.4 (m, 4H, CH_2); 1.0 (t, J_{HH} 7.1, 3H, CH_3); 0.8 (t, J_{HH} 7.1, 3H, CH_3)

[a] Spectra recorded in $CDCl_3$ (298 K) and referenced to 85% H_3PO_4.

[b] Spectra recorded in $CDCl_3$ (298 K) and referenced to $CHCl_3$, J in hertz; s, singlet, d, doublet, t, triplet, m, multiplet, b, broad.

troscopy, ^1H-, $^{31}P\{^1H\}$-, and $^{13}C\{^1H\}$-NMR spectroscopy (Tables 1–3). Compounds **1** and **3** have been further characterised by single crystal X-ray diffraction studies; see Table 4 for data collection and processing parameters and Table 5 for selected bond lengths. ORTEP representations of the molecular structures of **1** and **3**, are presented as Figs. 1 and 2, showing the atomic numbering scheme. Both structures are best described as being slightly distorted octahedral with the two PPh_3 ligands mutually trans and axial, and with the ortho-metallated azobenzene, thiocarbonyl and halide in the equatorial plane. The greatest deviation from the idealised geometry is in the C(3)–Ru–N(1) angle, 75.7(2)° **1**, 75.8(4)° **3**. This is commonly observed in complexes containing ortho-metallated azobenzene ligands, and is a result of the tight bite angle of the ligand [4], and this has the obvious knock-on effect of opening up of other angles in the equatorial plane from 90°. The most significant structural features of **1** and **3** relate to: (i) the Ru to azobenzene bond lengths; (ii) the bond lengths within the ortho-metallated azobenzene ligand; and (iii) the CS bond lengths: a detailed discussion that relates these data to the ν(CS) follows later.

The infrared spectra of **1**–**5** (Table 1) all display a strong ν(CS) around 1270 cm^{-1} and complex fingerprint regions. Compound **4** displays $\nu(CO_2)$ at 1524 and 1389 cm^{-1}, which implies a chelating coordination mode for the acetate ligand [9]. In **5** the ν(CN) for the coordinated diethyldithiocarbamate ligand is tentatively assigned to a band observed at 1485 cm^{-1}.

Caulton and coworkers reported [8b] in an infrared study to assess the degree of π-stabilisation in unsaturated complexes of the type $[RuHX(CO)(P^tBu_2Me)_2]$ that the ν(CO) was dependent upon the π-donor power of the ligand X. They also showed that this was also true in the coordinatively saturated pyridine containing adducts $[RuHX(CO)(py)(P^tBu_2Me)_2]$, although to a slightly lesser extent, and that this formally forbidden π-donation was possible because a trans-push–pull effect facilitated by the π-accepting properties of the CO ligand. Careful inspection of the ν(CS) stretching frequencies in **1**–**3**, Table 1, shows a similar pattern: the stronger π-donating halide (Cl) affects the lowest ν(CS), suggesting that the ν(CS) is dependent upon the π-donating power of the halide even though they have a cis rather than trans disposition. The relative values for the ν(CS) of **4** and **5**, when taken as a pair, are also consistent with this interpretation.

The $^{31}P\{^1H\}$-NMR spectra of **1**–**5** (Table 1) all show a singlet resonances, which for **1**–**3** suggest mutually trans-PPh_3 ligands. Slight shifts in resonance were observed on exchange of chloride by bromide or iodide. More significant shifts (20 ppm) occurred for **4** and **5**, where substitution of the chloride ligand and displacement of one of the PPh_3 ligands has taken place.

The ^1H-NMR spectra of **1**–**5** are consistent with their formulation (Scheme 1) and are also almost identical to those obtained for the analogous compounds $[RuCl(CO)(\eta^2\text{-}C,N\text{-}o\text{-}C_6H_4NNPh)(PPh_3)_2]$ [7]. The aromatic region is complex, with overlapping multiplets leaving individual proton assignment difficult; however, the doublet of doublets observed at ca 7.9 ppm can be assigned to the proton ortho to the ruthenated carbon of the azobenzene and integrates as expected to the remaining protons. The orientation of the chelating azobenzene, two phosphine and halide ligands is the same as has been observed in the analogous ruthenium complex $[RuCl(CO)(\eta^2\text{-}C,N\text{-}o\text{-}C_6H_4CNPh)(PPh_3)_2]$, which contains an orthometallated imine rather than azobenzene [10]. The data for **4** are also consistent (integration of $OC(O)CH_3$ to aryl-H) with the infrared data and suggest the acetate ligand is coordinated in a bidentate fashion as opposed to being bound monodentate in the related CO-containing complex $[Ru\{\eta^1\text{-}OC(O)Me\}(CO)(\eta^2\text{-}C,N\text{-}o\text{-}C_6H_4N{=}NPh)(PPh_3)_2]$ [7]. For compound **5** the integration suggests that the dithiocarbamate ligand is also coordinated in a bidentate fashion. The methyl protons of the ethyl groups appear as two ‘triplets’ and the methylene protons as a complex second-order multiplet, and this is consistent with its structure (Scheme 1) since there is no plane of symmetry through the CN bond. It is also directly comparable to the structurally characterised osmium

Table 3
^{13}C {^{1}H}-NMR data[a] for **1**–**5**

Compound	CS	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	Others
1	306.7 t(15.6)	184.6 t(9.6)	138.0	132.0	126.8	124.8	160.3	153.4	121.8	127.8	130.8	132.3 t(20.6)	134.3 t(5.0)	127.4 t(5.0)	129.3	
2	306.9 t(16.1)	184.8 t(9.0)	138.1	132.0	126.6	125.0	160.6	153.3	121.9	127.8	131.1	132.5 t(22.1)	134.4 t(5.0)	127.4 t(5.0)	129.3	
3	307.6 t(16.5)	185.2 t(8.6)	138.2	132.0	126.5	125.4	161.2	153.2	122.1	127.9	131.4	132.7 t(22.1)	134.7 t(5.0)	127.3 t(5.0)	129.3	
4	292.2 d(19.1)	168.5 d(8.0)	139.7	132.8	128.8	124.5	164.5	151.4	123.3	129.8	130.6	131.1 d(45.2)	134.6 d(13.1)	128.3 d(13.1)	130.4	185.2 CO 22.5 CH_3
5	303.2 d(18.1)	187.7 d(9.0)	139.4	132.8	126.8	124.5	162.3	151.6	122.4	127.8	129.0	134.0[b]	133.6 d(10.0)	127.9 d(10.0)	129.8	209.7 CS 44.3, 44.0 CH_2 12.2,12.0 CH_3

[a] Spectra recorded in $CDCl_3$ at 298 K, J_{CP} in hertz, t, triplet, d, doublet.

[b] Doublet expected but not observed, presumably because of signal overlap.

Table 4
Data collection and processing parameters

Compound	**1**	**3**
Formula	$C_{49}H_{39}ClN_2P_2RuS$	$C_{49}H_{39}IN_2P_2RuS$
Molecular weight	886.34	977.79
Temperature (K)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P21/c$	$P21/c$
a (Å)	10.140(2)	10.339(2)
b (Å)	17.525(4)	17.415(3)
c (Å)	22.906(3)	22.771(2)
β (°)	97.22(3)	96.99(2)
V (Å^3)	4038.3(13)	4069.5(11)
Z	4	4
D_{calc} (Mg m^{-3})	1.458	1.596
μ (mm^{-1})	5.274	1.312
F(000)	1816	1960
θ (min–max) (°)	3.18–65.13	1.80–24.98
Refections collected	7265	14102
Independent reflections	6840	7061
R_{int}	0.0683	0.0871
Crystal size	0.25 × 0.25 × 0.07	0.25 × 0.25 × 0.20
A (min, max)	0.7091, 0.3523	0.7793, 0.7350
Goodness of fit on F^2	1.117	1.019
R (observed data)	0.0612	0.693
wR_2 (all data)	0.1829	0.1960
Difference map (min, max) (e$^-$ Å^{-3})	1.923, −1.059	0.995, −1.290

complex [Os(CO)(η^2-*C*,*N*-C_6H_4-2-C_5H_4N)(S_2CNMe_2)(PPh_3)] reported by Roper and coworkers that has this structure [2g].

The $^{13}C\{^1H\}$-NMR spectra for **1**–**5** were very helpful in confirming their structures; see Fig. 3 for numbering scheme. For compounds **1**–**3** (Table 3) the mutually trans-PPh_3 ligands couple to the CS, and ruthenated carbon of the ortho-metallated azobenzene ligand and split the signals into triplets. Further, the resonances for the PPh_3 ligand carbon atoms appear as virtual triplets. For compounds **4** and **5**, which contain one PPh_3 ligand, the CS, ortho-ruthenated and PPh_3 signals are doublets. The molecular asymmetry also causes two sets of carbon signals for the ethyl groups in **5**. The ortho-metallated carbon resonances 168.5–187.7 ppm are at much lower field than might be expected when compared with the metallated carbon resonance for [RuCl(Ph)(CO)(P^tBu_2Me)$_2$] (155.7 ppm) [8c] but are comparable with the values for the CO-containing analogues [7]. All of the other resonances were assigned using substituent effects and previous assignments in related systems [11].

Confirmation of the solid-state structures of **1** and **3** were obtained from single crystal X-ray diffraction studies and the most significant structural features relate to the ortho-metallated azobenzene ring and the Ru(CS) moiety. The bond lengths in the ortho-ruthenated azobenzene are significantly different than those observed for uncoordinated azobenzene **I** [12] (Table 5). The Ru–C(3) bond lengths at 2.029(7) Å **1** and 2.045(9) Å **3** are at the short end of the observed range (2.01–2.20 Å) for complexes containing an Ru–C σ-aryl bond and are both longer than that observed for [RuCl(CO)(η^2-*C*,*N*-*o*-C_6H_4NNPh)(PPh_3)$_2$] **II** of 2.021(7) Å [7]. The Ru–N(1) bond lengths at 2.232(6) Å **1** and 2.242(8) Å **2** are longer than in **II**, 2.184(6) Å. In common with other structures containing an ortho-metallated azobenzene, the phenyl ring on the bonded nitrogen twists away from the plane defined by Ru, C(3), C(2), N(1), N(2) by approximately 40°. In a related paper [7] we showed that the perturbations of the bond lengths around the azobenzene moiety were akin to the well-known hydroxyazo/ketohydrazone tautomerisation observed in ortho-hydroxyazobenzenes, Scheme 2 [5,13–16], and was the result of a cis-push–pull effect. A similar argument can be invoked here to explain the bond length perturbations observed in **1** and **3**. A π-donation from the halide trans to the metallated carbon induces an electron flow around the ortho-ruthenated azobenzene and results in π-donation by the azo-nitrogen to the ruthenium centre, which is stabilised by the π-acid CS ligand, Fig. 4.

Theoretical calculations by Richards [17] suggested that the CS ligand has the capability of being both a better σ-donor and π-acceptor than the ubiquitous CO ligand in transition metal complexes; further, the possibility of CS behaving as a π-donor to a metal centre has been raised [18]. It seems reasonable to expect that if CS is a stronger π-acceptor than CO then the Ru–C(3) and Ru–N(1) bond lengths in **1** would be shorter than those reported for **II**; this is obviously not the case, since both bonds are longer (Table 5). Care has to be exercised here since the bond length differences are within the 3σ level of certainty; however, there is a

Table 5
Selected bond lengths for **1**, **3**, **I** and **II**

Compound	C(3)–M	C(3)–C(2)	C(2)–N(2)	N(2)–N(1)	N(1)–C(8)	N(1)–M	Ru–C(E)	CE	RuX	Ref.
1	2.029(7)	1.405(10)	1.393(8)	1.277(7)	1.454(8)	2.232(6)	1.788(6)	1.572(6)	2.4855(18)	This work
3	2.045(9)	1.407(13)	1.402(12)	1.265(11)	1.444(12)	2.242(8)	1.806(11)	1.520(11)	2.7136(12)	This work
I		1.395	1.429	1.241	1.429					[12]
II	2.021(7)	1.426(10)	1.363(9)	1.273(8)	1.427(9)	2.184(6)	1.834(8)	1.134(9)	2.4990(19)	[7]

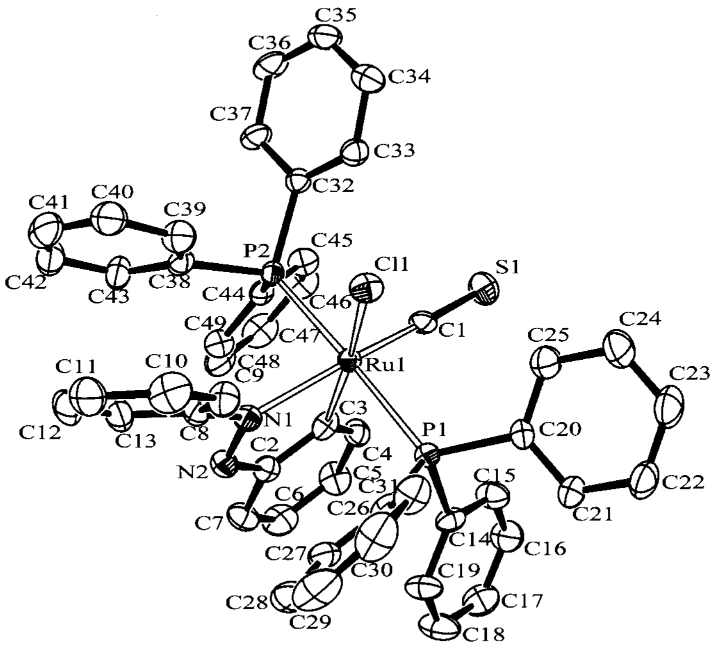


Fig. 1. ORTEP representation of **1** showing the atomic numbering scheme.

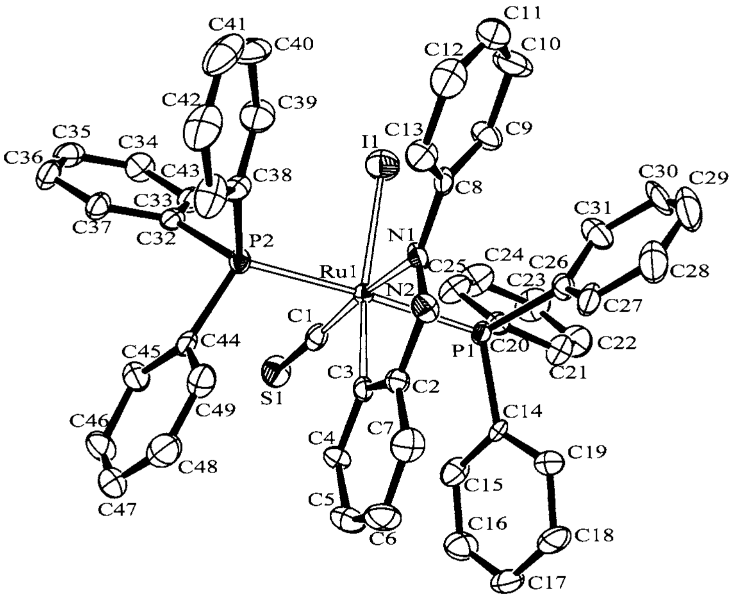


Fig. 2. ORTEP representation of **3** showing the atomic numbering scheme.

trend, and it is supported by the spectroscopic data. The perturbations in the cycloruthenated azobenzene bond lengths relative to free azobenzene are, however, good evidence for π-donation by the halide, and π-acceptance by the CS ligand is facilitated by the cycloruthenated azobenzene and results in a cis-push–pull effect. This observation is similar to that observed in analogous CO-containing complexes and was discussed at length in Ref. [7]. The magnitude of the cis-push–pull effect should be affected by the π-donor power of the halide and would be expected to be observable in the crystal structures. The Ru–C(3) and Ru–N(1) bond lengths for **1** should be shorter than for **3** because Cl is known to be a stronger π-donor than **I** [19]; they are, however, within the 3σ level of certainty. More significant though are the bond length differences between **3** and **II**, where the CO ligand has been replaced by CS too. This suggests that there is a moderation of the effect dependent not only on the π-donor strength of the halide but the π-acceptor capabilities of the accep-

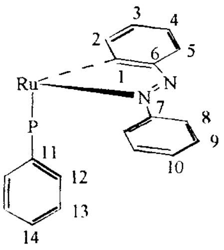
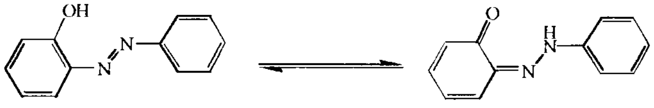


Fig. 3.



Scheme 2. Azo/hydrazone tautomerisation.

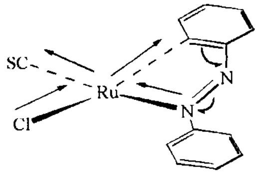


Fig. 4. Numbering scheme for ^{13}C-NMR data.

tor. The differences in the C–S bond lengths (Table 5) suggest that there is moderation of the effect depending upon the donor strength, and this is substantiated by the infrared data. The significant lengthening of the Ru–N(1) bond length for **1** relative to **II** is presumably due to the increased trans influence of the CS ligand, and the stronger trans influence of the CS versus CO ligand has been clearly shown in *cis-cis-trans*-[$OsCl_2(CO)(CS)(PPh_3)_2$], where the Os–Cl trans to CS is longer than that trans to CO [20]. The relevance of this is that the longer Ru–N bond means there is less potential for the side-on overlap necessary for the formation of the Ru–N π-interaction that is stabilised by the CS ligand. This will have the net effect of reducing the ability of the cycloruthenated azobenzene to facilitate stabilisation π-donation from the halide donor; hence the longer bond lengths in **1** relative to **II** suggest a weaker cis-push–pull effect.

3. Conclusion

It has been shown by a combination of infrared spectroscopy and X-ray crystallography that the CS ligand is capable of stabilising a cis-push–pull effect in 18 valence electron cycloruthenated azobenzene-containing complexes. It appears that the magnitude of the cis-push–pull effect appears to be less than in the corresponding CO-containing complexes as a direct result of the stronger trans influence of the CS ligand.

4. Experimental

All solvents were dried by refluxing over an appropriate drying agent and distilled prior to use. [$RuHCl(CS)(PPh_3)_3$] and $Hg(o\text{-}C_6H_4N{=}NPh)_2$ were prepared according to literature procedures [21,22]; all other chemicals were obtained from commercial sources and used as received, except for $RuCl_3$ which was loaned by Johnson Matthey. Melting points were measured on a Griffin melting point apparatus and are uncorrected. Infrared spectra were recorded as KBr discs on a Perkin Elmer spectrometer. ^{1}H-NMR (200.2 MHz) and $^{31}P\{^{1}H\}$-NMR (81.3 MHz) spectra were recorded on a Bruker AC200 spectrometer and $^{13}C\{^{1}H\}$-NMR (100.55 MHz) spectra were recorded on a Brucker AC400 spectrometer. ^{1}H- and $^{13}C\{^{1}H\}$-NMR spectra were referenced to $C\mathit{H}Cl_3$ ($\delta = 7.26$) and $\mathit{C}HCl_3$ ($\delta = 77.0$) and $^{31}P\{^{1}H\}$-NMR spectra were referenced externally to 85% H_3PO_4. Elemental analyses (C, H, N, S) were performed by the Microanalytical Service, Department of Chemistry, UMIST; solvates of crystallisation were confirmed by repeated elemental analysis and by NMR. The syntheses of all complexes were carried out under a dinitrogen atmosphere using standard Schlenk techniques. Work-ups were generally carried out in the open unless stated otherwise.

4.1. Complex syntheses

4.1.1. [$RuCl(CO)(\eta^2\text{-}C,N\text{-}C_6H_4N{=}NPh)(PPh_3)_2$] (1)

Caution: use of an organomercury reagent.

To [$RuHCl(CS)(PPh_3)_2$] (1 g, 1.03 mmol) suspended in toluene (40 cm^3) was added $Hg(o\text{-}C_6H_4N{=}NPh)_2$ (0.62 g, 1.15 mmol) and the solution was heated to reflux under N_2 with continuous stirring for 6 h. After cooling, the solution was filtered to remove Hg (**Caution**) and the solvent removed under reduced pressure. The crude material was then extracted with hot hexane (3 × 25 cm^3) to remove the azobenzene and PPh_3. Recrystallisation of the remaining purple solid from CH_2Cl_2–EtOH afforded **1** in good yield; see Table 1 for physical and analytical data.

4.1.2. [$RuBr(CO)(\eta^2\text{-}C,N\text{-}C_6H_4N{=}NPh)(PPh_3)_2$] (2) and 3

To **1** (0.1 g, 0.11 mmol) dissolved in CH_2Cl_2 (10 cm^3) was added $AgNO_3$ (0.017 g, 0.11 mmol) dissolved in H_2O–EtOH and the solution was stirred for 5 min. The solution was filtered to remove AgCl and to the filtrate was added NaBr (0.02 g, 0.2 mmol) dissolved in H_2O–EtOH and the solution stirred for 10 min. Reduction of the solvent under reduced pressure induced crystallisation of crude **2**. Recrystallisation from CH_2Cl_2–EtOH afforded **2**·$0.5CH_2Cl_2$; see Table 1 for physical and analytical data.

Complex **3** was prepared in an analogous manner; see Table 1 for physical and analytical data.

4.1.3. [Ru(η^2-O_2CMe)(CO)(η^2-C,N-C_6H_4N=NPh)(PPh_3)$_2$] (**4**) *and* **5**

To **1** (0.1 g, 0.1 mmol) dissolved in CH_2Cl_2 (10 cm^3) was added $AgOC(O)CH_3$ (0.017 g, 0.11 mmol) and the solution was stirred for 20 h. Filtration of the solution to remove AgCl and addition of hexane (20 cm^3) followed by slow evaporation of the CH_2Cl_2 afforded **4**; see Table 1 for physical and analytical data.

Complex **5** was prepared in an analogous manner; see Table 1 for physical and analytical data.

4.2. Crystallography

Suitable crystals of **1** and **3** were grown by the slow diffusion of ethanol into a solution of either **1** or **3** dissolved in CH_2Cl_2.

For **1** the data were collected on a Rigaku AFC6S diffractometer using Cu–K_α (1.541 78 Å) radiation and for **3** the data were collected on a Nonius Mach 3 diffractometer using Mo–K_α (0.710 73 Å) radiation. For both **1** and **3** the lattice constants were obtained from the setting angles of 25 accurately centred reflections. Reflection intensities were corrected for Lorenz polarisation and absorption. The SHELX97 suite of programs [23] was used to solve the structures by direct methods using full-matrix least-squares based on F^2. All non-hydrogen atoms were allowed to refine anisotropically and the hydrogen atoms were confined to chemically reasonable positions. See Table 4 for crystal data, collection parameters and refinement details

5. Supplementary material

All crystallographic data have been deposited at Cambridge Crystallographic Data Centre CCDC nos. 146923, **1**, and 146924, **3**. Copies of information can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1123-336033; e-mail: deposit@ccdc.ac.uk or www: http://www.ccdc.cam.ac.uk).

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