Synthesis and Characterization of Cycloruthenated 2-(Phenylimino)phenyls: A Useful Probe for the Elucidation of the Tautomeric Process in 2-Hydroxyphenyl-Schiff Bases

Kevin R. Flower,*,† Victoria J. Howard, Robin G. Pritchard, and John E. Warren

Department of Chemistry, UMIST, PO Box 88, Manchester, M60 1QD, U.K.

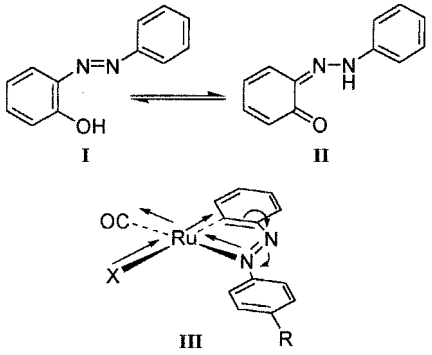
Received October 9, 2001

Treatment of [RuHCl(CO)(PPh_3)$_3$] with a 1:1 molar ratio of Hg{*o*-$C_6H_4C(H)$=NC_6H_4-4-R}$_2$ in refluxing toluene afforded the new compounds [RuCl(CO){η^2-*C,N*-$C_6H_4C(H)$=NC_6H_4-4-R}(PPh_3)$_2$] (R = NMe_2, **1a**; Me, **1b**; I, **1c**; NO_2, **1d**) in good yield. The new compounds have been fully characterized by elemental analysis, IR spectroscopy, and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy. A linear correlation in a Hammett plot of the metalated carbon resonance of the imine ligand versus σ^+-values is observed, and this is used to comment on, along with the reported ν(CO) data and data previously reported for analogous azo-containing complexes, the keto/enol tautomerization undergone by 2-hydroxyphenyl-Schiff bases. These data suggest that the position of the tautomeric equilibrium is affected by electron-withdrawing or -releasing substituents in the same way as for the analogous 2-phenylazophenols. During the purification of **1a** and **1b** small amounts of the bis-cyclometalated imine-containing complexes [Ru(CO){η^2-*C,N*-$C_6H_4C(H)$=NC_6H_4-4-R}$_2$(PPh_3)] (R = NMe_2, **2a**; Me, **2b**) were isolated. These compounds have been subsequently synthesized and fully spectroscopically characterized. The compounds **1a**, **1b**, **2a**, and **2b** have also been further characterized by single-crystal X-ray diffraction studies.

Introduction

The cyclometalation reaction has been known for a long time,[1] and compounds that contain a cyclometalated ligand continue to be of interest for the generation of catalysts,[2] compounds with interesting material properties,[3] and antitumor agents.[4] On the basis of methodology developed by Roper and Wright[5] we recently reported the preparation of some cycloruthenated azobenzene complexes of the type [RuX(CE)(η^2-*C,N*-C_6H_4N=NC_6H_5)(PPh_3)$_2$] (E = O, S; X =Cl, Br, I) and showed that the cycloruthenated azobenzene ligand facilitated a *cis*-push−pull effect,[6] which is analogous to the hydroxy-azo/keto-hydrazone tautomerization in 2-hydroxyazobenzene systems, Chart 1.[7] This effect can be briefly described as formally forbidden π-donation to an 18 valence electron organometallic complex by a π-donor *trans* to the metalated carbon atom, which is transmitted through the cyclometalated ligand to the π-accepting *cis* carbonyl ligand and hence stabilized. A recent report by Antonov et al.[8] described the keto/enol tautomerization for 2-hydroxynaphaldehyde-derived Schiff bases. Their data suggested that the relative position of the equilibrium, like in the azo analogues,[7] is affected by either electron-withdrawing or -releasing substituents; however, unlike the azo-based systems, they suggested that the keto form is favored in the presence of electron-releasing and the enol form in the

Chart 1



† E-mail: k.r.flower@ umist.ac.uk.

(1) Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139.

(2) (a) Dupont, J.; Pfeffer, M.; Spencer, J. *Eur. J. Inorg. Chem.* **2001**, 1917. (b) Kleij, A. W.; Gebbink, R. J. M. K.; van den Nieuwenhuijzen, P. A. J.; Kooijman, H.; Lutz, M.; Spek, A. L.; Van Koten, G. *Organometallics* **2001**, *20*, 634. (c) Dupont, J.; Gruber, A. S.; Fonseca, G. S.; Monteiro, A. L.; Ebling, G.; Burrow, R. A. *Organometallics* ***2001***, *20*, 171. (d) Sundermann, A.; Uzman, O.; Martin, J. M. L. *Chem. Eur. J.* **2001**, *7*, 1703. (e) Estevan, F.; Herbst, K.; Lahuerta, P.; Barberis, M.; Pérez-Prieto, J. *Organometallics* **2001**, *20*, 950.

(3) (a) Neve, F.; Crispini, A.; Serroni, S.; Loiseau, F.; Campagna, S. *Inorg. Chem.* **2001**, *40*, 1093. (b) Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzaq, F.; Kwong, R.; Tsyba, I.; Bortz, M.; Mui, B.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2001**, *40*, 1704. (c) Eran, B. B.; Singer, D.; Praefcke, K. *Eur. J. Inorg. Chem.* **2001**, 111. (d) Grushin, V. V.; Herron, N.; LeCloux, D. D.; Marshall, W. J.; Petrov, V. A.; Wang, Y. *Chem. Commun.* **2001**, 1494.

(4) (a) Bonnardel, P. A.; Parish, R. V.; Pritchard, R. G. *J. Chem. Soc., Dalton Trans.* **1996**, 3185. (b) Parish, R. V.; Howe, B. P.; Wright, J. P.; Mack, J.; Pritchard, R. G.; Buckley, R. G.; Elsome, A. M.; Fricker, S. P. *Inorg. Chem.* **1996**, *35*, 1659. (c) Dinger, M. B.; Henderson, W. *J. Organomet. Chem.* **1998**, *557*, 231. (d) Dinger, M. B.; Henderson, W. *J. Organomet. Chem.* **1998**, *560*, 233. (e) Abram, U.; Mack, J.; Ortner, K.; Müller, M. *J. Chem. Soc., Dalton Trans.* **1998**, 1101.

(5) Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1977**, *142*, C1.

(6) (a) Cross, W. I.; Flower, K. R.; Pritchard, R. G. *J. Organomet. Chem.* **2000**, *601*, 164. (b) Flower, K. R.; Pritchard, R. G. *J. Organomet. Chem.* **2001**, *620*, 60.

(7) (a) Venkataraman, K. *Synthetic Dyes*; Academic Press: New York, 1952; Vol. 1. (b) Zollinger, H. *Azo and Diazo Chemistry*; Wiley-Interscience: New York, 1961.

(8) Antonov, L.; Fabian, W. M. F.; Nedeltcheva, D.; Kamounah, F. S. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1173.

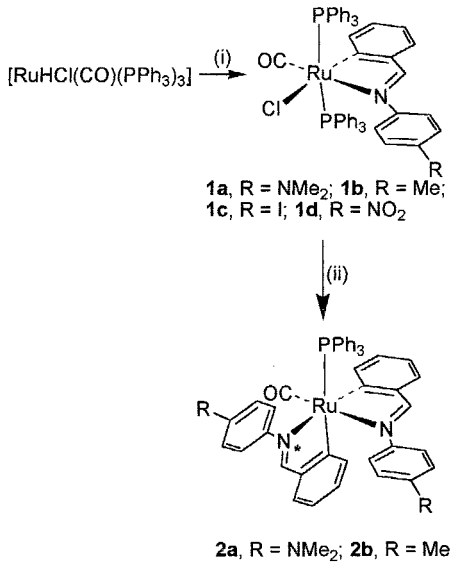
10.1021/om010883i CCC: $22.00
Publication on Web 02/16/2002

Table 1. Physical, Analytical,[a] and Infrared[b] Data for 1a−d and 2a,b

compound	color	yield (%)	mp (°C)	microanalytical data (%) C	H	N	Cl	IR ν(CO) cm^{-1}
1a [RuCl(CO){η^2-*C,N*-$C_6H_4C(H)$=NC_6H_4-4-NMe_2}$(PPh_3)_2$]·$2CH_3OH$	yellow	62	233	64.2 (63.9)	4.8 (4.6)	3.1 (2.9)	4.1 (3.7)	1935
1b [RuCl(CO){η^2-*C,N*-$C_6H_4C(H)$=NC_6H_4-4-Me}$(PPh_3)_2$]·$1.6CH_2Cl_2$	yellow	73	226	62.2 (62.0)	4.7 (4.5)	1.5 (1.4)	15.2 (14.6)	1934
1c [RuCl(CO){η^2-*C,N*-$C_6H_4C(H)$=NC_6H_4-4-I}$(PPh_3)_2$]·CH_2Cl_2	orange	72	238	54.7 (55.1)	3.4 (3.8)	1.4 (1.3)	10.4 (9.9)	1931
1d [RuCl(CO){η^2-*C,N*-$C_6H_4C(H)$=NC_6H_4-4-NO_2}$(PPh_3)_2$]·$1.5CH_2Cl_2$	red	75	232	61.0 (61.1)	4.2 (4.2)	2.9 (2.8)	13.6 (14.0)	1929
2a [Ru(CO){η^2-*C,N*-$C_6H_4C(H)$=NC_6H_4−4-NMe_2}$_2(PPh_3)$]	orange	10[c]	145	70.6 (70.2)	5.6 (5.4)	6.6 (6.7)	0.0 (0.0)	1913
2b [Ru(CO){η^2-*C,N*-$C_6H_4C(H)$=NC_6H_4−4-Me}$_2(PPh_3)$]·CH_2Cl_2	orange	65	142	66.6 (66.7)	4.4 (4.8)	3.1 (3.2)	7.9 (8.2)	1914

[a] Calculated values in parentheses. [b] Spectra recorded as KBr disks, all bands strong. [c] Isolated as second product in synthesis of **1a**.

Scheme 1[a]



[a] (i) Hg{*o*-$C_6H_4C(H)$=NC_6H_4-4-R}$_2$ (R = NMe_2, Me, I, NO_2), C_6H_5Me, reflux 6 h; (ii) Hg{*o*-$C_6H_4C(H)$=NC_6H_4-4-R}$_2$ (R = NMe_2, Me), C_6H_5Me, reflux 18 h.

Table 2. $^{31}P\{^1H\}$ NMR and Proton Data[a] for Compounds 1a−d and 2a,b

compd	^{31}P (δ)	^1H (δ)
1a	28.0	7.89 (t, J_{HP} = 1.7, 1H, CH=N); 7.44−6.90 (m, 31H, aryl-H); 6.76 (d, J_{HH} = 7.8, 1H, aryl-H); 6.50 (t, J_{HH} = 7.3, 1H, aryl-H); 6.23 (m, 5H, aryl-H); 3.48 (s, 6H, CH_3OH); 2.87 (s, 6H, NCH_3)
1b	28.3	7.98 (t, J_{HP} = 2.0, 1H, CH=N); 7.46−7.00 (m, 30H, aryl-H); 6.73, (d, J_{HH} = 7.8, 1H, aryl-H); 6.63 (d, J_{HH} = 8.4, 2H, aryl-H); 6.51 (t, J_{HH} = 7.0, 1H, aryl-H); 6.23 (d, J_{HH} = 8.4, 1H, aryl-H); 6.16 (m, 1H, aryl-H); 5.29 (s, 3H, CH_2Cl_2); 2.23 (s, 3H, CH_3).
1c	28.6	8.02 (t, J_{HP} = 1.9, 1H, CH=N); 7.45−7.04 (m, 33H, aryl-H); 6.66 (d, J_{HH} = 8.4, 1H, aryl-H); 6.51 (t, J_{HH} = 7.8, 1H, aryl-H); 6.10 (m, 1H, aryl-H); 6.02 (d, J_{HH} = 8.8, 2H, aryl-H); 5.29 (s, 2H, CH_2Cl_2)
1d	28.2	8.15 (t, J_{HP} = 2.0, 1H, CH=N); 7.59 (d, J_{HH} = 9.0, 2H, aryl-H)0.7.48−7.04 (m, 31H, aryl-H); 6.58 (m, 2H, aryl-H); 6.33 (d, J_{HH} = 9.0, 2H, aryl-H); 6.12 (m, 1H, aryl-H); 5.29 (s, 3H, CH_2Cl_2)
2a	30.5	8.29 (s, 1H, CH=N); 7.78 (d, J_{HP} = 2.4, 1H, CH=N); 7.62−6.73 (m, 25H, aryl-H); 6.32 (d, J_{HH} = 9.0, 2H, aryl-H); 6.20 (d, J_{HH} = 8.8, 2H, aryl-H); 5.92 (d, J_{HH} = 9.0, 2H, aryl-H); 2.82 (s, 6H, NCH_3); 2.75 (s, 6H, NCH_3)
2b	31.1	8.27 (s, 1H, CH=N); 7.83 (d, J_{HP} = 2.6, 1H, CH=N); 7.58−6.66 (m, 29H, aryl-H); 5.75 (d, J_{HH} = 8.4, 2H, aryl-H); 5.29 (s, 2H, CH_2Cl_2); 2.18 (s, 3H, CH_3); 2.09 (s, 3H, CH_3)

[a] Spectra recorded in $CDCl_3$ at 293 K; coupling constants (*J*) in Hz; s = singlet, d = doublet, t = triplet, m = multiplet.

presence of electron-withdrawing groups. We were somewhat surprised by these findings and herein report the synthesis of some cycloruthenated 2-phenylimines for which the data suggest that the position of the tautomerization is influenced by substituents in exactly the same way as in the analogous azo-containing systems.

Results and Discussion

Synthesis and Characterization of [RuCl(CO)-{η^2-*C,N*-$C_6H_4C(H)$=NC_6H_4-4-R}$(PPh_3)_2$] (R = NMe_2, 1a; Me, 1b; I, 1c; NO_2, 1d). The compounds [RuCl(CO)-{η^2-*C,N*-$C_6H_4C(H)$=NC_6H_4-4-R}$(PPh_3)_2$] (R = NMe_2, **1a**; Me, **1b**; I, **1c**; NO_2, **1d**) were prepared on treatment of [$RuHCl(CO)(PPh_3)_3$] with the diorganomercurials Hg-{*o*-$C_6H_4C(H)$=N−C_6H_4-4-R}$_2$,[9] in good yield, Scheme 1. The new compounds **1a**−**d** were all characterized by elemental analysis and infrared spectroscopy, Table 1, ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, Table 2, $^{13}C\{^1H\}$ NMR spectroscopy, Table 3; see Figure 1 for the numbering scheme. Compounds **1a** and **b** were also characterized by single-crystal X-ray diffraction studies; see Table 4 for data collection and processing parameters and Table 5 for selected bond lengths and angles. ORTEP[10] representations of the molecular structures of **1a** and **1b** are presented in Figures 2 and 3, respectively, and each shows the relevant atomic numbering scheme: the solvents of crystallization and protons are omitted for clarity. Both structures can best be described as slightly distorted octahedral with the two PPh_3 ligands mutually *trans* and axial with the orthometalated imine ligand, carbonyl, and halide in the equatorial plane. For a more detailed discussion see later.

The ^1H NMR data are consistent with the formulation of **1a**−**d**. All of the compounds show a triplet resonance for the imine CH (coupling to the mutually *trans* PPh_3 ligands). In the aromatic region, the ruthenated imine-ligand protons are to a large extent masked by the PPh_3 proton resonances: integrations are consistent with the imine proton and the methyl groups for **1a** and **1b**. The

(9) Flower, K. R.; Howard, V. J.; Naguthney, S.; Pritchard, R. G.; Warren, J. E.; McGown, A. T. *Inorg. Chem.* **2002**, in press.

(10) Johnson, C. K. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Table 3. $^{13}C\{^1H\}$ NMR Data[a] for 1a−d and 2a,b

compd	CO	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	others
1a	206.9 t J = 15.4	186.1 t J = 9.6	140.8	129.5	119.6	130.0	143.8	170.6	140.6	124.3	111.4	148.9	133.2 t J = 21.2	134.2 t J = 5.3	127.3 t J = 4.3	128.9	40.8 NCH_3
1b	206.9 t J = 15.9	188.3 t J = 9.6	140.7	129.0	119.7	129.6	143.4	172.8	147.5	125.2	127.7	135.2	133.2 t J = 21.1	134.2 t J = 5.3	127.4 t J = 4.3	128.9	20.9 CH_3
1c[b]	206.8 t J = 16.3	189.7 t J = 9.1	140.9	130.0	119.9	130.6	142.9	173.4	149.3	126.6	136.1	90.8	133.2 t J = 21.1	134.1 t J = 5.3	127.5 t J = 4.4	129.0	
1d	206.7 t J = 16.3	191.9 t J = 9.1	141.1	130.8	120.1	131.3	142.3	174.9	154.9	125.2	122.5	145.0	133.3 t J = 21.1	134.0 t J = 5.3	126.6 t J = 4.3	129.3	
2b	205.6 d J = 10.5	195.8 d J = 7.6	140.0	129.9	119.1	129.3	144.4	171.8	149.7	122.3	128.3	135.2	134.9 d J = 29.8	133.4 d J = 8.6	127.2 d J = 8.7	128.6	20.8 CH_3
		184.9 d J = 68.2	138.1	130.2 d J = 4.8	122.1	129.1 d J = 2.9	147.9	175.3 d J = 4.8	152.5		128.1	135.3					20.6 CH_3

[a] Spectra recorded in $CDCl_3$ at 298 K; all resonances singlets unless otherwise stated; all J = PC in Hz. [b] Poorly soluble.

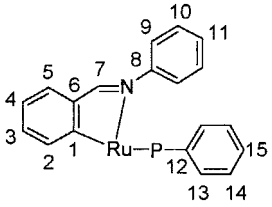


Figure 1. Numbering scheme for $^{13}C\{^1H\}$ NMR data.

solvents of crystallization are readily observed and integrate in the correct ratio. It should be noted here that the amount of solvent incorporated into the crystal lattice during recrystallization is variable and depends on the rapidity of the recrystallization and is best determined by running the proton NMR spectrum for each sample after recrystallization.

The compounds **1a**−**d** all show the expected singlet resonance in their $^{31}P\{^1H\}$ NMR spectra, which is little perturbed by changing the imine substituents.

The $^{13}C\{^1H\}$ NMR data have been assigned with the aid of DEPT 135 spectra, substituent effects,[11] and the data reported previously for the diorganomercurial precursors.[9] The use of $^{13}C\{^1H\}$ NMR data to study the position of the keto/enol tautomerization has been previously described[12] and further developed by us in a study of azo-containing naphthylphosphines.[13] During this study we noted that some caution needed to be applied in the interpretation of the position of the *ortho*-carbon resonance when used to calculate the position of the equilibrium; however, the most salient point to note from these studies is that the quinoid form **II** has the higher frequency resonance: the $^{13}C\{^1H\}$ NMR data obtained for the C(1) carbon atoms, Table 3, are consistent with this. We also carried out a plot of the metalated ligand C(1) resonances against Hammett σ^+-values[14] and obtained an essentially linear plot (LR = 0.92) with a positive slope, which is what is to be expected, i.e., more carbenic character[15] at C(1) for imine ligands bearing an electron-withdrawing group. Transposing this observation to the nonmetalated systems it appears that electron-withdrawing groups will stabilize the quinoid form **II**, and electron-withdrawing substituents the enol form **I**, Chart 1.

Further evidence to support this interpretation comes from the ν(CO) infrared data for **1a**−**d**, Table 1. Caulton et al have shown[16] that the ν(CO) is dependent upon π-donation of accompanying ligands and that the greater the π-donation, the lower the ν(CO); in addition the special π-acceptor properties of the CO ligand have been shown to stabilize π-donation in 18 valence electron species through a push−pull effect. The trend in the ν(CO) frequencies, Table 1, supports the observation that the more electron-withdrawing the substituent on the imine ring, the lower the ν(CO); this is consistent with a *cis*-push−pull effect facilitated by the cycloruthenated imine ligand, as it is consistent with greater π-donation from the imine-nitrogen and hence is consistent with the more quinoid character for the metalated imine ligand carbon atom observed in the $^{13}C\{^1H\}$ NMR spectrum and is directly analogous to that observed in related 2-phenylazophenyl-containing systems,[6] Chart 1. These data are all consistent with what has previously been observed for the keto/enol tautomerization process for 2-phenylazophenols,[17] but at odds with observations made by Antonov et al.[8] for analogous 2-hydroxy-Schiff bases.

Synthesis and Characterization of [Ru(CO){η^2-*C,N*-$C_6H_4C(H)$=NC_6H_4-4-R}$_2$(PPh_3)] (R = NMe_2, 2a; Me, 2b). After recrystallization of both **1a** and **1b** a second crop of orange crystals was obtained, and these were identified as [Ru(CO){η^2-*C,N*-$C_6H_4C(H)$=NC_6H_4-4-R}$_2$(PPh_3)] (R = NMe_2, **2a**; Me, **2b**), respectively. Both compounds were characterized by elemental analysis and infrared spectroscopy, Table 1, ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, Table 2, and for **2b** $^{13}C\{^1H\}$ NMR spectroscopy, Table 3. In addition both compounds were characterized by single-crystal X-ray diffraction studies;

(11) Kalinowski, H. O.; Berger, S.: Braun, S. *Carbon-13 NMR Spectroscopy*; Wiley-Interscience: New York, 1988.

(12) (a) Olivieri, A. C.; Wilson, R. B.; Paul, I. C.; Curtin, D. Y. *J. Am. Chem. Soc.* **1989**, *111*, 5525. (b) Lycka, A.; Snobl, D.; Machacek, V.; Vecera, M. *Org. Magn. Reson.* **1981**, *15*, 392. (c) Harris, R. K.; Jonsen, P.; Packer, K. J.; Campbell, C. D. *Magn. Reson. Chem.* **1986**, *24*, 977. (d) Hansen, P. E.; Lycka, A. *Magn. Reson. Chem.* **1986**, *24*, 772.

(13) Alder, M. J.; Cross, W. I.; Flower, K. R.; Pritchard, R. G. *J. Chem. Soc., Dalton Trans.* **1999**, 2563.

(14) March, J. *Advanced Organic Chemistry, Structure, Reaction, and Mechanisms*, 4th ed.; Wiley-Interscience: New York, 1992; p 280.

(15) Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, *25*, 121.

(16) (a) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25, and references therein. (b) Poulton, H. J. T.; Folting, K.; Streib, W. E.; K. G. Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 3190. (c) Heyn, R. H.; Macgregor, S. A.; Nadasdi, T. T.; Ogasawara, M.; Eisenstein, O.; Caulton, K. G. *Inorg. Chim. Acta* **1997**, *259*, 5. (d) Yandulov, D. V.; Caulton, K. G.; Bekova, N. V.; Shubina, E. S.; Epstein, L. M.; Khoroshun, D. M.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1998**, *120*, 12553. (e) Huang, D.; Gerard, H.; Clot, E.; Young, V.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1999**, *18*, 5441.

(17) (a) Bouwstra, J. A.; Schouten, A.; Kroon, J. *Acta Crystallogr. Sect. C* **1983**, *39*, 1121. (b) Whitaker, A. *J. Soc. Dyers Colour* **1978** 431. (c) Kelemen, J.; Moss, S.; Sauter, H.; Winkler, T. *Dyes Pigments* **1982**, *3*, 27. (d) Kelemen, J. *Dyes Pigments* **1981**, *2*, 73. (e) Burowoy, A.; Salem, A. G.; Thompson, A. R. *J. Chem. Soc.* **1952**, 4793. (f) Bekarek, V.; Rothschein, K.; Vetesnik, P.; Vecera, M. *Tetrahedron Lett.* **1968**, 3711. (g) Berrie, A. H.; Hampson, P.; Longworth, S. W.; Mathias, A. *J. Chem. Soc. B* **1968**, 1308.

Table 4. Crystal Data and Data Collection and Refinement Details for 1a,b and 2a,b

	1a·$2CH_3OH$	**1b**·$1.68CH_2Cl_2$	**2a**	**2b**·CH_2Cl_2
empirical formula	$C_{54}H_{53}ClN_2O_3P_2Ru$	$C_{52.68}H_{45.37}Cl_{4.37}NOP_2Ru$	$C_{49}H_{45}N_4OPRu$	$C_{48}H_{41}Cl_2N_2OPRu$
fw	976.44	1026.51	837.93	864.77
T, K	150(2)	150(2)	150(2)	150(2)
cryst size, mm	0.40 × 0.25 × 0.07	0.35 × 0.15 × 0.08	0.10 × 0.06 × 0.05	0.22 × 0.20 × 0.20
λ(Mo Kα), Å	0.71073	0.71073	0.71073	0.71073
cryst syst	orthorhombic	monoclinic	triclinic	monoclinic
space group	*Pna*21	*P*21/*n*	$P\bar{1}$	*P*21/*n*
a, Å	27.0186(9)	11.0538(2)	9.9947(3)	9.6899(19)
b, Å	10.7026(5)	27.3616(4)	11.7234(4)	21.164(4)
c, Å	16.3688(5)	15.6546(3)	17.9092(8)	20.198(4)
α, deg	90		82.1240(2)	
β, deg	90	90.8810(4)	78.533(2)	99.4510(5)
γ, deg	90		77.575(2)	
vol, Å^3	4733.4(3)	4734.17(14)	1998.64(13)	4085.9(14)
Z	4	4	2	4
d(calcd), Mg/m^3	1.370	1.440	1.392	1.406
F(000)	2024	2099	868	1776
2ϑ range, deg	2.91 to 27.46	2.98 to 27.47	2.98 to 27.55	3.06 to 27.47
total reflns colld	12 334	45 860	27 595	33 694
no. of ind reflns	6657	10 534	8938	9155
R(int)	0.0729	0.0957	0.1309	0.0781
compl to ϑ, %	94	97	96.8	97.7
no. of data/restrs/params	6657/1/555	10534/0/738	8938/0/685	9155/0/662
gof	1.003	0.985	0.894	1.020
R1 [$I>2\sigma(I)$]	0.0602	0.0457	0.0550	0.0427
wR2	0.1319	0.1020	0.0765	0.1033
R1 (all data)	0.0883	0.0772	0.1419	0.0617
wR2	0.1443	0.1140	0.0961	0.1132

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 1a and 1b.

1a	Ru(1)−C(1) 2.050(4); C(7)−N(1) 1.285(6); Ru(1)−N(1) 2.240(4); Ru(1)−C(16) 1.825(5); C(16)−O(1) 1.157(5); Ru(1)−Cl(1) 2.5158(11); Ru(1)−P(1) 2.3748(14); Ru(1)−P(2) 2.3856(14) C(1)−Ru(1)−N(1) 75.55(10); C(1)−Ru(1)−Cl(1) 170.07(12); N(1)−Ru(1)−C(16) 168.90(18); N(1)−Ru(1)−Cl(1) 92.62(10); Cl(1)−Ru(1)−C(16) 98.39(15); C(1)−Ru(1)−C(16) 91.48(19); P(1)−Ru(1)−P(2) 173.81(4)
1b	Ru(1)−C(1) 2.048(3); C(7)−N(1) 1.302(4); Ru(1)−N(1) 2.218(2);Ru(1)−C(15) 1.830(3); C(15)−O(1) 1.157(3); Ru(1)−Cl(1) 2.5196(7); Ru(1)−P(1) 2.3781(8); Ru(1)−P(2) 2.3761(8) C(1)−Ru(1)−N(1) 78.57(10); C(1)−Ru(1)−Cl(1) 170.19(8); N(1)−Ru(1)−C(15) 167.87(11); N(1)−Ru(1)−Cl(1) 92.13(6); Cl(1)−Ru(1)−C(15) 99.79(9); C(1)−Ru(1)−C(16) 89.65(12); P(1)−Ru(1)−P(2) 174.71(4)

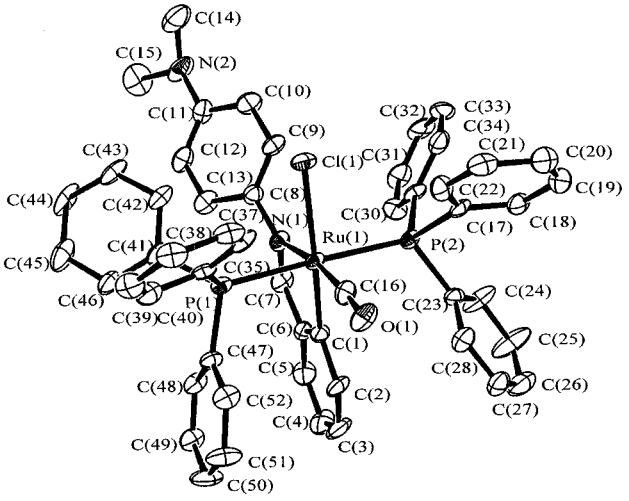


Figure 2. ORTEP representation of **1a** showing the atomic numbering scheme, thermal ellipsoids at 50%.

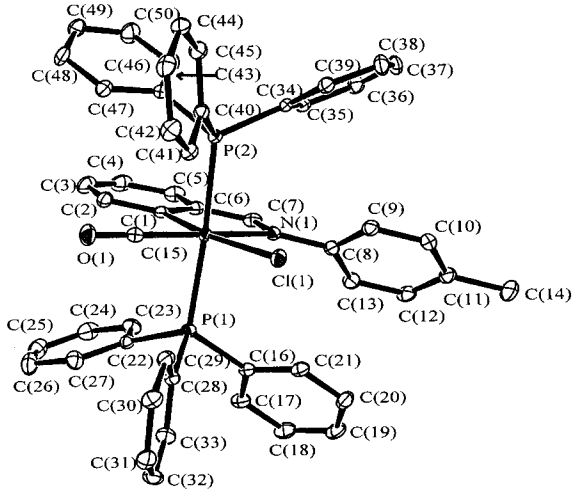


Figure 3. ORTEP representation of **1b** showing the atomic numbering scheme, thermal ellipsoids at 50%.

see Table 4 for data collection and processing parameters and Table 6 for selected bond lengths and angles. ORTEP[10] representations of the molecular structures of **2a** and **2b** are presented in Figures 4 and 5, respectively, and each shows the relevant atomic numbering scheme: the solvents of crystallization and protons have been omitted for clarity.

This second transfer of an organic group by the organomercurial has not been previously reported in detailed studies of related systems carried out by Roper et al.[18] So we repeated the reaction between [RuHCl(CO)(PPh_3)$_3$] and Hg{*o*-$C_6H_4C(H)$=NC_6H_4-4-R}$_2$ in a 1:2 ratio under the same conditions used to prepare **1a**−**d**. For (R = NO_2, I) only the monoimine-containing complexes **1c**−**d** were obtained in essentially the same yield as the original preparation. This we presume was due to the insolubility of **1a** and **1b** in toluene, which causes

Table 6. Selected Bond Lengths (Å) and Angles (deg) for 2a and 2b

2a	Ru(1)−C(1) 2.033(3); C(7)−N(1) 1.289(4); Ru(1)−N(1) 2.167(2); Ru(1)−C(21) 2.101(3); C(27)−N(3) 1.292(4); Ru(1)−N(3) 2.260(2); Ru(1)−C(16) 1.833(3); C(16)−O(1) 1.157(3); Ru(1)−P(1) 2.3910(9) C(1)−Ru(1)−N(1) 78.56(10); C(21)−Ru(1)−N(3) 77.67(10); N(1)−Ru(1)−N(3) 92.39(8); C(1)−Ru(1)−C(21) 91.06(11); C(1)−Ru(1)−N(3) 166.42(11); P(1)−Ru(1)−C(21) 179.24(8); N(1)−Ru(1)−C(16) 167.60(12)
2b	Ru(1)−C(1) 2.042(3); C(7)−N(1) 1.293(3); Ru(1)−N(1) 2.177(2); Ru(1)−C(21) 2.098(2); C(27)−N(2) 1.289(3); Ru(1)−N(2) 2.259(2); Ru(1)−C(15) 1.820(3); C(15)−O(1) 1.161(3); Ru(1)−P(1) 2.3947(7) C(1)−Ru(1)−N(1) 78.85(9); C(21)−Ru(1)−N(2) 77.10(9); N(1)−Ru(1)−N(2) 92.92(8); C(1)−Ru(1)−C(21) 89.67(10); C(1)−Ru(1)−N(2) 165.21(8); P(1)−Ru(1)−C(21) 178.09(7); N(1)−Ru(1)−C(15) 168.02(10)

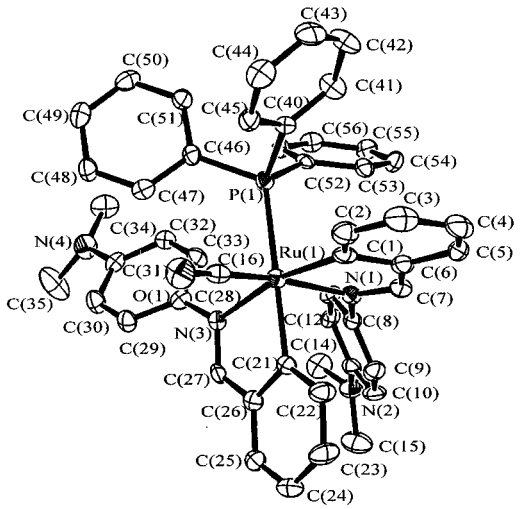


Figure 4. ORTEP representation of **2a** showing the atomic numbering scheme, thermal ellipsoids at 50%.

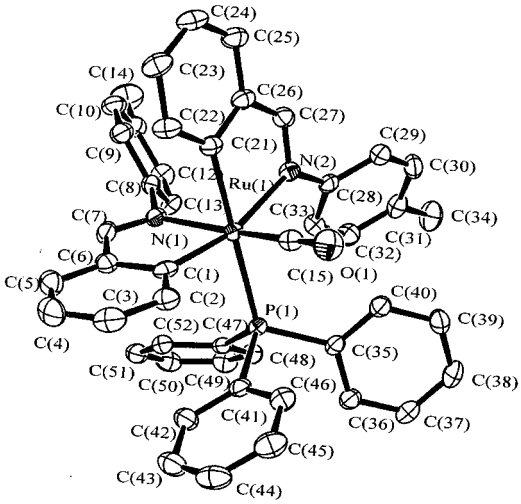
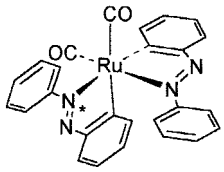


Figure 5. ORTEP representation of **2b** showing the atomic numbering scheme, thermal ellipsoids at 50%.

them to precipitate from solution on formation and are thus unable to react with the additional diorganomercurial. When R = NMe_2, **1a** was obtained in 75% yield along with a small amount of **2b**, again essentially the same result as in the original preparation. However, on treatment of [RuHCl(CO)(PPh_3)$_3$] with Hg{*o*-$C_6H_4C(H)$=NC_6H_4-4-Me}$_2$, **2b** was isolated in a reasonable yield of 65%. Several repetitions of these reactions gave the same results. It is clear that the transfer of the second organic group is not as facile as the first, and we are currently investigating this reaction further to try and optimize the conditions.

Chart 2



IV

All of the NMR data in Tables 2 and 3 are consistent with the formulation of the new complexes. The assignments of the imine CH resonance in the proton spectrum and the carbon atoms of the * ruthenated imine ring, Scheme 1, were aided by the larger magnitude of the *trans* coupling to the spin-active phosphorus nucleus. It is useful to note here that the ruthenated-imine, which contains more quinoid character (see crystallographic discussion), has the lower field C(1) resonance as expected.[6,16]

Solid-State Structures of 1a, 1b, 2a, and 2b. The Ru(1)−C(1) bond lengths for **1a** and **1b** of 2.050(4) and 2.048(3) Å, respectively, are comparable with, but longer than, those observed in the structures of [RuCl(CE)(η^2-*C,N*-C_6H_5N=NC_6H_5)(PPh_3)$_2$] {E = O, 2.021(7) Å; and E = S, 2.029(7) Å}.[6] Similarly, the Ru(1)−N(1) distances of 2.240(4) and 2.218(2) Å are comparable to those observed for the azo-containing analogues {E = O, 2.184(6) Å; and E = S, 2.232(6) Å}. The angles about the equatorial plane are influenced by the tight C(1)−Ru(1)−N(1) angles of 75.55(10)° and 78.57(10)°, respectively, having the effect of opening up the other angles. The structures of **2a** and **2b** are essentially the same, and the discussion will focus on **2a.** The complex contains two cyclometalated imine ligands, which show distinct structural differences from each other and which are remarkably similar to the differences displayed by the azo-containing complex **IV** (Chart 2) reported by Bruce et al.[19] The Ru(1)−C(1) bond length of 2.033(3) Å is "slightly" shorter than that observed in **1a**, and Ru(1)−C(21) at 2.101(3) Å is slightly longer. Similarly Ru(1)−N(1) at 2.167(2) Å is shorter than for **1a**, and Ru(1)−N(3) at 2.260(2) Å is similar. The bond lengths reported in Bruce's structure for comparison are Ru−C 2.052(7) Å; Ru−C* 2.103(8) Å; Ru−N 2.103(6) Å; Ru−N* 2.155(7) Å. In both the imine and azo-containing structures the similarity of the structural differences in the two cyclometalated ligands is striking. This

(18) (a) Rickard, C. E. F.; Roper, W. R.; Taylor, G. E.; Walters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1990**, *389*, 375. (b) Clark, G. R.; Hedford, C. E. L.; Roper, W. R.; Wright, L. J.; Yap, V. P. D. *Inorg. Chim. Acta* **1994**, *220*, 261. (c) Clark, G. R.; Ng, M. M. P.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1995**, *491*, 219. (d) Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J.; Yap, V. P. D. *Inorg. Chim. Acta* **1996**, *251*, 65. (e) Clark, A. M.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1997**, *545*−*546*, 619. (f) Clark, A. M.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *Organometallics* **1998**, *17*, 4535. (g) Clark, A. M.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *Organometallics* **1999**, *18*, 2813. (h) Clark, A. M.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **2000**, *598*, 262.
(19) Bruce, M. I.; Shawkataly, O. B.; Snow, M. R.; Tiekink, E. R. T. *Acta Crystallogr. Sect. C* **1987**, *43*, 243.

suggests, just like the cyclometalated 2-phenylazophenyl ligand, that the cycloruthenated imine is capable of behaving as both a π-acceptor and π-donor via a *cis*-push−pull effect: a detailed justification for this can be found in a previous report.[6a] These structural data are therefore consistent with a contribution to the overall structure of the quinoid form. Bearing in mind the results of the Hammett plot, it appears that the relative contribution is dependent upon the imine ring substituents and that the more electron withdrawing the group, the greater the contribution of the quinoid form: this is consistent with all previous reports for 2-phenylazophenols.[6,12,17]

Conclusion

We have prepared a series of cycloruthenared 2-(phenylimino)phenyl-containing complexes and have shown that the $^{13}C\{^1H\}$ NMR resonance of the ruthenated carbon can be used as a probe of the relative effect substituents have on the position of the keto/enol tautomeric process in 2-hydroxyphenyl-Schiff bases. The data are consistent with those previously reported for analogous azobenzene-containing systems;[6,12,17] the quinoid form is favored by electron-withdrawing groups and is the reverse conclusion contained in the recent report of Antonov et al.,[8] who suggest that the quinoid form is favored by electron-releasing substituents.

Experimental Section

General Comments. All solvents, except alcohols, were dried by refluxing over an appropriate drying agent (toluene, Na; CH_2Cl_2, P_4O_{10}; hexane, NaK) and distilled prior to use. $[RuHCl(CO)(PPh_3)_3]$ and $Hg\{o\text{-}C_6H_4CH{=}NPh\text{-}4\text{-}R\}_2$ were prepared according to literature procedures;[9,20] all other chemicals were obtained from commercial sources and used as received except for $RuCl_3$, which was loaned by Johnson Matthey. Infrared spectra were recorded as Nujol mulls between KBr plates on a Nicolett 5PC spectrometer. ^1H NMR (200.2 MHz) and $^{31}P\{^1H\}$ NMR (81.3 MHz) were recorded on a Bruker DPX200 spectrometer, and $^{13}C\{^1H\}$ NMR (100.55 MHz) were recorded on a Brucker DPX400 spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to $CHCl_3$ ($\delta = 7.26$) and $CHCl_3$ ($\delta = 77.0$), and $^{31}P\{^1H\}$ NMR were referenced externally to 85% H_3PO_4 ($\delta = 0.0$). Elemental analyses were performed by the Microanalytical Service, Department of Chemistry, UMIST; solvates of crystallization were confirmed by repeated elemental analysis and confirmed by ^1H NMR. Melting points were obtained using a Griffin melting point apparatus and are uncorrected. The syntheses of all complexes were carried out under a dinitrogen atmosphere using standard Schlenk techniques. Workups were generally carried out in the open unless otherwise stated.

Synthesis of $[RuCl(CO)(\eta^2\text{-}C,N\text{-}C_6H_4CH{=}NPh\text{-}4\text{-}NMe_2)(PPh_3)_2]$ (1a). Caution: *use of an organomercurial reagent*. To $[RuHCl(CO)(PPh_3)_2]$ (0.5 g, 0.52 mmol) suspended in toluene (20 mL) was added $Hg(o\text{-}C_6H_4CH{=}NPh\text{-}4\text{-}NMe_2)_2$ (0.35 g, 0.58 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 and the solvent removed under reduced pressure. The crude material was then extracted with hot hexane (3 × 25 mL) to remove the imine and PPh_3. Recrystallization of the remaining yellow solid from CH_2Cl_2/EtOH afforded **1a**·CH_2Cl_2 in good yield; see Table 1 for physical and analytical data.

In an analogous manner compounds **1b**−**d** were prepared. See Table 1 for physical and analytical data.

Synthesis of $[Ru(CO)(\eta^2\text{-}C,N\text{-}C_6H_4CH{=}NPh\text{-}4\text{-}Me)_2(PPh_3)]$(2b). Caution: *use of an organomercurial reagent*. To **1b** (0.25 g, 0.29 mmol) dissolved in toluene (20 mL) was added $Hg(o\text{-}C_6H_4CH{=}NPh\text{-}4\text{-}Me)_2$ (0.18 g, 0.31 mmol) and the solution heated to reflux for 18 h. After cooling, the solution was filtered through Celite, and the solvent removed under reduced pressure, followed by extraction of the crude material with hot hexane (3 × 25 mL), afforded crude **2b** as an orange powder. Recrystallization from CH_2Cl_2/EtOH afforded an analytically pure sample. See Table 1 for physical and analytical data.

X-ray Crystallography. All crystals were grown by dissolving approximately 10 mg of the compound in 0.2 mL of CH_2Cl_2 in a glass vial (10 mm × 50 mm) and layering on top MeOH for **1a** and EtOH for **1b** and **2a**,**b** and leaving the mixture stand for several days at room temperature.

All X-ray diffraction measurements were carried out on the National Crystallographic Service Nonius Kappa CCD diffractometer, University of Southampton, England. Monochromatic X-rays generated by a Nonius FR591 rotating anode source were used to record phi scans and omega scans to fill the Ewald sphere. An Oxford crysostream cooler was used to maintain the crystals at 150 K. The structures were solved using direct methods and refined using full-matrix least-squares (SHELX-97).[21] Crystallographic details are presented in Table 4

Acknowledgment. J.E.W. thanks the EPSRC for the award of a postgraduate studentship, and K.R.F. thanks the EPSRC National Crystallographic Service, Department of Southampton, for data collections for compounds **1a**, **1b**, **2a**, and **2b** through project no. 01XR10 and Johnson Matthey for the loan of $RuCl_3$.

Supporting Information Available: Tables of atomic coordinates, displacement parameters, and bond distances and angles for **1a**−**d** and **2a**,**b** are available free of charge via the Internet at http://pubs.acs.org.

OM010883I

(20) Ahmad, N.; Levison, J. J.; Robinson S. D.; Uttley, M. J. *Inorg. Synth.* **1974**, *15*, 48.

(21) Sheldrick, G. M. *SHELX-97*, Programs for crystal structure analysis (release 97-2); University of Göttingen, 1998.