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Synthesis and characterisation of cyclometallated orthoazobenzene complexes of Ru(II): crystal and molecular structure of [RuCl(CO)(η^2-*C*,*N*-$C_6H_4N{=}NPh$)(PPh_3)$_2$]·0.5$CHCl_3$·0.5Et_2O. Is there a similarity to the hydroxyazo/ketohydrazone tautomerisation in *ortho*-hydroxyazobenzenes?

Wendy I. Cross, Kevin R. Flower *, R.G. Pritchard

Department of Chemistry, UMIST, PO Box 88, Manchester M60 1QD, UK

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Abstract

Treatment of [RuHCl(CO)(PPh_3)$_3$] with Hg(*o*-$C_6H_4NNC_6H_5$)$_2$ affords [RuCl(CO)(η^2-*C*,*N*-*o*-$C_6H_4NNC_6H_5$)(PPh_3)$_2$] (**1**) in good yield, where the cyclometallated azobenzene ligand coordinates through an *ortho*-C and 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)(η^2-*C*,*N*-*o*-$C_6H_4NNC_6H_5$)(PPh_3)$_2$] (**2** and **3**), while reaction of **1** with AgOC(O)Me gives the monondentate acetate complex [Ru{η^1-OC(O)Me}(CO)(η^2-*C*,*N*-*o*-$C_6H_4NNC_6H_5$)(PPh_3)$_2$] (**4**), and reaction with NaS_2CNEt_2·$2H_2O$ gives the chelate complex [Ru(CO)(S_2CNEt_2)(η^2-*C*,*N*-*o*-$C_6H_4NNC_6H_5$)(PPh_3)] (**5**). The cationic complex [Ru (CO)(bipy)(η^2-*C*,*N*-*o*-$C_6H_4NNC_6H_5$)-(PPh_3)][BF_4] (**6**) is obtained on treatment of **1** with $AgNO_3$, followed by bipy and $NaBF_4$. In the solid-state structure of **1**, significant changes in the bond lengths for the cyclometallated azobenzene ligand are observed and are discussed with the aid of a range of related examples, and compared with those observed in the well-known hydroxyazo/ketohydrazone tautomeric process in azodyes. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Azobenzene; Tautomerisation; Crystal structure

1. Introduction

Roper and Wright first reported the transfer of organic groups to ruthenium or osmium using organomercurials in 1977 [1], and since then they have developed extensive chemistry based upon this methodology [2]. For example, compounds that contain chelating C, N systems such as [MCl(CO)(η^2-*C*,*N*-2-C_6H_4-Py)(PPh_3)$_2$] (M = Ru, Os) and [OsCl(CO)(η^2-*C*,*N*-Qn)(PPh_3)$_2$] (Qn = 8-quinolyl) have been reported and their chemistry investigated [2e,f,g]. 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 this paper we wish to draw attention to the similarity in the structural changes that occur on cyclometallation of azobenzene and this process.

2. Results and discussion

Treatment of [RuHCl(CO)(PPh_3)$_3$] with Hg(*o*-$C_6H_4NNC_6H_5$)$_2$ in refluxing toluene afforded [Ru-

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* Corresponding author. Tel.: +44-161-2004538.
E-mail address: k.r.flower@umist.ac.uk (K.R. Flower)

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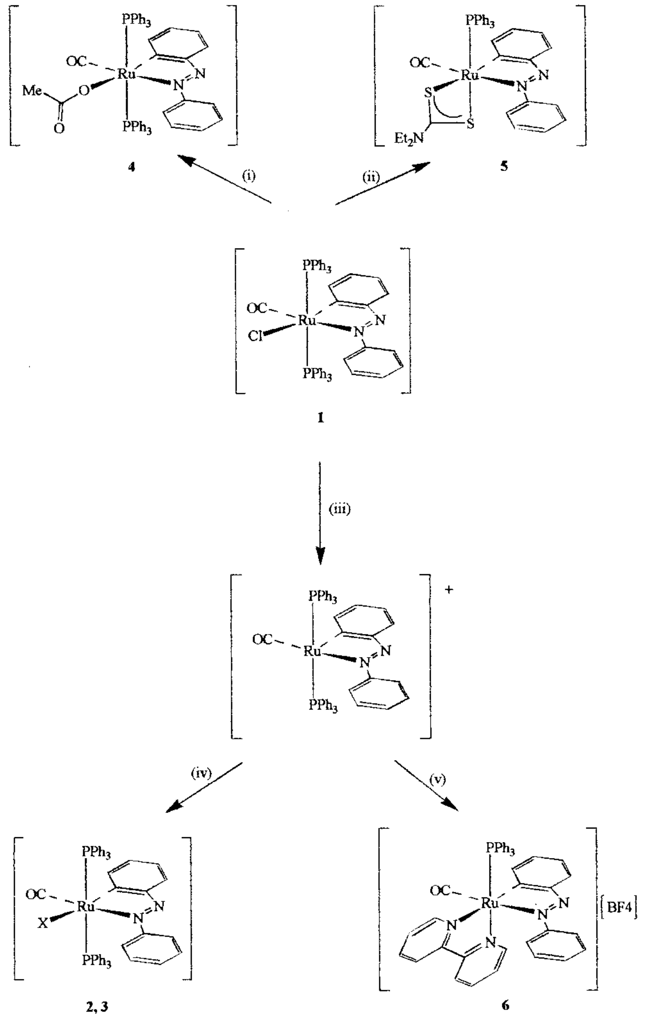

Scheme 1. (i) $AgOC(O)Me$, CH_2Cl_2; (ii) $NaS_2CNEt_2{\cdot}2H_2O$, CH_2Cl_2, EtOH, H_2O; (iii) $AgNO_3$, CH_2Cl_2, EtOH, H_2O; (iv) NaX (X = Br, I); (v) bipy, $NaBF_4$, H_2O, EtOH.

$Cl(CO)(\eta^2\text{-}C,N\text{-}o\text{-}C_6H_4NNC_6H_5)(PPh_3)_2]$ (**1**) in good yield according to Eq. (1).

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

After removal of elemental mercury, and then the solvent under reduced pressure, extraction of the crude reaction mixture with hot hexane allowed isolation of one molar equivalent of azobenzene and PPh_3, which were characterised by comparison with authentic specimens[1]; recrystallisation of the remaining 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**–**6** have been characterised by elemental analysis, IR spectroscopy, ^1H-, $^{31}P\{^1H\}$-, and $^{13}C\{^1H\}$-NMR spectroscopy (Tables 1–3). Compound $\mathbf{1}{\cdot}0.5CHCl_3{\cdot}0.5(C_2H_5)_2O$ was further characterised by a single-crystal X-ray diffraction study, see Section 4 and Table 4 for selected bond lengths (Å) and angles (°) and Fig. 1 for an ORTEP representation of the molecule with the atomic numbering scheme; the solvents of crystallisation and hydrogen atoms have been omitted for clarity. The structure is best described as a slightly distorted octahedral with the two PPh_3 ligands mutually *trans* and axial, with the *ortho*-metallated azobenzene, carbon monoxide and chloride in the equatorial plane. The greatest deviation from the idealised geometry is in the C(3)–Ru–N(1) angle, 76.6(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

Table 1
Physical [a] and analytical data [b] and infrared data for complexes **1**–**6**

Complex	Colour	Yield (%)	M.p. (°)	Microanalytical data				ν(CO) (cm^{-1})	Others
				C (%)	H (%)	N (%)	S (%)		
$\mathbf{1}{\cdot}CHCl_2$	Purple	87	218	62.5 (62.9)	3.9 (4.3)	3.0 (2.9)		1938s	
$\mathbf{2}{\cdot}CHCl_2$	Purple	95	214	58.9 (60.0)	3.8 (4.1)	2.7 (2.8)		1944s	
$\mathbf{3}{\cdot}0.5CHCl_2$	Purple	95	212	59.6 (59.2)	3.7 (4.0)	2.8 (2.8)		1940s	
$\mathbf{4}{\cdot}CHCl_2$	Purple	68	200	64.5 (63.8)	4.6 (4.5)	3.0 (2.9)		1948s	1610s, 1340s
$\mathbf{5}{\cdot}CHCl_2$	Red	77	174	59.5 (59.9)	4.5 (4.8)	5.8 (5.8)	8.5 (8.8)	1943s	1490msh
$\mathbf{6}{\cdot}CHCl_2$	Red	72	205	56.0 (56.0)	3.7 (3.8)	6.1 (6.2)		1952s	1056brs

[a] All compounds soften before melting. Spectra recorded as KBr discs, s, strong; m, medium; sh, shoulder; br, broad.
[b] Calculated values in parentheses.

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[1] Azobenzene: m.p. 69; PPh: m.p. 80; $^{31}P\{^1H\}$-NMR δ -5.0.

Table 2
$^{31}P\{^1H\}$-NMR [a] and proton [b] data for complexes **1**–**6**

Complex	^{31}P (δ) ppm	^1H (δ) ppm
1	27.8	7.8 (dd, J_{HH} 8.0, 2.0, 1H, aryl H); 7.5–6.8 (bm 36H, aryl H); 6.6 (m, 1H, aryl H); 6.1 (m, 1H, aryl H).
2	27.0	7.8 (dd, J_{HH} 8.0, 2.0, 1H, aryl H); 7.5–6.8 (bm 36H, aryl H); 6.7 (m, 1H, aryl H); 6.2 (m, 1H, aryl H).
3	25.5	7.8 (dd, J_{HH} 8.0, 2.0, 1H, aryl H); 7.5–6.8 (bm 36H, aryl H); 6.7 (m, 1H, aryl H); 6.2 (m, 1H, aryl H).
4	31.8	7.7 (d, J_{HH} 8.0, 1H, aryl H); 7.6 (d, J_{HH} 8.0, 1H, aryl H); 7.5–6.9 (bm 35H, aryl H); 6.8 (m, 1H, aryl H); 6.7 (m, 1H, aryl H); 1.6 (s, 3H, CH_3).
5	43.7	8.2 (dd, J_{HH} 8.0, 2.0, 1H, aryl H); 7.8 (d, J_{HH} 8.0, 1H, aryl H); 7.4–6.9 (bm 21H, aryl H); 6.7 (m, 1H, aryl H); 3.4 (m, 4H, CH_2); 1.1 (t, J_{HH} 7.1, 3H, CH_3); 0.8 (t, J_{HH} 7.1, 3H, CH_3).
6	46.1	8.7 (d, J_{HH} 6.0, 1H, aryl H); 8.4–8.0 (bm 6H, aryl H); 7.4–7.3 (bm 19H, aryl H); 6.9–6.6 (m, 5H, aryl H); 5.4 (d, J_{HH} 6.5, 1H, aryl H)

[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 = Hz; s, singlet; d, doublet; t, triplet; m, multiplet; b, broad.

of other angles in the equatorial plane from 90°. The most significant structural feature relates to the bond lengths of the *ortho*-metallated azobenzene ligand and a detailed discussion follows later.

The infrared spectra of **1**–**6** (Table 1) all display a strong ν(CO) around 1940 cm^{-1} and complex fingerprint regions. Compound **4** displays $\nu(CO_2)$ at 1610 and 1340 cm^{-1}, and the $\Delta\nu$ of 270 cm^{-1} implies monodentate coordination for the acetate ligand [7]. In **5** the ν(CN) for the coordinated diethyldithiocarbamate ligand is tentatively assigned to a band observed at 1490 cm^{-1}. For **6** a broad and strong absorption was observed at 1056 cm^{-1} and confirms the presence of the uncoordinated $[BF_4]^-$ group.

The $^{31}P\{^1H\}$-NMR spectra of **1**–**6** (Table 1) all show a singlet resonance, which for **1**–**4** suggest mutually *trans*-PPh_3 ligands. Slight shifts in resonance were observed on exchange of chloride by bromide, iodide or acetate. More significant shifts (20 ppm) occurred for **5** and **6**, where substitution of the chloride ligand and displacement of one of the PPh_3 ligands took place.

The ^1H-NMR spectra of **1**–**4** are consistent with their formulation, Scheme 1. 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 [8]. The data for **4** are also consistent (integration of $OC(O)CH_3$ to aryl-H) with the IR data and suggest the acetate ligand is monodentate. For compound **5** the integration suggests that the dithiocarbamate ligand is bidentate. The methyl protons of the ethyl groups appear as two 'triplets' and the methylene protons as a complex second order multiplet and is consistent with its structure (Scheme 1), since there is no plane of symmetry through the CN bond. It is also directly analogous to the structurally characterised osmium complex $[Os(CO)(\eta^2\text{-}C,N\text{-}C_6H_4\text{-}2\text{-}C_5H_4N)(S_2CNMe_2)(PPh_3)]$ reported by Roper and co-workers, which has this structure [2g].

The $^{13}C\{^1H\}$-NMR spectra for **1**–**6** were very helpful in confirming their structures, see Fig. 2 for numbering scheme. For compounds **1**–**4** (Table 3) the mutually *trans*-PPh_3 ligands couple to the CO and ruthenated carbon of the *ortho*-metallated azobenzene ligand and split the signals into triplets. Further, the resonances for the PPh_3 ligand carbons appear as virtual triplets. For compounds **5** and **6**, which contain one PPh_3 ligand, the CO and *ortho*-ruthenated and PPh_3 signals are doublets. The molecular asymmetry causes two sets of carbon signals for the ethyl groups in **5** and one signal for each of the carbons of the bipy ligand in **6**. The *ortho*-metallated carbon resonances 184.0–192.3 ppm

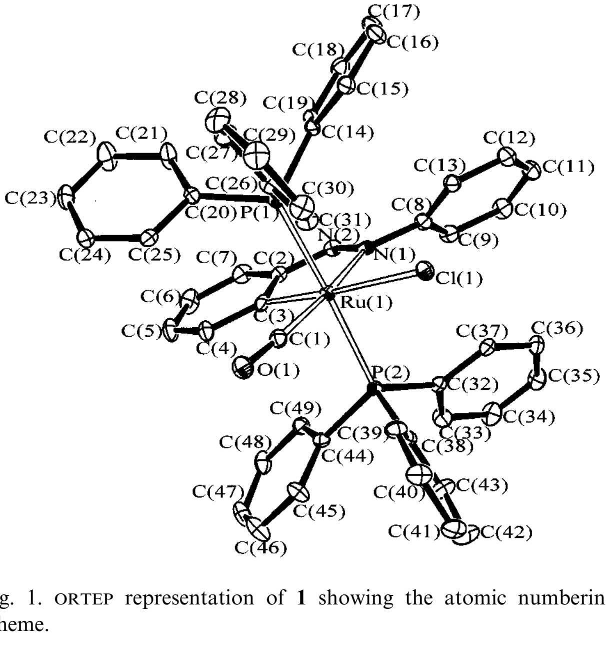


Fig. 1. ORTEP representation of **1** showing the atomic numbering scheme.

Table 3
$^{13}C\{^1H\}$-NMR data [a] for **1**–**6**

Compound	CO	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	Others
1	207.4 t(16.1)	188.9 t(7.6)	140.1	131.8	126.8	125.1	160.8	153.5	121.0	127.9	130.5	132.9 t(22.1)	133.9 t(4.5)	127.5 t(4.5)	129.2	
2	207.6 t(16.1)	189.2 t(8.6)	140.1	131.9	126.8	125.3	161.0	153.5	121.2	128.0	130.8	133.0 t(22.6)	134.0 t(5.0)	127.5 t(4.5)	129.2	
3	208.3 t(15.1)	188.9 t(8.6)	140.0	131.8	126.8	125.8	161.5	153.5	121.4	128.1	131.1	133.2 t(22.1)	134.2 t(5.1)	127.4 t(4.0)	129.2	
4	208.3 t(15.1)	190.9 t(9.0)	140.6	133.4	127.4	125.1	162.8	154.0	121.4	128.1	130.3	130.9 t(21.1)	133.8 t(5.5)	127.4 t(4.5)	129.4	179.6CO 25.3CH$_3$
5	205.4 d(16.1)	192.3 d(10.8)	140.0	132.7	126.9	124.5	162.8	152.1	121.8	127.8	128.7	134.6 d(43.8)	133.2 d(13.2)	128.0 d(11.1)	129.6	209.5CS; 44.2, 43.8 CH$_2$; 12.2,12.1 CH$_3$
6	203.5 t(19.1)	184.1 t(12.1)	140.4	133.6	126.9	124.5	162.2	153.6	120.8	128.2	130.9	132.1 d(22.1)	133.4 d(4.5)	128.9 d(4.5)	129.4	155.8, 155.6, 150.3, 149.9, 140.6, 139.9, 132.5, 127.0, 124.4, 123.7.

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

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) [9]. All of the other azobenzene resonances were assigned using substituent effects and previous assignments in related systems [10].

Confirmation of the solid-state structure of **1** was obtained from a single-crystal X-ray diffraction study and the most significant structural feature relates to the *ortho*-metallated azobenzene ring. The bond lengths are significantly different from those observed for uncoordinated azobenzene [11] (Table 5). For **1**: N(2)–C(2) 1.363(9) Å is short; N(2)–N(1) 1.273(8) Å is long; N(1)–C(8) 1.427(9) Å is as expected. Furthermore, statistically significant changes in the bond lengths in the ruthenated phenyl ring are evident: C(2)–C(7) 1.398(10), C(3)–C(4) 1.369(10), C(4)–C(5) 1.398(11), C(5)–C(6) 1.390(12), C(6)–C(7) 1.363(12) Å: all other C_{ar}–C_{ar} bond lengths in the molecule are as expected, 1.38 Å. The Ru–C(3) bond at 2.021(7) Å is at the short end of the observed range (2.01–2.20 Å) for complexes containing a Ru–C σ-aryl bond. 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 40.6°. These observations raise the question: what is responsible for the structural changes on complexation of the azobenzene as an *ortho*-metallated ligand? Perusal of the literature shows that a number of complexes that contain an *ortho*-metallated azobenzene ligand display bond-length patterns similar to that of **1**; others show patterns similar to free azobenzene [4]. To our knowledge no uniform explanation has been proffered to explain these observations and we wish to propose here that a similarity may be drawn between a chelating *ortho*-metallated azobenzene ligand and the well-known tautomeric process undergone by *ortho*-hydroxyazobenzenes (see Scheme 2). This tautomeric process has been studied by X-ray crystallography [12], and a variety of spectroscopic techniques including IR [13], UV–vis [14], ^{13}C- [10], ^{14}N- [15], and ^{15}N-NMR [16]. It has been shown that in the phenylazophenol systems the equilibrium lies to the left and is not greatly perturbed by substituents on the phenyl rings, whereas in the 1-phenylazonaphthalen-2-ol series the equilibrium is very sensitive to substituents in the 4-position of the phenylazo group.

To support this proposal, Table 5 collects together pertinent bond lengths for a selection of compounds derived from azobenzene (Fig. 3), along with those for free azobenzene and **1**. The numbering scheme used in the Table is that reported for **1** and has been transposed to all of the other compounds for comparative purposes: this numbering scheme is not necessarily that used in all of the original reports. The selection of these compounds is to a certain extent arbitrary and limited

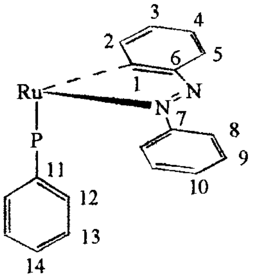


Fig. 2. Numbering scheme for ^{13}C-NMR data.

by the number of available examples, but is focused to aid in illustrating certain key points that will be used to support the argument that follows.

Compounds **A**–**C** are necessarily in the azo form, in **D** the azobenzene is orthometallated and there is no appreciable interaction between the azo-nitrogen and the mercury, in **E** the azobenzene behaves as a simple 2e σ donor to the metal centre through the azo nitrogen, compounds **F** and **G** are hydrazone tautomers, **H** has slight (< 2%) hydrazone tendencies, and **I** contains two orthometallated azobenzenes, both as chelates but *trans* to different ligands.

The structures of the organic compounds **A**–**C** and the metal complexes **D** and **E**, where the azobenzene behaves as a monodentate ligand, all have similar bond lengths around the azo moiety, whereas those in **1** are significantly different from free azobenzene and tend towards those of the hydrazone tautomers **F**–**H**. At this point it is important to note that for the hydrazone tautomer (Scheme 2) the lone pair that was initially on the azo nitrogen is now part of the σ bond to hydrogen and the necessary 'electron movement' results in there still being a lone pair on this nitrogen.

If a process similar to that of the azo/hydrazone tautomerisation (Scheme 2) is applied to **1**, the Cl ligand *trans* to the metallated carbon behaves as a π donor, the metallated carbon acts as a π acceptor with the resulting 'electron movement' the azo-nitrogen becomes a π donor and this is stabilised by the *trans*-CO ligand (Fig. 4). Classically the argument falters here because **1** is an 18-valence-electron organometallic, and standard valence-electron counting procedures preclude

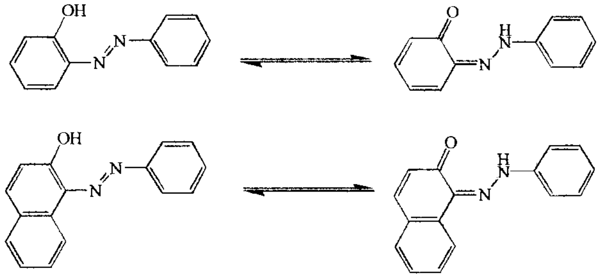
Table 4
Selected bond lengths (Å) and angles (°) for **1**

Bond lengths					
Ru(1)–C(1)	1.834(8)	Ru(1)–C(3)	2.021(7)	Ru(1)–N(1)	2.184(6)
Ru(1)–P(2)	2.3750(18)	Ru(1)–P(1)	2.3748(19)	Ru(1)–Cl(1)	2.4990(19)
N(1)–C(8)	1.427(9)	N(2)–C(2)	1.363(9)	C(2)–C(7)	1.398(10)
C(2)–C(3)	1.426(10)	C(3)–C(4)	1.369(10)	C(4)–C(5)	1.398(11)
C(5)–C(6)	1.390(12)	C(6)–C(7)	1.363(12)	C(8)–C(13)	1.376(10)
C(8)–C(9)	1.381(10)	C(9)–C(10)	1.381(11)	C(10)–C(11)	1.372(13)
C(11)–C(12)	1.374(12)	C(12)–C(13)	1.371(10)		
Bond angles					
C(1)–Ru(1)–C(3)	89.9(3)	C(1)–Ru(1)–N(1)	166.4(3)	C(3)–Ru(1)–N(1)	76.6(3)
C(1)–Ru(1)–P(2)	86.7(2)	C(3)–Ru(1)–P(2)	92.7(2)	N(1)–Ru(1)–P(2)	92.28(15)
C(1)–Ru(1)–P(1)	87.2(2)	C(3)–Ru(1)–P(1)	90.2(2)	N(1)–Ru(1)–P(1)	94.34(15)
P(2)–Ru(1)–P(1)	173.23(7)	C(1)–Ru(1)–Cl(1)	99.9(2)	C(3)–Ru(1)–Cl(1)	170.2(2)
N(1)–Ru(1)–Cl(1)	93.59(16)	P(2)–Ru(1)–Cl(1)	87.10(6)	P(1)–Ru(1)–Cl(1)	91.08(6)
N(2)–N(1)–C(8)	110.9(6)	N(2)–N(1)–Ru(1)	116.3(4)	C(8)–N(1)–Ru(1)	132.7(5)
N(1)–N(2)–C(2)	113.9(6)	N(2)–C(2)–C(7)	116.6(7)	N(2)–C(2)–C(3)	120.8(6)

Table 5
Selected bond lengths for **1** and **A**–**I**

Compound	C(3)–O	C(3)–M	C(3)–C(2)	C(2)–N(2)	N(2)–N(1)	N(1)–C(8)	N(1)–M	Ru–CO	Refs.
1		2.021(7)	1.426(10)	1.363(9)	1.273(8)	1.427(9)	2.184(6)		This work
A			1.395	1.429	1.241	1.429			[11]
B	1.390(4)		1.368(5)	1.413(5)	1.240(4)	1.424(5)			[6b]
C	1.395(5)		1.389(5)	1.424(5)	1.257(4)	1.423(5)			[6b]
D[a]		2.01(2)	1.46	1.41	1.24	1.40			[17]
E			1.375(8)	1.450(6)	1.225(6)	1.478(7)	2.057(4)		[18]
F	1.267		1.453	1.340	1.314	1.415			[19]
G	1.234(4)		1.467(4)	1.312(4)	1.317(4)	1.405(5)			[16]
H	1.344(4)		1.402(4)	1.405(4)	1.256(3)	1.419(4)			[6b]
I*		2.103(8)	1.39(1)	1.45(1)	1.240(8)	1.50(1)	2.155(7)	1.930(8)	[4c]
I		2.052(7)	1.40(1)	1.368(8)	1.289(7)	1.424(8)	2.103(6)	1.879(9)	[4c]

[a] The C(2)–C(3) bond length is much longer than expected, but is consistent with the large estimated S.D.s for this structure.



Scheme 2. Azo/hydrazone tautomerisation.

π donation as destabilisation of the complex would result. However, Caulton and co-workers [9,20] have used an alternative approach to the 'all or nothing' view of valence-electron counting to understand the effect of π donation in the pyridine adducts [RuH(X)(CO)(py)(P^{t}Bu$_2$Me)$_2$] (X = a selection of π donors) using a multicentre molecular orbital approach. This procedure relies on the special acceptor properties of the CO ligand when it is found *trans* to a π donor. The overall effect is that the CO ligand absorbs the π donation and prevents destabilisation of the complex by setting up a 'push–pull' process: a direct analogy can be seen in **1**.

The implied double-bond character of the Ru–C(3) bond is supported by the ^{13}C{^{1}H}-NMR shift for the *ortho*-ruthenated carbon in **1**, which appears at 188.9 ppm and is at noticeably lower field than the metallated carbon in the σ-aryl complex [Ru(Ph)Cl(CO)(P^{t}Bu$_2$Me)$_2$] (155 ppm) [9]. Heteroatom-stabilised carbene complexes of Ru(II) with similar ligand sets have ^{13}C resonances for the carbene carbon around 220 ppm [21], and the implication of this is that there is some carbenic (double bond) character in the Ru–C(3) bond in **1**. Further, the Ru–C(3) bond length of 2.021(7) Å is comparable to Ru–C bond lengths of heteroatom-stabilised carbene complexes of Ru(II) [21].

To further illustrate this point we shall now consider **I**. In this complex there are two *ortho*-metallated azobenzene ligands and two *cis*-CO ligands. The * azobenzene has bond lengths around the azo moiety that are comparable to those of free azobenzene, whereas those of the second azobenzene are perturbed (Table 5), and this is easily understood from the previous discussion. The * azobenzene ligand acts in a manner comparable to **D** and **E**, i.e. the Ru–C bond is a pure σ bond and the azo-nitrogen behaves as a pure 2e donor. The principal reason for this being that the metallated carbon is *trans* to a CO ligand and is not capable of competing effectively for back donation. There is, however, evidence (bond asymmetry) that a 'push–pull' system is in operation in the second azobenzene: the metallated carbon acts as an acceptor and the azo N as a π donor, and this donation is stabilised by the *trans* CO.

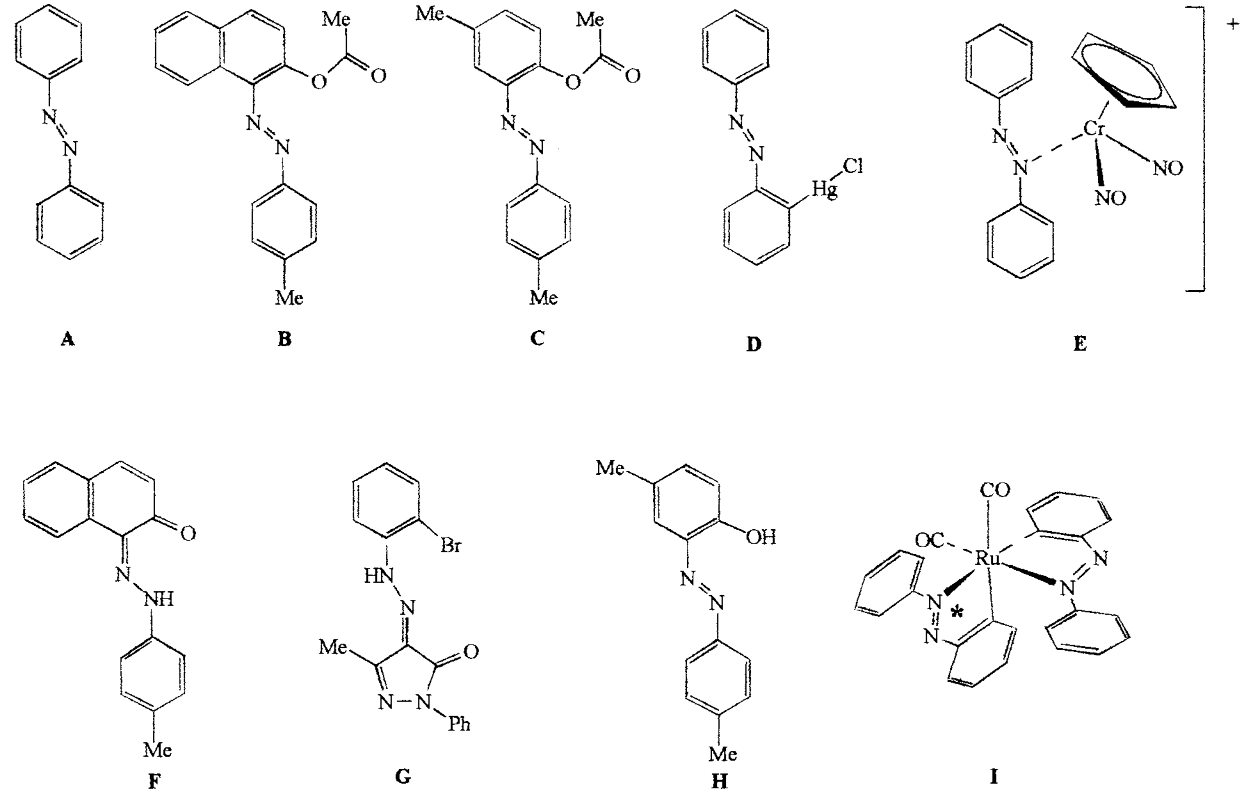


Fig. 3.

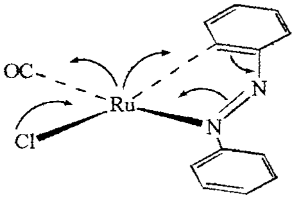


Fig. 4.

3. Conclusions

From this study it has become apparent that an *ortho*-metallated azobenzene ligand is capable of behaving as both a π acceptor and π donor ligand to a metal centre and that acceptance is through the metallated carbon and donation through the azo nitrogen: a process that bears many similarities to the tautomeric process observed in *ortho*-hydroxyazobenzenes.

4. Experimental

All solvents were dried by refluxing over an appropriate drying agent and distilled prior to use. [RuHCl(CO)(PPh$_3$)$_3$], Hg(o-C$_6$H$_4$N=NPh)$_2$ were prepared according to literature procedures [22,23]; 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. IR 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) were recorded on a Bruker AC200 spectrometer and ^{13}C{^{1}H}-NMR (100.55MHz) were recorded on a Bruker AC400 spectrometer. ^{1}H- and ^{13}C{^{1}H}-NMR spectra were referenced to C*H*Cl$_3$ ($\delta = 7.26$) and *C*HCl$_3$ ($\delta = 77.0$) and ^{31}P{^{1}H}-NMR was referenced externally to 85% H$_3$PO$_4$. Elemental analyses were performed by the Microanalytical service, Department of Chemistry, UMIST; solvates of crystallisation were confirmed by repeated elemental analysis and confirmed by NMR. The synthesis of all complexes were carried out under a dinitrogen atmosphere using standard Schlenk techniques. Work-ups were generally carried out in the open unless otherwise stated.

4.1. [RuCl(CO)(η^2-C,N-C$_6$H$_4$N=NPh)(PPh$_3$)$_2$] (**1**)

Caution: use of an organomercury reagent.

To [RuHCl(CO)(PPh$_3$)$_2$] (1 g, 1.04 mmol) suspended in toluene (40 cm^3) was added Hg(o-C$_6$H$_4$N=NPh)$_2$ (0.62 g, 1.15 mmol) and the solution was heated to reflux under N$_2$ with continuous stirring for 3 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$_2$Cl$_2$–EtOH afforded **1**·CH$_2$Cl$_2$ in good yield, see Table 1 for physical and analytical data.

4.2. [RuBr(CO)(η^2-C,N-C$_6$H$_4$N=NPh)(PPh$_3$)$_2$] (**2**)

To **1**·CH$_2$Cl$_2$ (0.096 g, 0.1 mmol) dissolved in CH$_2$Cl$_2$ (10 cm^3) was added AgNO$_3$ (0.017 g, 0.1 mmol) dissolved in H$_2$O–EtOH and the solution was stirred 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$_2$O–EtOH and the solution stirred for 10 min. Reduction of the solvent under reduced pressure induced crystallisation of crude **2**. Recrystallisation from CH$_2$Cl$_2$–EtOH afforded **2**·CH$_2$Cl$_2$; see Table 1 for physical and analytical data.

In an analogous manner **3**·CH$_2$Cl$_2$ was prepared; see Table 1 for physical and analytical data.

4.3. [Ru{η^1-OC(O)Me}(CO)(η^2-C,N-C$_6$H$_4$N=NPh)(PPh$_3$)$_2$] (**4**)

To **1**·CH$_2$Cl$_2$ (0.096 g, 0.1 mmol) dissolved in CH$_2$Cl$_2$ (10 cm^3) was added AgOC(O)CH$_3$ (0.017 g, 0.1 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$_2$Cl$_2$, afforded **4**·CH$_2$Cl$_2$; see Table 1 for physical and analytical data.

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

4.4. [Ru(CO)(η^2-C,N-C$_6$H$_4$N=NPh)(PPh$_3$)(bipy)][BF$_4$] (**6**)

To **1**·CH$_2$Cl$_2$ (0.096 g, 0.1 mmol) dissolved in CH$_2$Cl$_2$ (10 cm^3) was added AgNO$_3$ (0.017 g, 0.1 mmol) dissolved in H$_2$O–EtOH and the solution was stirred 5 min. The solution was filtered to remove AgCl and to the filtrate was added bipy (0.016 g, 0.1 mmol) and the solution was stirred for 20 h. Removal of the solvent under reduced pressure, extraction into CH$_2$Cl$_2$ and filtering through Celite, to remove inorganics, afforded a deep red solution. To this solution was added NaBF$_4$ (0.1 g, 1 mmol) dissolved in H$_2$O–EtOH and the solution was stirred for 1 h. Removal of the solvent, extraction into CH$_2$Cl$_2$, filtration through Celite and reduction of the solvent volume to ca. 0.5 cm^3, followed by the addition of Et$_2$O (50 cm^3), afforded crude **2**. Recrystallisation from CH$_2$Cl$_2$–Et$_2$O afforded **6**·CH$_2$Cl$_2$; see Table 1 for physical and analytical data.

4.5. Crystallography

A purple tablet ($0.2 \times 0.14 \times 0.12$ mm^3) of **1**·0.5CHCl$_3$·0.5Et$_2$O: M_w 986.49, which was obtained on diffusion of Et$_2$O into a saturated solution of **1** in CHCl$_3$, was mounted on a Nonius MACH four-circle diffractometer using graphite monochromated Mo–K$_\alpha$ (0.71069 Å) radiation. Lattice constants were determined from the setting angles of 25 accurately controlled reflections: monoclinic; $P2_1/n$; $a = 10.824(2)$, $b = 25.887(5)$, $c = 15.697(3)$ Å; $\beta = 92.234(15)°$, $Z = 4$. The $\omega/2\theta$ scan technique was used with a ω scan width of $0.9° + 0.35 \tan \theta$ to collect reflections with $2\theta \leq 50°$. The intensities were corrected for Lorenz, polarisation and absorption (0.651 mm^{-1}). The SHELX97 suite of programs [24] was used to solve the structure by direct methods and refined using full-matrix least-squares based on F^2, hydrogen atoms were constrained to chemically reasonable positions, the lattice solvent molecules were found to occupy the same crystallographic site and on refinement each was found to have half occupancy: R $[I > 2\sigma(I)]$; $R_1 = 0.0638$, $wR_2 = 0.1436$; R (all data), $R_1 = 0.1085$, $wR_2 = 0.1718$. Selected bond lengths and angles can be found in Table 4.

5. Supplementary material

All crystallographic data have been deposited at Cambridge Crystallographic Data Centre, CCDC no. 137488. Copies of this 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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