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# Directed Metal Oxidation Levels in Azo–Ruthenium Cyclometalates. Synthesis and Structure of a Trivalent Family

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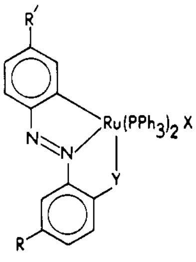
Substituted azobenzenes react with $Ru(PPh_3)_3X_2$ (X = Cl, Br) to afford complexes (**3**–**6**) of type A in which the metal oxidation state is directed by the donor group Y. When Y = O, the metal is trivalent (**3**, **4**, **6**), and when Y = OMe, SMe, it is bivalent (**5**). The Y = O complexes represent the first example of cyclometalated ruthenium(III). The structure of **4b**, i.e., A with Y = O, R = Me, R′ = H, and X = Br, $RuC_{49}H_{40}N_2OP_2Br$, has been determined by X-ray crystallography. The crystals of **4b** are monoclinic in the space group $P2_1/c$ with $Z = 4$ and unit cell dimensions $a = 12.361$ (2) Å, $b = 19.091$ (3) Å, $c = 18.560$ (4) Å, $\beta = 108.30$ (1)°, and $V = 4158.3$ (13) Å$^3$. The structure was refined to $R = 0.046$ and $R_w = 0.059$. The azo ligand and the bromide are bound in approximately planar C, N, O, Br tetracoordination, and the $PPh_3$ ligands occupy trans positions. The coordination sphere is highly distorted octahedral. The EPR spectra of **4b** and other Y = O complexes (low-spin $d^5$) are uniformly rhombic (77 K, frozen solution). The magnitude of axial ($\Delta$) and rhombic ($V$) distortion parameters and the optical transition energies ($\nu_1$ and $\nu_2$) among Kramers doublets are computed to be ~12 000, ~9000, ~7000, and ~16 000 $cm^{-1}$, respectively. The $\nu_1$ transition is experimentally observed at ~8000 $cm^{-1}$. Results are rationalized in terms of the orbital energy order $d_{xy} > d_{xz} > d_{yz}$. The redox potentials of the Y = O complexes in dichloromethane lie in the following ranges (vs. SCE): ruthenium(IV)–ruthenium(III), +1.0 to +0.6 V; ruthenium(III)–ruthenium(II), −0.3 to −0.7 V. In contrast, the Y = OMe, SMe complexes display only the latter couple but at much higher potentials: ~0.7 V (OMe) and ~1.0 V (SMe).



A

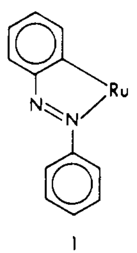
## Introduction

The usefulness of ruthenium as a catalyst in photochemical and thermal processes depends upon its ability to vary oxidation states. Indeed, variable valence pervades the chemistry of ruthenium. Yet virtually all the known cyclometalated derivatives of ruthenium involve the bivalent state.[2-7] We therefore set out to explore possible ways for modulating the metal oxidation state in such species.

Herein we apply an approach based on ligand modification to a group of azobenzene complexes. Both ruthenium(III) and ruthenium(II) cyclometalates have been isolated, and the formation of an unstable ruthenium(IV) species in solution has been indicated. The molecular and electronic structures of the trivalent complexes are probed with the help of X-ray crystallography in combination with EPR and near-IR spectroscopy. The relative stabilities of oxidation states are probed electrochemically.

## Results and Discussion

**A. Formation of Complexes.** The affinity of ruthenium for the azo function is well-documented.[7-9] It is also known that azobenzene is readily ortho ruthenated to form the chelate ring **1**.[6,10]



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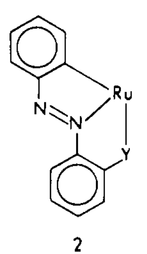

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(1) (a) Department of Inorganic Chemistry, Indian Association for the Cultivation of Science. (b) Department of Magnetism, Indian Association for the Cultivation of Science. (c) Jadavpur University.

(2) A large number of compounds are reported in the review by: Bennett, M. A.; Bruce, M. I.; Matheson, T. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 4, Section 32.3, pp 691–820. Selected references not appearing in this collection are cited below.[3-6]

(3) C, N coordination: (a) Jameson, G. B.; Muster, A.; Robinson, S. D.; Wingfield, J. N.; Ibers, J. A. *Inorg. Chem.* **1981**, *20*, 2448–2456. (b) Patrick, J. M.; White, A. H.; Bruce, M. I.; Beatson, M. J.; Black, D. S. C.; Deacon, G. B.; Thomas, N. C. *J. Chem. Soc., Dalton Trans.* **1983**, 2121–2124. (c) Reveco, P.; Schmehl, R. H.; Cherry, W. R.; Fronczek, F. R.; Selbin, J. *Inorg. Chem.* **1985**, *24*, 4078–4082. (d) Nouoyama, M. *Inorg. Chim. Acta* **1986**, *115*, 169–172.

(4) C, O coordination: (a) McGuiggan, M. F.; Pignolet, L. H. *Inorg. Chem.* **1982**, *21*, 2523–2526. (b) Saunders, D. R.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1984**, 2133–2136. (c) Gopinathan, S.; Joseph, K.; Gopinathan, C. *J. Organomet. Chem.* **1984**, *269*, 273–275. (d) Bruce, M. I.; Duffy, D. N.; Humphery, M. G.; Swincer, A. G. *J. Organomet. Chem.* **1985**, *285*, 383–397.

(5) C, P coordination: (a) Garbukas, M. F.; Kasper, J. S.; Lewis, L. N. *J. Organomet. Chem.* **1984**, *276*, 241–248. (b) Rosete, R. O.; Cole-Hamilton, D. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1984**, 2067–2071. (c) Lewis, L. N. *J. Am. Chem. Soc.* **1986**, *108*, 743–749.

(6) A presumably dimeric trivalent complex is reported by: Gilbert, J. D.; Rose, D.; Wilkinson, G. *J. Chem. Soc. A* **1970**, 2765–2769.

(7) Unstable electrogenerated ruthenium(III) species are described by: (a) Mahapatra, A. K.; Datta, S.; Goswami, S.; Mukherjee, M.; Mukherjee, A. K.; Chakravorty, A. *Inorg. Chem.* **1986**, *25*, 1715–1721. (b) Mukherjee, A. K.; Mukherjee, M.; Das, P. K.; Mahapatra, A. K.; Goswami, S.; Chakravorty, A. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *C42*, 793–796.

(8) Arylazo oxime complexes: (a) Chakravarty, A. R.; Chakravorty, A. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 307–310. (b) Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 3138–3143. (c) Chakravarty, A. R.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1983**, 961–966. (d) Chakravarty, A. R.; Chakravorty, A.; Cotton, F. A.; Falvello, L. R.; Ghosh, B. K.; Thomas, M. *Inorg. Chem.* **1983**, *22*, 1892–1896.

(9) 2-(Arylazo)pyridine complexes: (a) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 2246–2250. (b) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1982**, *21*, 2737–2742. (c) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *J. Chem. Soc., Chem. Commun.* **1982**, 1288–1289. (d) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1983**, *22*, 602–609. (e) Goswami, S.; Mukherjee, R. N.; Chakravorty, A. *Inorg. Chem.* **1983**, *22*, 2825–2832. (f) Ghosh, P.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1985**, 361–367. (g) Mahapatra, A. K.; Ghosh, B. K.; Goswami, S.; Chakravorty, A. *J. Indian Chem. Soc.* **1986**, *63*, 101–104.

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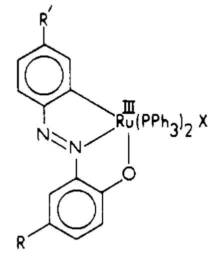
**Table I.** Spectral, Electrochemical, and Microanalytical Data

| compd | electronic spectral data[a] $\lambda_{max}$, nm ($\epsilon$,[b] $M^{-1}\ cm^{-1}$) | electrochemical data[c-e] $E°_{298}$, V: Ru(IV)–Ru(III) | electrochemical data[c-e] $E°_{298}$, V: Ru(III)–Ru(II) | anal. data[f]: % C | anal. data[f]: % H | anal. data[f]: % N |
|---|---|---|---|---|---|---|
| **3a** | 640 (2600), 430 (5000), 370 (9300), 270 (26 000) | 0.76 | −0.57 | 67.17 (67.24) | 4.39 (4.44) | 3.25 (3.20) |
| **3b** | 647 (3300), 415 (5600), 350 (10 600), 275 (30 100) | 0.70[h] | −0.55[i] | 67.56 (67.54) | 4.63 (4.59) | 3.30 (3.22) |
| **3c** | 642 (3500), 412 (5800), 350 (12 000), 270 (30 000) | 0.65 | −0.59 | 67.97 (67.83) | 4.79 (4.75) | 3.22 (3.17) |
| **3d** | 630 (3900), 420[g] (6100), 358 (13 300), 315 (15 900), 270 (31 700) | 0.58 | −0.59 | 66.66 (66.62) | 4.71 (4.66) | 3.15 (3.11) |
| **3e** | 652 (3700), 430 (6300), 350[g] (11 000), 270 (25 000) | 0.76 | −0.47 | 65.08 (64.96) | 4.33 (4.31) | 3.11 (3.09) |
| **3f** | 745[g] (4200), 710 (4300), 440[g] (6700), 670 (12 700), 272 (31 800) | 0.90 | −0.35 | 64.36 (64.22) | 4.37 (4.26) | 3.10 (3.06) |
| **4a** | 640 (2500), 425 (6000), 370 (9700), 265 (27 300) | 0.74 | −0.55 | 63.83 (63.92) | 4.39 (4.42) | 3.15 (3.11) |
| **4b** | 650 (3400), 410 (6300), 365 (10 400), 272 (28 400) | 0.70 | −0.53 | 64.27 (64.25) | 4.40 (4.37) | 3.10 (3.06) |
| **4c** | 640 (3200), 415 (5800), 366 (10 200), 268 (27 900) | 0.68 | −0.61 | 64.62 (64.58) | 4.41 (4.52) | 3.09 (3.01) |
| **4d** | 630 (4300), 410[g] (6500), 355 (10 100), 275 (27 800) | 0.65 | −0.62 | 63.53 (63.49) | 4.43 (4.44) | 2.95 (2.96) |
| **4e** | 652 (3400), 410 (6100), 350 (9800), 275 (30 200) | 0.77 | −0.45 | 62.08 (61.92) | 4.06 (4.11) | 3.02 (2.95) |
| **4f** | 745[g] (4700), 710 (5000), 435[g] (7100), 380 (12 600), 272 (32 100) | 0.96 | −0.35 | 61.29 (61.24) | 4.07 (4.06) | 4.39 (4.37) |
| **5a** | 620 (700), 455 (5300), 340 (11 900), 255 (17 400) | | 0.72 | 67.40 (67.46) | 4.82 (4.70) | 3.25 (3.21) |
| **5b** | 610 (800), 455 (5400), 345 (13 300), 260 (20 500) | | 0.73[j] | 67.68 (67.75) | 4.88 (4.85) | 3.14 (3.16) |
| **5c** | 620 (1000), 455 (3400), 350 (11 100), 255 (21 400) | | 0.97 | 66.24 (66.25) | 4.63 (4.62) | 3.28 (3.15) |
| **6** | 642 (2700), 440 (7450), 370 (11 700), 310 (15 400), 270 (30 100) | 0.73 | −0.52 | 66.08 (66.00) | 4.41 (4.35) | 3.13 (3.20) |

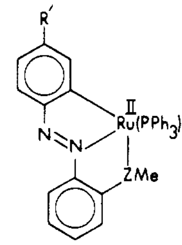
[a] In dichloromethane. [b] Extinction coefficient. [c] Conditions: solvent, dichloromethane; supporting electrolyte, TEAP (0.1 M); working electrode, platinum; reference electrode, SCE; solute concentration, ~$10^{-3}$ M. [d] Cyclic voltammetric data: $E°_{298} = 0.5(E_{pa} + E_{pc})$, where $E_{pa}$ and $E_{pc}$ are anodic and cathodic peak potentials, respectively; scan rate 50 mV $s^{-1}$. [e] Constant-potential coulometry (oxidation done at potential $E°_{298}$ + 200 mV, reduction at $E°_{298}$ − 200 mV) was performed in selected cases: $n = Q/Q'$, where $Q'$ is the calculated coulomb count for 1e transfer and $Q$ is the coulomb count found after exhaustive electrolysis of 0.01 mmol of solute. [f] Calculated values are in parentheses. [g] Shoulder. [h] $n$ = 1.02. [i] $n$ = 1.03. [j] $n$ = 1.07.

If the bicyclic system **2** can be assembled, different metal oxidation states could possibly be stabilized by choosing the donor substituent Y for strong specific-oxidation-state affinities. For example, phenoxide oxygen has[11] a high affinity for ruthenium(III) while thioether sulfur prefers[7] ruthenium(II). This simple strategy has successfully afforded the first systematic group of stable mononuclear ruthenium(III) cyclometalates (Y = O). The corresponding Y = OMe and SMe species contain bivalent metal.

Fifteen complexes (**3a–f**, **4a–f**, and **5a–c**) were synthesized.



| R | R' | X=Cl | X=Br |
|---|---|---|---|
| H | H | 3a | 4a |
| Me | H | 3b | 4b |
| Me | Me | 3c | 4c |
| Me | OMe | 3d | 4d |
| Me | Cl | 3e | 4e |
| Me | NO2 | 3f | 4f |



| R' | Z | |
|---|---|---|
| H | O | 5a |
| Me | O | 5b |
| H | S | 5c |

The general method of synthesis consisted of heating $Ru(PPh_3)_3X_2$ (X = Cl, Br)[12] and the azo ligand in ethanol. The resultant green solution afforded the dark-colored solid chelate, which is soluble in dichloromethane and chloroform.

The bivalent complexes **5** are diamagnetic as expected ($t_2^6$). The two $PPh_3$ units are believed to be trans in analogy with the known structures[3a,4a] of other cyclometalated $Ru^{II}(PPh_3)_2$ systems.

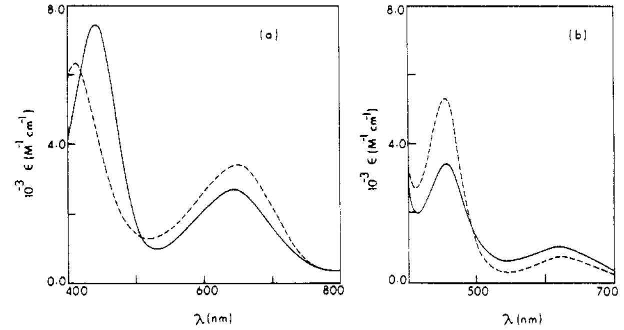


**Figure 1.** (a) Electronic spectra in dichloromethane of ruthenium(III) complexes: (---) **4b**, CNOBr donors; (—) **6**, CNOCl donors. (b) Electronic spectra of Ruthenium(II) complexes: (---) **5a**, CN(OMe)Cl donors; (—) **5c**, CN(SMe)Cl donors.

**Table II.** Bulk Magnetic Moments[a] and EPR *g* Values[b]

| compd | $\mu_{eff}$, $\mu_B$ | $g_1$ | $g_2$ | $g_3$ |
|---|---|---|---|---|
| **3a** | 1.92 | 2.298 | 2.106 | 1.962 |
| **3b** | 1.94 | 2.282 | 2.108 | 1.958 |
| **3c** | 1.97 | 2.280 | 2.118 | 1.963 |
| **3d** | 1.95 | 2.310 | 2.116 | 1.958 |
| **3e** | 1.93 | 2.277 | 2.112 | 1.961 |
| **3f** | 1.96 | 2.288 | 2.113 | 1.960 |
| **4a** | 1.97 | 2.315 | 2.120 | 1.972 |
| **4b** | 1.91 | 2.289 | 2.126 | 1.969 |
| **4c** | 1.90 | 2.287 | 2.128 | 1.970 |
| **4d** | 1.91 | 2.323 | 2.116 | 1.968 |
| **4e** | 1.94 | 2.283 | 2.120 | 1.968 |
| **4f** | 1.95 | 2.300 | 2.115 | 1.966 |
| **6** | 1.90 | 2.304 | 2.096 | 1.948 |

[a] In solid states at 298 K. [b] Measurements were made in 1:1 chloroform–toluene glass at 77 K.

In the synthesis of the trivalent complexes (**3**, **4**) from $Ru^{II}(PPh_3)_3X_2$, chelation is attended with metal oxidation. In view of the low (vide infra) ruthenium(III)–ruthenium(II) reduction potentials of the chelates, aerial oxygen is the most probable oxidant. The chloro complexes display a single RuCl stretch in the range 320–330 $cm^{-1}$, which is expectedly absent in **4**. The complexes absorb strongly in the visible region presumably due to charge-transfer transitions. The spectra are characteristically different from those of **5** (Figure 1, Table I). The trivalent complexes are low-spin $d^5$ one-electron paramagnets with rhombic EPR spectra in 1:1 chloroform–toluene glassy solution (77 K).

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(10) (a) Bruce, M. I.; Iqbal, M. Z.; Stone, F. G. A. *J. Chem. Soc. A* **1970**, 3204–3209. (b) Bruce, M. I.; Iqbal, M. Z.; Stone, F. G. A. *J. Organomet. Chem.* **1971**, *31*, 275–281. (c) Bruce, M. I.; Iqbal, M. Z.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 2820–2828. (d) Bruce, M. I.; Iqbal, M. Z.; Stone, F. G. A. *J. Chem. Soc. D* **1970**, 1325–1327.

(11) Lahiri, G. K.; Bhattacharya, S.; Ghosh, B. K.; Chakravorty, A., unpublished results.

(12) Stephenson, T. A.; Wilkinson, G. *J. inorg. Nucl. Chem.* **1966**, *28*, 945–956.

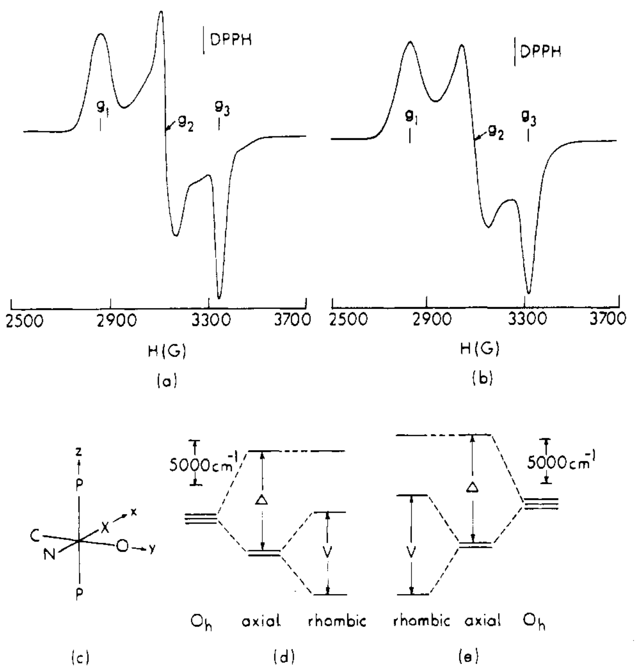


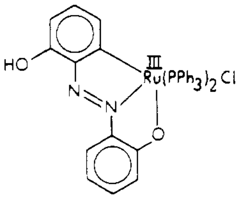
**Figure 2.** X-Band EPR spectra in 1:1 chloroform–toluene glass (77 K), system of axes, and computed $t_2$ splittings: (a) spectrum of **3a**, CNOCl donors; (b) spectrum of **4a**, CNOBr donors; (c) system of axes; (d) splitting of **3a**; (e) splitting of **4a**.

**Table III.** Selected Bond Distances (Å) and Angles (deg) in **4b** (with Estimated Standard Deviations in Parentheses)

| | | | |
|---|---|---|---|
| Ru–Br | 2.485 (1) | Ru–N(1) | 2.007 (5) |
| Ru–P(1) | 2.407 (2) | Ru–C(8) | 2.028 (8) |
| Ru–P(2) | 2.395 (2) | N(1)–N(2) | 1.276 (8) |
| Ru–O | 2.112 (5) | O–C(1) | 1.322 (8) |
| P(1)–Ru–C(8) | 92.2 (2) | N(1)–Ru–C(8) | 75.7 (2) |
| P(1)–Ru–N(1) | 96.0 (2) | O–Ru–N(1) | 78.4 (2) |
| P(1)–Ru–O | 86.4 (1) | Br–Ru–O | 103.4 (1) |
| P(1)–Ru–Br | 85.9 (1) | Br–Ru–C(8) | 102.7 (2) |
| P(2)–Ru–C(8) | 90.5 (2) | P(1)–Ru–P(2) | 174.4 (1) |
| P(2)–Ru–N(1) | 89.5 (2) | O–Ru–C(8) | 153.7 (2) |
| P(2)–Ru–O | 93.3 (2) | Br–Ru–N(1) | 177.5 (2) |
| P(2)–Ru–Br | 88.7 (1) | | |

EPR spectra are shown in Figure 2 and the data summarized in Table II. These will be examined further in a later section of this work.

The reaction of Ru(PPh$_3$)$_3$Cl$_2$ with 2,2′-dihydroxyazobenzene affords **6** and the isomeric complex **7**. In **6** a phenolic OH stretch



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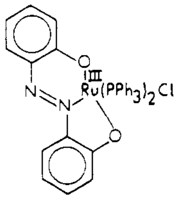

7

is clearly observable at 3430 cm$^{-1}$ and its spectral and magnetic properties are entirely analogous to those of **3** (Figure 1, Tables I and II). The red complex **7** does not involve cyclometalation and will not be considered any further in this work.

**B. Crystal and Molecular Structure of 4b.** A view of **4b** is displayed in Figure 3, and selected bond parameters are listed in Table III. The two tertiary phosphine molecules are located trans to each other in a distorted-octahedral coordination sphere. The hydroxyazobenzene ligand acts in a tridentate fashion (**2**), binding the metal center at O, N(1), and C(8).

The entire tridentate ligand skeleton together with the metal is approximately planar with no atom deviating from the least-squares plane by >0.15 Å. Among the four constituent rings of this skeleton, the two benzene rings are highly planar as is the chelate ring of Ru, N(1), N(2), C(9), and C(8), where all deviations are <0.013 Å. The ring of Ru, O, C(1), C(2), and N(1) is also a good plane (deviations <0.065 Å). The dihedral angle between the two chelate rings is 3.4 (2)°.

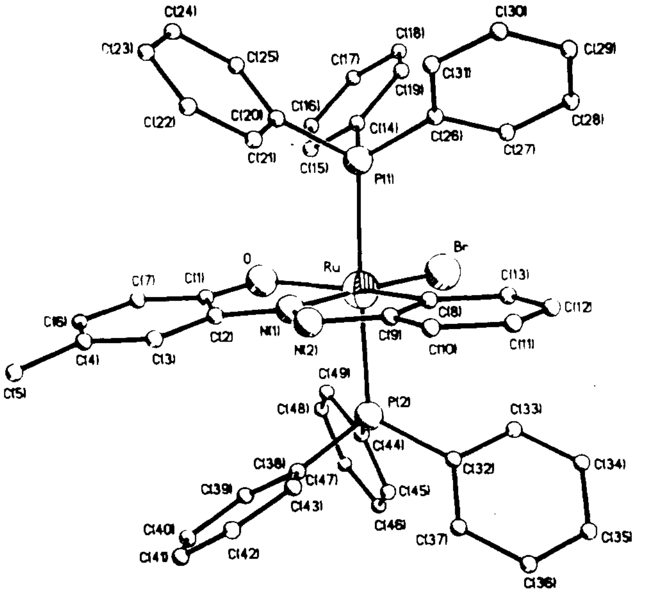

**Figure 3.** Perspective drawing of the molecular structure of **4b**.

As can be seen from bond angle data (Table III), the metal coordination sphere is rather severely distorted from octahedral geometry. For example, the O–Ru–C(8) angle shows a large (~26°) deviation from 180°. However, the P(1)–Ru–P(2) and N(1)–Ru–Br angles lie within 6° of the optimum value. In the first case *both* the ligand atoms belong to chelate rings while in the second case at least one atom is not part of the chelate.

The distortion of the coordination sphere is caused by the two acute (~77°) bite angles of the two juxtaposed chelate rings. The distortion can also be depicted by the degree of planarity of three groups of atoms. Two sets of these, Ru, O, N(1), C(8), Br and Ru, N(1), Br, P(1), P(2), separately define two nearly orthogonal (dihedral angle 92.9 (1)°) least-squares planes with no atom deviating by >0.08 Å in either case. On the other hand, in the third group, Ru, O, C(8), P(1), P(2), the deviations of O and C(8) are respectively 0.25 and 0.71 Å from the least-squares plane.

The Ru–Br distance of 2.485 (1) Å in **4b** can be compared with 2.514 (5) Å, found in a RuBr$_6^{3-}$ salt.[13] The lengths of the Ru–P bonds in our complex lie close to the value (2.414 (0) Å) found in RuCl$_2$(PPh$_3$)$_2$(C$_6$H$_5$CO$_2$), which has trans phosphine moieties.[14] The Ru–C(8) distance of 2.028 (9) Å in **4b** appears reasonable, although no data for other ruthenium(III) cyclometalates are available for comparison. In ruthenium(II) cyclometalates Ru–C distances lie in the range 2 ± 0.1 Å.[3a,c,4a,7b] In a dimeric metal-metal-bonded ruthenium(III) species containing coordinated phenyl groups the Ru–C length is 2.104 (6) Å.[15] The Ru$^{III}$–O bond distances in salts of Ru(OH$_2$)$_6^{3+}$ and *trans*-Ru(bpy)$_2$(OH)(OH$_2$)$^{2+}$ are respectively 2.029 (7) and 2.007 (3) Å.[16,17] The corresponding bond in **4b** is significantly longer. The trans effect of the C(8) atom could be a contributing factor, but a definitive assessment is vitiated by the lack of structural information on other compounds having the Ru$^{III}$–O(phenolato) bond. Lengthening of bonds trans to Ru–C is however documented in ruthenium(II)

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(13) Drew, M. G. B.; Rice, D. A.; Jimewell, C. W. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 59–62.

(14) McGuiggan, M. F.; Pignolet, L. H. *Cryst. Struct. Commun.* **1981**, *10*, 1227–1232.

(15) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 6409–6413.

(16) Bernhard, P.; Burgi, H. B.; Hauser, J.; Lehmann, H.; Ludi, A. *Inorg. Chem.* **1982**, *21*, 3936–3941.

(17) Durham, B.; Wilson, S. R.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 600–607.

**Table IV.** Assignments of $g$ Values and Values of Parameters[a]

| compd | soln no. | $g_x$ | $g_y$ | $g_z$ | $p$ | $q$ | $r$ | $k^b$ | $\Delta/\lambda$ | $V/\lambda$ | $\nu_1/\lambda$ | $\nu_2/\lambda$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **3e** | 1 | −2.277 | −2.112 | 1.961 | 0.080 | 0.996 | 0.028 | 0.924 | 10.593 | −7.829 | 6.746 (7.9)[c] | 14.612 |
| | 2 | −2.277 | −2.112 | −1.961 | 0.800 | 0.599 | 0.016 | 1.089 | 0.084 | −0.062 | 1.469 | 1.536 |
| **4b** | 1 | −2.289 | −2.126 | 1.969 | 0.069 | 0.997 | 0.024 | 1.122 | 12.180 | −8.713 | 7.880 (8.8)[c] | 16.628 |
| | 2 | −2.289 | −2.126 | −1.969 | 0.800 | 0.599 | 0.016 | 1.098 | 0.086 | −0.061 | 1.469 | 1.536 |

[a] Symbols have the same meaning as in the text. [b] If admixture with excited states ($t_2^4e$) is considered, the true orbital reduction factor is expected to be ~20% less than $k$ (see ref 7a and 22b). The true factors are therefore all <1. [c] Values obtained by Gaussian analysis of experimental spectra ($\lambda = 1000$ cm$^{-1}$, see text).

systems.[3a,7b] The Ru–N(1) distance in **4b** merits scrutiny. No information on the Ru$^{III}$–N(azo) bond lengths is available in the literature, but the case of Ru$^{II}$–N(azo) has been examined in complexes of arylazo oximes,[8d] 2-(arylazo)pyridines[18] and (benzylthio)azobenzenes.[7b] The mean Ru$^{II}$–N(azo) distances in these systems are 1.98 (1), 1.98 (1), and 2.00 (1) Å, respectively. Within experimental error the Ru–N(1) bond in **4b** is no shorter than the average of these values. The lack of back-bonding in the Ru$^{III}$–azo situation may offset the expected small decrease in the Ru–N distance upon metal oxidation.[19] In 2,2′-bipyridine complexes it is known that metal oxidation (Ru(II) → Ru(III)) leads to an increase of Ru–N distances.[20]

**C. Structure of Other Trivalent Complexes.** The EPR and electronic spectra as well as electrochemical redox responses (vide infra) of all **3** and **4** complexes are closely akin to those of **4b**. It is therefore reasonable to assume that all the complexes belong to the same structural type having planar tridentate azobenzene coordination and trans phosphine binding. This analogy can be similarly extended to **6**.

**D. Distortion of Electronic Structure.** The severe distortion from $O_h$ symmetry of **4b**, and by inference of the other trivalent complexes, should correspondingly distort the electronic structure of the central metal ion. The latter distortion can be quantitated with the help of EPR and near-IR spectra.[7a,11,21,22] The EPR spectra of **3**, **4**, and **6** are systematically rhombic (Table II, Figure 2), and the three experimental $g$ values are designated $g_1$, $g_2$, and $g_3$ in order of decreasing magnitude (Table II, Figure 2).

In $O_h$ symmetry the ground state of ruthenium(III) ($t_2^5$) is $T_2$. In view of the trans configuration of the Ru(PPh$_3$)$_2$ fragment it is appropriate to consider axial distortion ($\Delta$) as tetragonal in the present complexes. This splits $t_2$ into b and e (consisting of the degenerate pair $e_+$ and $e_-$)[23] and $T_2$ into B and E ($E_+$ and $E_-$) components. When rhombic distortion ($V$) is superposed, all degeneracies are lifted (Figure 2). Spin–orbit coupling ($\lambda$) mixed the six component functions B, $\bar{B}$, $E_+$, $\bar{E}_+$, $E_-$, and $\bar{E}_-$, affording three Kramers doublets (a bar on the top of the symbol means $\beta$ spin). The ground-state doublet is represented by eq 1. The

$$\varphi_{\rm i} = p|E_+\rangle + q|\bar{B}\rangle + r|E_-\rangle$$
$$\varphi_{\rm ii} = p|\bar{E}_-\rangle + q|B\rangle + r|\bar{E}_+\rangle \qquad (1)$$

experimental $g$ factors afford values of the parameters $k$, $p$, $q$, $r$, $\Delta/\lambda$, $V/\lambda$, $\nu_1/\lambda$, and $\nu_2/\lambda$, where $k$ is the orbital reduction factor and $\nu_1$ and $\nu_2$ are the energies of transitions from the ground Kramers doublet to the two upper doublets ($\nu_1 < \nu_2$). Ideally $k$ is a measure of covalency. However, $k$ as determined from EPR analysis of the present type acts as a sink for various unaccounted effects and its values span the range 0.4–1.2.[22]

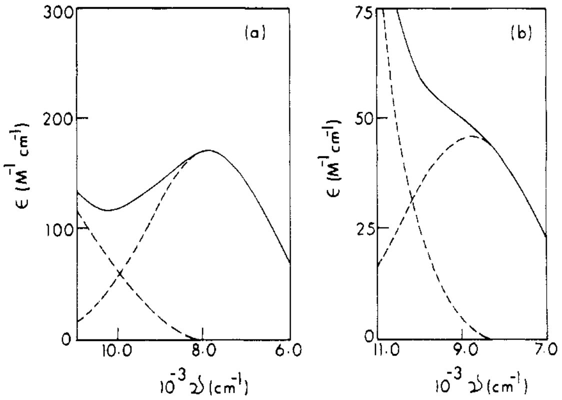

**Figure 4.** Low-energy optical spectra in dichloromethane: (a) **3e**, CNOCl donors; (b) **4b**, CNOBr donors.

For simplicity the RuP$_2$CNOX coordination sphere is idealized as shown in Figure 2. The relative energy ordering of the $t_2$ components can be logically deduced from ligand field considerations.[22a,b] With the P–Ru–P axis identified as the tetragonal ($z$) axis, $\Delta$ should be positive, corresponding to $b(d_{xy}) > e(d_{xz,yz})$. Rhombic distortion is expected to place $d_{xz}$ above $d_{yz}$ due to the different ligand fields in the $xz$ (P$_2$NX) and $yz$ (P$_2$CO) planes. The energy order $d_{xy} > d_{xz} > d_{yz}$ corresponds to $g_1 = |g_x|$, $g_2 = |g_y|$, and $g_3 = |g_z|$. Two alternative solutions differing in the sign of $g_z$ arise, and two representative cases are shown in Table IV. Details of the procedure used for analyses of EPR data and a listing of solutions for all complexes are deposited as supplementary material. If the order $d_{xy} > d_{yz} > d_{xz}$ were chosen ($g_1 = |g_y|$, $g_2 = |g_x|$, and $g_3 = |g_z|$), merely the names of the $x$ and $y$ axes would be interchanged. Apart from reversal of the signs of $V$ and $r$, this interchange would leave all other parameters unaffected.

Solution 1 of Table IV corresponds to $\nu_1 \approx 7000$ cm$^{-1}$ and $\nu_2 \approx 16\,000$ cm$^{-1}$, while in solution 2, $\nu_1 \approx \nu_2 \approx 1500$ cm$^{-1}$ ($\lambda \approx 1000$ cm$^{-1}$).[7a,11,22g,i,j] The trivalent complexes display a relatively weak band in the near-IR region. The cases of **3e** and **4b** are shown in Figure 4, and the transition energies are stated in parentheses in Table IV. The observed near-IR transitions in **3e** and **4b** thus correspond to $\nu_1$ of solution 1 representing large distortion. The $\nu_2$ transition cannot be observed due to the presence of strong absorption from allowed transitions. The orbital splittings of **3a** and **4a** are shown in Figure 2. The bromo complex is electronically more distorted than the chloro complex. Due to the lower ligand field strength of Br$^-$ compared to that of Cl$^-$, the $d_{xy}$ and $d_{xz}$ orbitals in **4a** should lie above those in **3a**. This could produce the observed effect.

**E. Redox Stability.** In order to assess the relative redox stabilities of ruthenium(III) in **3**, **4**, and **6** and ruthenium(II) in **5**, the chelates were examined voltammetrically in dichloromethane solution at a platinum electrode. Potential data are summarized in Table I, and representative cyclic voltammograms are displayed in Figure 5. All potentials are referenced to the saturated calomel electrode (SCE).

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(18) (a) Ghosh, B. K.; Mukhopadhyay, A.; Goswami, S.; Ray, S.; Chakravorty, A. *Inorg. Chem.* **1984**, *23*, 4633–4639. (b) Seal, A.; Ray, S. *Acta Crystallogr., Sect C: Cryst. Struct. Commun.* **1984**, *C40*, 929–932.

(19) Stynes, H. C.; Ibers, J. A. *Inorg. Chem.* **1971**, *10*, 2304–2308.

(20) Egglestone, D. S.; Goldspy, K. A.; Hodgson, D. J.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 4573–4580.

(21) (a) Bleaney, B.; O'Brien, M. C. M. *Proc. Phys. Soc., London, Sect. B* **1956**, *69*, 1216–1230. (b) Griffith, J. S. *The Theory of Transition Metal Ions*; Cambridge University Press: London, 1961; p 364.

(22) (a) Hudson, A.; Kennedy, M. J. *J. Chem. Soc. A.* **1969**, 1116–1120. (b) Hill, N. J. *J. Chem. Soc., Faraday Trans. 2* **1972**, 427–434. (c) Desimone, R. E. *J. Am. Chem. Soc.* **1973**, *95*, 6238–6244. (d) Stanko, J. A.; Peresie, H. J.; Bernheim, R. A.; Wang, P. S. *Inorg. Chem.* **1973**, *12*, 634–639. (e) Kaplan, D.; Navon, G. *J. Phys. Chem.* **1974**, *78*, 700–703. (f) Chakravarty, A. R.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1982**, 615–622. (g) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 1614–1616. (h) Bhattacharya, S.; Chakravorty, A. *Proc.—Indian Acad. Sci., Chem. Sci.* **1985**, *95*, 159–167. (i) Bhattacharya, S.; Ghosh, P.; Chakravorty, A. *Inorg. Chem.* **1985**, *24*, 3224–3230. (j) Daul, C.; Goursot, A. *Inorg. Chem.* **1985**, *24*, 3554–3558.

(23) Sugano, S.; Tanabe, Y.; Kamimura, H. *Multiplets of Transition Metal Ions in Crystals*; Academic: New York, 1970; p 131.

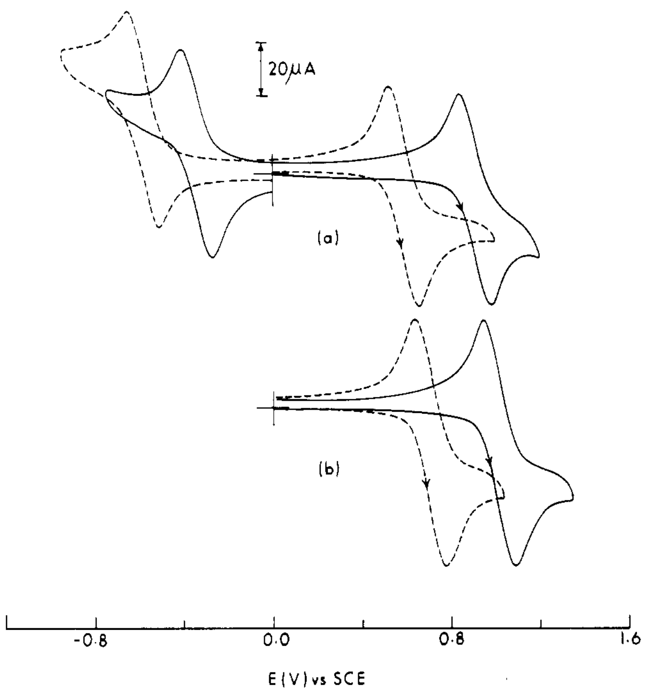

**Figure 5.** Cyclic voltammograms (298 K) in dichloromethane (0.1 M TEAP) at platinum electrodes illustrating substituent effects: (a) R′ = OMe (**3d**, ---), R′ = $NO_2$ (**3f**, —); (b) Z = O (**5a**, ---), Z = S (**5c**, —). In each case solute concentration and scan rate are $\sim 10^{-3}$ M and 50 mV $s^{-1}$, respectively.

Complexes **3** and **4** systematically show two quasi-reversible (peak-to-peak separation 90–300 mV) responses separated by ~1.3 V. Both responses are one-electron in nature, as confirmed coulometrically in representative cases (Table I). The two complexes are given in eq 2 and 3, where $\mathbf{3}^+$ ($\mathbf{4}^+$) and $\mathbf{3}^-$ ($\mathbf{4}^-$) are

$$\mathbf{3}^+ (\mathbf{4}^+) + e^- \rightleftharpoons \mathbf{3}\ (\mathbf{4}) \qquad (2)$$

$$\mathbf{3}\ (\mathbf{4}) + e^- \rightleftharpoons \mathbf{3}^- (\mathbf{4}^-) \qquad (3)$$

believed to contain ruthenium in the +4 and +2 states, respectively.[11] The oxidized and reduced species are quite unstable and could not be characterized. Attempted coulometric rereduction after initial coulometric oxidation (eq 2) and reoxidation after initial reduction (eq 3) gave very small coulomb counts. The potentials ($E°_{298}$) of the couples are sensitive to the substituent R′, shifting to higher potentials as R′ is made progressively more electron withdrawing. The potentials correlate linearly with the Hammett $\sigma$ value of R′. The electrochemical behavior of **6** is similar to that of **3** and **4**.

In the case of **5** only the ruthenium(III)–ruthenium(II) couple (eq 4) is observed at potentials that approach or even surpass the $E°_{298}$ value of the ruthenium(IV)–ruthenium(III) couple of eq 2. In going from **5a** to **5c** the $E°_{298}$ value of eq 4 shifts upward

$$\mathbf{5}^+ + e^- \rightleftharpoons \mathbf{5} \qquad (4)$$

by ~250 mV. Thus, ruthenium(II) is better stabilized by the softer (compared to OMe) SMe donor. The stabilization of ruthenium(II) by thioether coordination has been documented earlier.[7a]

The oxidized complex $\mathbf{5}^+$ is unstable, and its EPR detection in the coulometrically oxidized solution has not been achievable even when coulometry is performed at 268 K. Attempted coulometric reduction of the initially oxidized solution affords very small coulomb counts. The ruthenium(IV)–rutheniun(III) couple based on $\mathbf{5}^{2+}$ and $\mathbf{5}^+$ will probably occur above 2 V—a region not accessible due to solvent cutoff. The figure 2 V is arrived at by adding 1.3 V (difference in the $E°_{298}$ values of the couples in eq 2 and 3) to the $E°_{298}$ value of the couple of eq 4.

The $E°_{298}$ values of **3a** and **5a** demonstrate the effect of O-methylation on the stability of ruthenium oxidation states. The formal potential of the ruthenium(III)–ruthenium(II) couple is shifted positively by ~1.3 V upon such methylation. As a result the phenolato complex **3a** is stable in the trivalent state while the bivalent state is stabilized in the methyl ether complex **5a**.

**F. Concluding Remarks.** It is demonstrated that the group Y in **2** can be used to control the stability of the +3 and +2 oxidation states of ruthenium. The stability shifts dramatically from the +3 to the +2 state in switching from Y = O to Y = $OCH_3$. With Y = O it has been possible to generate the first mononuclear ruthenium(III) cyclometalates, **3**, **4**, and **6**. These complexes are characterized by high stability, severe distortion from octahedral geometry, and electrochemical conversion to unstable tetravalent and bivalent congeners.

## Experimental Section

**Materials.** Commercial ruthenium trichloride received from Arora-Matthey, Calcutta, India, was purified by repeated evaporation to dryness with concentrated hydrochloric acid.[24] The complexes $[Ru(PPh_3)_3X_2]$ (X = Cl, Br) were prepared according to the reported procedure.[12] BDH aluminum oxide (neutral) was used for chromatography. Acetonitrile was treated with $CaH_2$ (overnight) followed by successive distillations over $LiCO_3$–$KMnO_4$ and $P_2O_5$.[25,26] Dichloromethane was purified by treatment with $NaHCO_3$ and anhydrous $CaCl_2$.[27] The solvents were stored over 4A molecular sieves. Commercial tetraethylammonium bromide was converted to the perchlorate salt (TEAP).[25] Dinitrogen gas was purified by successively bubbling it through alkaline dithionite and concentrated sulfuric acid. All other chemicals and solvents used for preparative work were of reagent grade and were used without further purification.

**Physical Measurements.** UV-vis-near-IR spectra were recorded by using a Hitachi 330 spectrophotometer fitted with a thermostated cell compartment. Gaussian analysis of bands where required was performed as before.[7a,22c] Infrared (4000–300 $cm^{-1}$) spectra were taken on a Perkin-Elmer 783 spectrophotometer. The magnetic susceptibility was measured on a PAR 155 vibrating-sample magnetometer fitted with a Walker Scientific L75FBAL Magnet. Electrochemical measurements were done by using the PAR Model 370-4 electrochemistry system incorporating the following: Model 174A, polarographic analyzer; Model 175, universal programmer; Model RE0074, XY recorder; Model 173, potentiostat; Model 179, digital coulometer; Model 377, cell system. All experiments were performed under dinitrogen atmospheres. A planar Beckman Model 39273 platinum-inlay working electrode, a platinum-wire auxiliary electrode, and an aqueous saturated calomel reference electrode (SCE) were used. A platinum-gauze working electrode was used in coulometric experiments. All cyclic voltammetric data were collected at 298 K and are uncorrected for junction potentials. Low-temperature coulometry, where required, was performed by using a jacketed cell. EPR measurements were made with a Varian Model 109CE-line X-band spectrometer fitted with a quartz Dewar for measurements at 77 K (liquid dinitrogen). All spectra were calibrated with the help of DPPH (*g* = 2.0037). Microanalyses (C, H, N) were done by using a Perkin-Elmer 240C elemental analyzer. The following Hammett $\sigma$ values for para substituents were used: H, 0.00; Me, −0.17; OMe, −0.27; Cl, +0.23; $NO_2$, +0.78.[28]

**Treatment of EPR Data.** An outline of the procedure can be found in our recent publications,[22h,i] and further details are deposited as supplementary material.

**Synthesis of Compounds. Azobenzenes.** These are identified as L-(complex). For example, the free azobenzene ligand corresponding to **3a** is designated L(**3a**). The azobenzenes L(**3b**)–L(**3f**) were prepared by coupling diazotized anilines with *p*-cresol. The other ligands were prepared by using literature procedures.[29]

**Complexes.** The syntheses of complexes of type **3** and **4** were achieved by using a general method. Yields varied in the range 75–85%. Specific details are given for one complex.

**Chlorobis(triphenylphosphine)(2-(phenylazo)phenolato-$C^2$,*N*,*O*)ruthenium(III) (3a).** $Ru(PPh_3)_3Cl_2$ (100 mg, 0.10 mmol) was suspended

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(24) Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 275–278.

(25) Sawyer, D. T.; Roberts, J. L., Jr. *Experimental Electrochemistry for Chemists*; Wiley: New York, 1974; p 167–215.

(26) Walter, M.; Ramaley, L. *Anal. Chem.* **1973**, *45*, 165–166.

(27) Vogel, A. I. *Practical Organic Chemistry*, 3rd ed.; ELBS and Longman Group Ltd.: London, 1965; Chapter 2, pp 176–177.

(28) Hammett, L. P. *Physical Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1970.

(29) (a) Drew, H. D. K.; Landguist, J. K. *J. Chem. Soc.* **1938**, 292–304. Sciarini, L. J. *Arch. Biochem. Biophys.* **1957**, *71*, 437–441; *Chem. Abstr.* **1958**, *52*, 4567d. (c) Shriner, R. L.; Struck, H. C.; Jorrison, W. J. *J. Am. Chem. Soc.* **1930**, *52*, 2060–2069. Buraway, A.; Vellins, C. E. *J. Chem. Soc.* **1954**, 90–94. Livingstone, S. E. *J. Chem. Soc.* **1956**, 437–440. (d) Schetty, G. *Helv. Chim. Acta* **1970**, *53*, 1437–1459.

**Table V.** Selected Crystal Data, Data Collection Parameters, and Least-Squares Residuals for Complex **4b**

| | |
|---|---|
| formula | $RuC_{49}H_{40}N_2OP_2Br$ |
| fw | 915.1 |
| space group | $P2_1/c$ |
| $a$, Å | 12.361 (2) |
| $b$, Å | 19.091 (3) |
| $c$, Å | 18.560 (4) |
| $\beta$, deg | 108.30 (1) |
| $V$, Å$^3$ | 4158.3 (13) |
| $Z$ | 4 |
| $d_{calcd}$, g cm$^{-3}$ | 1.463 |
| data collecn instrum | Enraf-Nonius CAD-4 |
| radiation | graphite-monochromatized CuK$\alpha$ ($\lambda_\alpha$ = 1.54178 Å) |
| scan method | $\omega$–$2\theta$ scan |
| cryst size, mm | 0.20 × 0.15 × 0.15 |
| $\mu$(Cu K$\alpha$), cm$^{-1}$ | 52.96 |
| range of $\theta$, deg | $2 \leqslant \theta \leqslant 55$ |
| no. of data, $I > 2\sigma(I)$ | 3995 |
| no. of params refined | 505 |
| $R^a$ | 0.046 |
| $R_w{}^b$ | 0.059 |
| quality of fit indicator[c] | 1.034 |
| largest shift/esd | 0.968 |

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = \sigma^{-2}(F_o)$. [c] Quality of fit indicator $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

in 35 mL of ethanol. This mixture was warmed, and to this was added L(**3a**) (50 mg, 0.23 mmol). The whole mixture was heated to reflux for 1 h. A greenish brown solution was formed, from which dark-colored crystals started depositing. The solution was cooled to complete the deposition and was then filtered. The solid residue was washed thoroughly with ethanol and dried in vacuo over $P_2O_5$. The yield was 80%. The synthesis of complexes of type **4** was achieved similarly by using $Ru(PPh_3)_3Br_2$ in place of $Ru(PPh_3)_3Cl_2$.

Complexes of type **5** were prepared by the same general procedure and purified by chromatography. The crude product obtained after drying over $P_2O_5$ in vacuo was dissolved in a small volume of dichloromethane and chromatographed on an alumina column (20 × 1 cm). Upon elution with benzene a green band appeared, which afforded the crystalline complex in ~60–70% yield. Separation of complexes **6** and **7** (prepared as a mixture by the same general procedure used for **3**) was achieved by chromatography on alumina. Elution with benzene afforded a red band, from which **7** was isolated. Benzene–acetonitrile (9:1) gave a deep green band consisting of **6**. Yields were as follows: **6**, 70%; **7**, 15%.

**Preparation of Crystals of 4b for X-ray Analysis.** Hexane (25 mL) was layered over a solution of 20 mg of **4b** in 20 mL of pure dichloromethane. The system was allowed to evaporate very slowly. Dark crystals deposited within a few days.

**X-ray Structure Determination.** Crystal data, collection parameters, and least-squares residuals are given in Table V. The unit cell dimensions were derived from a least-squares fit of 25 randomly chosen reflections. The space group was determined unambiguously from the systematic absences of $0k0$ ($k$ odd) and $h0l$ ($l$ odd) reflections. Intensity values were corrected for Lorentz and polarization effects but not for absorption.

The position of the ruthenium atom was derived from the highest peaks of the Patterson map. The remaining 55 non-hydrogen atoms were located from successive Fourier maps and difference Fourier syntheses. Block-matrix least-squares refinement of the overall scale factor and positional and individual isotropic temperature factors of all non-hydrogen atoms afforded an $R$ factor of ~0.10. Methyl hydrogen atoms were located from the difference Fourier map, but the other hydrogen atoms were placed in calculated positions (C–H = 1.05 Å). All hydrogen contributions were included in structure factor calculations with isotropic temperature factors of the corresponding C atoms to which they are attached. The final refinement involving only the positional and anisotropic thermal parameters for all non-hydrogen atoms as well as an overall scale factor converged to $R = 0.046$, $R_w = 0.059$ with $w = [\sigma^2|F_o| + 0.04|F_o|^2]^{-1}$. The ruthenium and bromine atoms were treated as anomalous scatterers (Ru, $\Delta f' = -0.105$, $\Delta f'' = 3.296$; Br, $\Delta f' = -0.767$, $\Delta f'' = 1.283$).[30] A difference Fourier map after convergence of the refinement contained no features of chemical interest, the highest peak around ruthenium and bromine positions being no denser than 0.7 e/Å$^3$.

**Table VI.** Fractional Atomic Coordinates and Isotropic-Equivalent Temperature Factors (Å$^2$) for Non-Hydrogen Atoms[a,b] in Complex **4b**

| atom | $x$ | $y$ | $z$ | $10^3U_{eqv}$ |
|---|---|---|---|---|
| Ru | 0.15654 (4) | 0.20628 (3) | 0.21690 (3) | 28 |
| Br | 0.14615 (7) | 0.32912 (4) | 0.17095 (5) | 52 |
| P(1) | 0.3601 (2) | 0.2219 (1) | 0.2578 (1) | 32 |
| P(2) | −0.0475 (1) | 0.2031 (1) | 0.1752 (1) | 30 |
| O | 0.1680 (4) | 0.2175 (2) | 0.3323 (3) | 42 |
| N(1) | 0.1595 (4) | 0.1060 (3) | 0.2498 (3) | 32 |
| N(2) | 0.1589 (4) | 0.0532 (3) | 0.2076 (3) | 36 |
| C(1) | 0.1602 (6) | 0.1571 (4) | 0.3651 (4) | 38 |
| C(2) | 0.1528 (6) | 0.0951 (3) | 0.3231 (4) | 34 |
| C(3) | 0.1401 (6) | 0.0288 (4) | 0.3529 (4) | 38 |
| C(4) | 0.1369 (6) | 0.0238 (4) | 0.4265 (4) | 44 |
| C(5) | 0.1152 (7) | −0.0462 (4) | 0.4582 (5) | 62 |
| C(6) | 0.1458 (6) | 0.0857 (4) | 0.4684 (4) | 53 |
| C(7) | 0.1580 (7) | 0.1510 (4) | 0.4397 (4) | 48 |
| C(8) | 0.1593 (6) | 0.1504 (4) | 0.1246 (4) | 39 |
| C(9) | 0.1598 (6) | 0.0765 (4) | 0.1360 (4) | 38 |
| C(10) | 0.1607 (7) | 0.0296 (4) | 0.0794 (4) | 55 |
| C(11) | 0.1590 (8) | 0.0532 (4 | 0.0103 (5) | 67 |
| C(12) | 0.1570 (8) | 0.1250 (4) | 0.0042 (4) | 59 |
| C(13) | 0.1577 (7) | 0.1731 (4) | 0.0527 (4) | 52 |
| C(14) | 0.4038 (6) | 0.3079 (3) | 0.3004 (4) | 35 |
| C(15) | 0.3595 (6) | 0.3305 (4) | 0.3561 (4) | 47 |
| C(16) | 0.3876 (7) | 0.3972 (4) | 0.3882 (5) | 62 |
| C(17) | 0.4601 (7) | 0.4400 (4) | 0.3664 (5) | 56 |
| C(18) | 0.5032 (7) | 0.4173 (4) | 0.3110 (5) | 63 |
| C(19) | 0.4789 (6) | 0.3511 (4) | 0.2791 (5) | 50 |
| C(20) | 0.4413 (6) | 0.1600 (4) | 0.3303 (4) | 39 |
| C(21) | 0.4237 (6) | 0.0882 (4) | 0.3185 (5) | 56 |
| C(22) | 0.4846 (7) | 0.0402 (4) | 0.3712 (6) | 68 |
| C(23) | 0.5631 (7) | 0.0635 (5) | 0.4375 (5) | 73 |
| C(24) | 0.5831 (8) | 0.1327 (5) | 0.4489 (5) | 68 |
| C(25) | 0.5222 (7) | 0.1821 (4) | 0.3960 (5) | 53 |
| C(26) | 0.4260 (6) | 0.2146 (4) | 0.1845 (4) | 37 |
| C(27) | 0.3905 (6) | 0.2582 (5) | 0.1197 (5) | 63 |
| C(28) | 0.4340 (6) | 0.2545 (5) | 0.0618 (5) | 66 |
| C(29) | 0.5157 (7) | 0.2023 (5) | 0.0633 (5) | 75 |
| C(30) | 0.5514 (7) | 0.1585 (5) | 0.1234 (5) | 74 |
| C(31) | 0.5093 (6) | 0.1648 (4) | 0.1839 (5) | 53 |
| C(32) | −0.1166 (6) | 0.2017 (4) | 0.0722 (4) | 37 |
| C(33) | −0.0874 (7) | 0.2517 (5) | 0.0291 (5) | 56 |
| C(34) | −0.1410 (8) | 0.2573 (5) | −0.0481 (5) | 72 |
| C(35) | −0.2268 (8) | 0.2111 (5) | −0.0824 (5) | 68 |
| C(36) | −0.2566 (7) | 0.1599 (5) | −0.0416 (5) | 63 |
| C(37) | −0.2017 (6) | 0.1537 (4) | 0.0363 (4) | 62 |
| C(38) | −0.1091 (6) | 0.1309 (4) | 0.2127 (4) | 35 |
| C(39) | −0.1596 (7) | 0.1415 (4) | 0.2681 (4) | 51 |
| C(40) | −0.2028 (8) | 0.0845 (5) | 0.2981 (5) | 71 |
| C(41) | −0.1933 (8) | 0.0157 (4) | 0.2721 (6) | 69 |
| C(42) | −0.1403 (7) | 0.0053 (4) | 0.2194 (5) | 62 |
| C(43) | −0.0992 (6) | 0.0611 (4) | 0.1880 (5) | 49 |
| C(44) | −0.1148 (5) | 0.2788 (3) | 0.2027 (4) | 32 |
| C(45) | −0.2251 (6) | 0.2978 (4) | 0.1622 (4) | 42 |
| C(46) | −0.2795 (7) | 0.3522 (4) | 0.1860 (5) | 54 |
| C(47) | −0.2228 (6) | 0.3888 (4) | 0.2509 (5) | 53 |
| C(48) | −0.1134 (7) | 0.3727 (4) | 0.2898 (5) | 54 |
| C(49) | −0.0583 (6) | 0.3170 (4) | 0.2677 (5) | 45 |

[a] $U_{eqv} = {}^1/_3\sum U_{ii}$. [b] Numbers in parentheses are estimated standard deviations in the least significant digits.

Atomic coordinates and isotropic-equivalent thermal parameters for non-hydrogen atoms are in Table VI.

Crystallographic calculations were done on a Burroughs 6700 computer at the Regional Computer Centre, Calcutta, India. Programs used were from the X-ray ARC package modified for local use.[31] The NOR-

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(30) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.

(31) (a) Vickery, B. L.; Bright, D.; Mallinson, P. R. "XRAY ARC: IBM 1130 Program System for Crystallography Modified for B6700 Computer", 1971. (b) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. "MULTAN 78: A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data"; University of York, York, England, and University of Louvain, Louvain, Belgium; 1978. (c) Nardelli, M. "PARST: A System of Computer Routines for Calculating Molecular Parameters from Results of Crystal Structure Analyses"; University of Parma, Parma, Italy; 1982.

MAL-EXFFT-SEARCH programs of the MULTAN 78 package were used for weighted Fourier synthesis.

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**Registry No.** **3a**, 110078-21-2; **3b**, 110078-22-3; **3c**, 110078-23-4; **3d**, 110078-24-5; **3e**, 110078-25-6; **3f**, 110078-26-7; **4a**, 110078-27-8; **4b**, 110078-28-9; **4c**, 110078-29-0; **4d**, 110078-30-3; **4e**, 110078-31-4; **4f**, 110078-32-5; **5a**, 110078-33-6; **5b**, 110078-34-7; L(**5b**), 29418-41-5; **5c**, 110078-35-8; **6**, 110078-36-9; **7**, 110078-37-0; $Ru(PPh_3)_3Cl_2$, 15529-49-4; $Ru(PPh_3)_3Br_2$, 15709-75-8; 2,2′-azophenol, 2050-14-8.

**Supplementary Material Available:** A discussion on treatment of EPR data and listings of EPR analysis for all compounds (Table VII), anisotropic thermal parameters of **4b** (Table VIII), bond distances and bond angles of **4b** (Table IX), and least-squares planes and dihedral angles of **4b** (Table X) (15 pages); a listing of observed and calculated structure factors of **4b** (27 pages). Ordering information is given on any current masthead page.

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# A New Family of Semibent Rhenium(V) Arylimides Formed by Azo Splitting. Structure, Bonding, and Electrooxidation to Rhenium(VI) Congeners

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The reaction of 2-(arylazo)pyridines, $YH_4C_6N{=}NC_5H_4N$ (**1**, Y = H, *m*-Me, *p*-Me, *p*-Cl) with $K_2ReCl_6$ in boiling 2-methoxyethanol affords violet complexes of the type $Re(YH_4C_6N{=}NC_5H_4N)(YC_6H_4N)Cl_3$ (**2**). The coordinated arylimide moiety originates from the splitting of the azo function of a second azopyridine ligand. The structure of the Y = H complex (**2a**) has been determined by three-dimensional X-ray crystallography. The crystals are triclinic in the space group $P\bar{1}$ with $Z = 2$ and unit cell dimensions $a = 9.960$ (3) Å, $b = 11.173$ (3) Å, $c = 9.535$ (3) Å, $\alpha = 106.06$ (3)°, $\beta = 91.10$ (3)°, $\gamma = 113.35$ (2)°, and $V = 926.2$ (6) Å$^3$. The structure was refined to $R = 0.0318$ and $R_w = 0.0455$. The coordination sphere is distorted octahedral $ReN_3Cl_3$. The arylimide moiety is coordinated in the semibent fashion with a Re–N–C angle of 159.9 (4)°. The azopyridine ligand forms a five-membered chelate ring coordinated at the azo (N(3)) and pyridine (N(1)) nitrogen atoms. The N(1) atom is located trans to the N(4) (arylimido nitrogen) atom. The Re–N(1), Re–N(3), and Re–N(4) distances are respectively 2.152 (4), 2.021 (4), and 1.724 (4) Å. The Re–N(1) and Re–N(4) bond orders are estimated to be 1 and 2.7 ± 0.1, respectively. The Re–N(3) bond order is >1 due to the presence of $d_{xy}(Re)\rightarrow\pi^*(azo)$ back-bonding, which couples synergetically with $\pi$-$(NC_6H_5)\rightarrow d_{xz},d_{yz}(Re)$ bonding. This is consistent with the observed configuration of the nitrogen atoms in the coordination sphere. The high-resolution $^1H$ NMR spectra of the complexes have been fully assigned in most cases. The meridional $ReCl_3$ geometry is reflected in the triplet nature of Re–Cl stretch (300–360 cm$^{-1}$). Metal–azo back-bonding finds expression in N–N bond (1.289 (5) Å) lengthening and $\nu_{N{=}N}$ (~1300 cm$^{-1}$) lowering. The complexes display a nearly reversible one-electron cyclic voltammetric oxidation ($E^\circ_{298}$ = 1.3–1.4 V vs. SCE) in acetonitrile at a platinum electrode: $\mathbf{2}^+ + e^- \rightleftharpoons \mathbf{2}$, where $\mathbf{2}^+$ is the rhenium(VI) congener of **2**. This is supported by the six-line EPR spectra of the coulometrically oxidized solution (Y = *p*-Me: $g = 1.96$, $A = 450$ G).

## Introduction

This work stems from our interest in the transition-metal chemistry of azo ligands in general and 2-(arylazo)pyridines, $ArN{=}NC_5H_4N$, in particular.[2-5] The richness of this chemistry in the cases of ruthenium[2] and osmium[3] prompted us to seek parallel developments for the neighboring element rhenium. Unexpectedly, this led us to a family of novel violet complexes of composition $Re(ArNNC_5H_4N)(ArN)Cl_3$, which contain the coordinated arylimide ligand apparently formed by the splitting of the parent azopyridine.

The complexes have been characterized with the help of spectroscopic and other techniques. The structure of a representative complex has been determined by three-dimensional X-ray crystallography. This has revealed that the ArN moiety is bound to the metal in the bent configuration, which is very rare among rhenium(V) organoimide, $Re^VNR$, species.[6-10] The bonding and the atomic arrangement in the coordination sphere are qualitatively rationalized. The feasibility of generating the rhenium(VI) congeners of the complexes is successfully examined with help of electrochemical and EPR techniques.

## Results and Discussion

**A. Synthesis.** The specific ligands used in the present work are **1a–d**. In boiling 2-methoxyethanol **1** reacts slowly with

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(1) (a) Indian Association for the Cultivation of Science. (b) Texas A&M University.

(2) (a) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 2246–2250. (b) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1982**, *21*, 2737–2742. (c) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *J. Chem. Soc., Chem. Commun.* **1982**, 1288–1289. (d) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1983**, *22*, 602–609. (e) Goswami, S.; Mukherjee, R. N.; Chakravorty, A. *Inorg. Chem.* **1983**, *22*, 2825–2832. (f) Ghosh, P.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1985**, 361–367. (g) Mahapatra, A. K.; Ghosh, B. K.; Goswami, S.; Chakravorty, A. *J. Indian Chem. Soc.* **1986**, *63*, 101–104. (h) Seal, A.; Ray, S. *Acta Crystallogr., Sect. C: Struct. Commun.* **1984**, *C40*, 929–932. (i) Krause, R. A.; Krause, K. *Inorg. Chem.* **1980**, *19*, 2600. (j) Krause, R. A.; Krause, K. *Inorg. Chem.* **1982**, *21*, 1714. (k) Krause, R. A.; Krause, K. *Inorg. Chem.* **1984**, *23*, 2195–2198.

(3) (a) Ghosh, B. K.; Goswami, S.; Chakravorty, A. *Inorg. Chem.* **1983**, *22*, 3358–3360. (b) Ghosh, B. K.; Mukhopadhyay, A.; Goswami, S.; Ray, S.; Chakravorty, A. *Inorg. Chem.* **1984**, *23*, 4633–4639.

(4) (a) Datta, D.; Chakravorty, A. *Inorg. Chem.* **1983**, *22*, 1085–1090. (b) Raghavendra, B. S.; Chakravorty, A. *Indian J. Chem. Sect. A* **1976**, *14A*, 166–169.

(5) Bandyopadhyay, P.; Bandyopadhyay, D.; Chakravorty, A.; Cotton, F. A.; Falvello, L. R.; Han, S. *J. Am. Chem. Soc.* **1983**, *105*, 6327–6329 and unpublished results.

(6) The only known example, viz. $Re(NC_6H_4CH_3)(OEt)(S_2CNMe_2)_2$, is reported by: Haymore, B. L.; Goeden, G. V. *Inorg. Chem.* **1983**, *22*, 157–167.

(7) Bent organoimido bonding in one trinuclear rhenium(VII) complex is reported by: Nugent, W. A.; Harlow, R. L. *J. Chem. Soc., Chem. Commun.* **1979**, 1105–1106.

(8) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123–175.

(9) (a) Chatt, J.; Garforth, J. D.; Johnson, N. P.; Rowe, G. A. *J. Chem. Soc.* **1964**, 1012–1020. (b) Chatt, J.; Dilworth, J. R.; Leigh, G. J. *J. Chem. Soc. A* **1970**, 2239–2243. (c) Chatt, J.; Dosser, R. J.; King, F.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2435–2440. (d) Shandles, R.; Murmann, R. K. *J. Inorg. Nucl. Chem.* **1965**, *27*, 1869–1871. (e) Rowbottom, J. F.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1972**, 826–830.

(10) (a) Bright, D.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 703–709. (b) Bright, D.; Ibers, J. A. *Inorg. Chem.* **1968**, *7*, 1099–1111. (c) Shandles, R. S.; Murmann, R. K.; Schlemper, E. *Inorg. Chem.* **1974**, *13*, 1373–1377.

0020-1669/87/1326-3365$01.50/0