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.

Contribution from the Department of Inorganic Chemistry, Indian Association for the Cultivation of Science,
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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 π-$(NC_6H_5)\rightarrow d_{xz},d_{yz}(Re)$ 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 ($E°_{298} = 1.3$–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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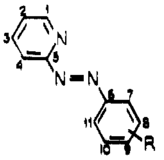
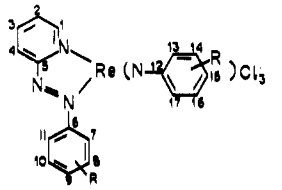
Table I. Selected Bond Distances (Å) and Angles (deg) in **2a** (with Estimated Standard Deviations in Parentheses)

Re–Cl(1)	2.351 (1)	Re–N(3)	2.021 (4)
Re–Cl(2)	2.362 (1)	Re–N(4)	1.724 (4)
Re–Cl(3)	2.395 (1)	N(2)–N(3)	1.289 (5)
Re–N(1)	2.152 (4)		
Cl(1)–Re–Cl(2)	85.26 (5)	Cl(3)–Re–N(3)	95.3 (1
Cl(1)–Re–Cl(3)	164.29 (5)	Cl(3)–Re–N(4)	89.1 (1)
Cl(1)–Re–N(1)	86.5 (1)	N(1)–Re–N(3)	72.5 (2)
Cl(1)–Re–N(3)	87.7 (1)	N(1)–Re–N(4)	160.9 (2)
Cl(1)–Re–N(4)	106.2 (1)	N(3)–Re–N(4)	93.3 (3)
Cl(2)–Re–Cl(3)	87.62 (5)	Re–N(1)–C(1)	127.3 (3)
Cl(2)–Re–N(1)	92.1 (1)	Re–N(1)–C(5)	114.2 (3)
Cl(2)–Re–N(3)	163.5 (1)	Re–N(3)–N(2)	124.5 (3)
Cl(2)–Re–N(4)	103.0 (1)	Re–N(3)–C(6)	123.7 (3)
Cl(3)–Re–N(1)	79.8 (1)	Re–N(4)–C(12)	159.9 (4)

K_2ReCl_6, affording a violet solution, from which dark-colored crystals of composition **2** (the atom-numbering scheme shown will be used throughout) are isolated after chromatographic workup.



1a, R = H
1b, R = 8-Me
1c, R = 9-Me
1d, R = 9-Cl



2a, R = H
2b, R = 8-Me, 14-Me
2c, R = 9-Me, 15-Me
2d, R = 9-Cl, 15-Cl

Other rhenium-containing products are also formed during the synthesis of **2**, but their nature is unknown at present (see Experimental Section).

The conversion **1** → **2** examplifies a rare reaction wherein a metal organoimido species is formed by the reductive cleavage of an azo function.[11] The transformation of eq 1 requires four

$$RN{=}NR' + 4e^- \rightarrow RN^{2-} + R'N^{2-} \qquad (1)$$

electrons. The metal oxidation levels in $ReCl_6^{2-}$ and **2** differ by only one unit. Therefore, the formation of **2** from **1** and $ReCl_6^{2-}$ must involve complex reactions. The ill-defined nature of the other products formed during synthesis of **2** has precluded electron accounting and possible elucidation of the reaction stoichiometry. Keeping the four-electron stoichiometry of eq 1 in mind, we examined whether the rhenium(III) dimer[12] $Re_2Cl_8^{2-}$ would smoothly cleave **1** (eq 2), affording identifiable complexes of the

$$\mathbf{1} + Re^{III}{}_2Cl_8^{2-} \rightarrow Re^{V}(NC_6H_4R) + Re^{V}(NC_5H_4N) \qquad (2)$$

arylimido moieties of eq 2. In practice, however, $K_2Re_2Cl_8$ failed altogether to react with **1** under the conditions used for the synthesis of **2** from **1** and K_2ReCl_6.

B. Structure of $Re(PhNNC_5H_4N)(PhN)Cl_3$ (2a). a. Coordination Sphere and Its Distortions. The crystal lattice consists of discrete molecules of one type. A view of the molecule is shown in Figure 1, and selected bond parameters are in Table I. The $ReCl_3N_3$ coordination sphere is severely distorted from regular octahedral geometry. The ligands NPh and **1a** account for the three nitrogen atoms with N(phenylimide) trans to N(pyridine). Remarkable features of the structure are the three distinctly different Re–N distances and the bent nature of the ReNPh function.

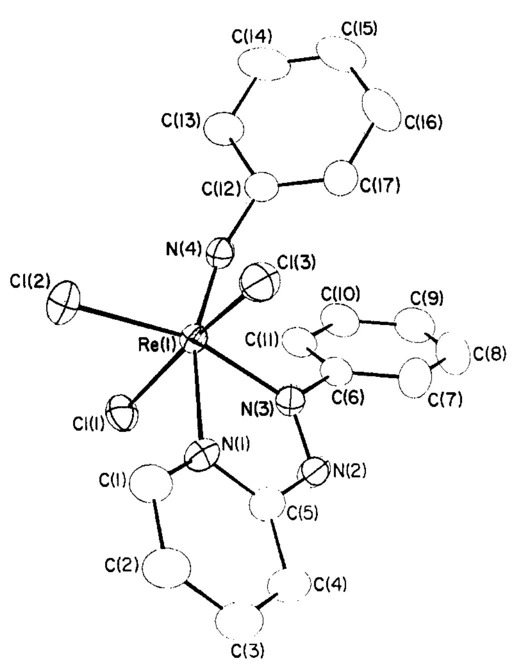


Figure 1. ORTEP plot of the molecular structure of **2a**, with the atom-labeling scheme indicated. All atoms are represented by their 50% probability ellipsoids.

The coordinated chloride ions are meridionally disposed and so are the three nitrogen atoms—the two meridional planes thus defined are nearly orthogonal to each other. The five-membered chelate ring is highly planar, and the pyridine ring is virtually coplanar with it. The acute chelate bite angle of 72.5 (2)° is one of the major distorting factors in the structure. The dimensions of the chelate ring compare well with those found in the ruthenium and osmium chelates of **1**.[2,3]

The Cl(1), Cl(2), Cl(3), and N(3) atoms define a perfect plane from which the Re atom is shifted by 0.301 (0) Å toward the N(4) atom. This type of shift that arises from the shortness of the Re–NPh bond is a common feature of all structurally characterized $Re^{V}NR$ complexes.[10] As a result of the shift the trans angles Cl(1)–Re–Cl(3) and Cl(2)–Re–Cl(3)—164.3 (1) and 163.5 (1)°, respectively—deviate considerably from 180°. Another feature of the structure is the bending of the N(1) and N(4) atoms toward each other in the direction of the Cl(3)–N(3) line, resulting in an N(1)–Re–N(4) angle of 160.9 (2)°. The effect of this bending is discernible in several cis angles around Re such as Cl(1)–Re–N(4) = 106.2 (1)° and Cl(3)–Re–N(4) = 89.1 (1)° or Cl(1)–Re–N(1) = 86.5 (1)° and Cl(3)–Re–N(1) = 79.8 (1)°. The combination of the distorting factors—chelate bite angle, shift of the metal atom, and bending of trans nitrogen donors—can be observed in the sizable (0.1–0.2 Å) deviations of Cl(1), Cl(3), N(1), and N(4) as well as of Cl(2), N(1), N(3), and N(4) from their respective least-squares planes. The two planes are, however, nearly orthogonal (dihedral angles 92.4 and 87.9°) to the plane of Cl(1), Cl(2), Cl(3), and N(3).

b. Single Bonds. Reported Re–Cl distances in chloro–$Re^{V}NR$ complexes lie in the range 2.40–2.43 Å.[10] The average Re–Cl length in **2a** is only slightly shorter. No structural data are available on any ReNR complex also containing coordinated pyridine (py). However, in $Re(O)(OEt)(py)_2Cl_2$ the average Re–N distance is 2.14 (1) Å.[13] The Re–N(1) distance of 2.152 (4) Å in **2a** compares very favorably with this. The Re–N(1) bond is considered to be essentially a single bond between rhenium(V) and the sp^2 nitrogen of pyridine. For sp^3 nitrogen the Re–N distance may be expected to be slightly longer—in $Re(MeNH_2)_4(MeN)Cl^{2+}$ the average $Re–NH_2Me$ length is 2.18 (1) Å.[10c]

c. Re–Azo Fragment. Like N(1), the N(3) nitrogen in **2a** is also approximately sp^2 hybridized. Yet the Re–N(3) distance in

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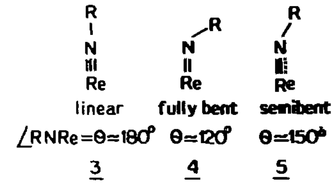
2a is only 2.021 (4) Å. Clearly the order of this bond is higher than 1. Associated with this is the significant lengthening of the N–N distance to 1.289 (5) Å in **2a** from the value expected for uncoordinated **1**. The N=N distance in free L is not directly known, but it is estimated to be ~1.25 Å on the basis of available data on PhN=NPh, MeN=NMe, and MeC(=NOH)N=NPh (1.253 (3), 1.254 (3), and 1.256 (2) Å, respectively).[14] These results strongly suggest the presence of sizable π back-bonding of the type dπ(Re)→pπ*(azo) in **2a**. IR data and the proposed bonding model support this (vide infra). With regard to metal–azo back-bonding **2a** is analogous to the ruthenium(II)[2] and osmium(II)[3] complexes of **1**.

d. ReNPh Fragment. Limiting linear and bent ReNR fragments are depicted in **3** and **4**, respectively. The intermediate *semibent* situation is shown by **5**, in which the dotted line represents a bond of order <1.



The structures of five Re^VNR complexes have been reported to date.[6,10] In four of these, θ lies in the range 171–180° and the range for Re–NR distances is 1.69–1.71 Å.[10] These exemplify the linear moiety **3**. On the basis of spectroscopic and other evidences it is generally believed that most Re^VNR complexes have such linear organoimido binding.[8] In the fifth reported structure, viz. that of $Re(S_2CNMe_2)_2(p\text{-}MeC_6H_4N)(EtO)$, θ and Re–NAr are respectively equal to 155.5 (5)° and 1.745 (5) Å.[6] The latter corresponds to a bond order of ~2.5. This has been the only known example of the semibent situation, **5**. The fully bent configuration **4** has not been diagnosed in any complex so far.

The Re–N(4) distance and the Re–N(4)–C(12) angle in **2a** are 1.724 (4) Å and 159.9 (4)°, respectively. We thus have here the second example of a semibent Re^VNR complex. The Re–N(4) bond order in **2a** is estimated to be 2.7 ± 0.1. This estimate is based on interpolation with the help of idealized single-, double-, and triple-bonded Re–NR distances of 2.14, 1.84, and 1.69 Å, respectively.[6] If we take the corresponding θ values for sp^3, sp^2, and sp nitrogen hybridization and interpolate the observed θ value, the hybridization of the NPh nitrogen in **2a** corresponds to $sp^{1.2}$. Since π bonds are formed (see below) out of the remaining 1.8 p orbitals, the Re–NPh bond order of 2.7 ± 0.1 in **2a** is internally consistent.

e. Bonding. Certain qualitative aspects of bonding in **2a** can now be considered. With the Re–N(4) direction taken as the *z* axis, the p_z orbital of N(4) is used for σ hybridization, which also uses a small fraction of p_x/p_y orbitals (vide supra), resulting in the observed bent geometry of ReNPh. But most of these last two orbitals are available for π bonding with metal d_{xz} and d_{yz} orbitals, the sense of donation being Re←NPh. The p_x/p_y orbitals are thus destabilized, setting the two metal electrons (rhenium(V), $5d^2$) in the low-lying d_{xy} orbital in a paired configuration.

A special feature of **2a** is that the filled metal d_{xy} orbital can interact with the empty pπ* orbital of the azo function, shifting electrons in the sense Re→azo. This stabilizes the d_{xy} orbital further. It is believed that Re–azo π back-bonding constitutes a necessary stabilizing factor that determines the relative arrangement of donor atoms in **2a**. It is only in the experimentally observed configuration (azo and PhN nitrogens cis to each other) that the synergetic π interactions azo←Re←NPh can get optimally expressed. This advantage is lost upon interchanging the positions of pyridine and azo nitrogens (i.e., placing the latter trans to the PhN nitrogen) since the azo π* orbital then fails to interact with the metal d_{xy} orbital. It is also lost for the same reason in the hypothetical facial ReN_3 configuration, in which ligand **1a** would approximately define the *xy* plane.

In the case of $Re(S_2CNMe_2)_2(p\text{-}MeC_6H_4N)(EtO)$, it has been argued that the bending of ReNAr is associated with an effective atomic number >18 arising out of π donation by OEt.[6] A similar situation is hard to conceive for **2a** since no potent π donors other than PhN exist in the molecule. Here the observed bending apparently results from optimization of the bonding process in the entire molecule. Semibending of Re^VNR may have several origins, and further scrutiny with the help of newer structures as they are discovered is called for.

C. Spectra. The IR, electronic, and ^1H NMR spectra as well as the electrochemical reactivity of **2a** are akin to those of the other **2** complexes, and it is inferred that **2a–d** have very similar structures.

Two notable features of the IR spectra of **2** (Table II) are (i) shift of the azo stretching frequency to lower values (1300–1340 cm^{-1}) compared to that in the free ligand (1425 cm^{-1} in **1a**[4b]) due to the π-back-bonding phenomenon and (ii) three distinct Re–Cl stretching frequencies (300–360 cm^{-1}) in each case, as expected of the meridional $ReCl_3$ configuration (see the figure in the supplementary material).[15]

The electronic spectra of the complexes in the visible region are dominated by two allowed transitions near 500 and 660 nm (Table II), precluding the possible observation of ligand field transitions of the type $d_{xy} \rightarrow d_{xz}$, d_{yz}. Such transitions may be the origin of the two relatively weak bands observed in the visible spectrum of $Re(MeNH_2)_4(MeN)Cl^{2+}$.[9d]

The high-resolution (270-MHz) ^1H NMR spectra of **2** have been assigned (Table III, Figure 2). The two expected methyl signals are seen for both **2b** and **2c**. The pyridine proton signals occur in isolated regions and are easily identified. The signals from the benzene rings of coordinated **1** and NAr partially overlap, but only in the case of **2a** is such overlap too serious for individual assignments. In other cases the individual signals can be sorted out on the basis of intensity, spin–spin structure, and substituent effects. For example, the azo group shifts H(7) and H(11) to relatively low fields, the methyl group shifts H(8) and H(10) (as well as H(14) and H(16)) to higher fields (compare **2c** and **2d**), and in **2b** H(7) and H(13) are singlets, etc. In this manner an internally consistent assignment scheme emerged for the complexes.

D. Electrogeneration of Rhenium(VI) Arylimide Species. In the bonding scheme noted earlier, d_{xy}^2 electrons constitute the HOMO of **2**. Even though this orbital should be quite stable, we considered the possibility that it may still undergo electrochemical oxidation to the half-filled configuration (d_{xy}^1) within the accessible upper potential limit (+2.2 V vs. SCE) of acetonitrile solvent at the platinum working electrode. The resultant species would then represent hitherto unreported $Re^{VI}NAr$ complexes.

The type **2** complexes indeed display a one-electron cyclic voltammetric response near 1.3 V vs. SCE. A representative voltammogram is shown in Figure 3. The $E°_{298}$ values of the various complexes are as follows: **2a**, 1.35 V; **2b**, 1.33 V; **2c**, 1.33 V; **2d**, 1.39 V. The expected para substituent effect ($E°_{298}$ order **2d** > **2a** > **2c**) is discernible.[16] The peak-to-peak separation in each case is ~70 mV, showing that the electrode process (eq 3)

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

lies close to the reversible limit. On the negative side of the SCE (−0.5 to −1.0 V) two responses are observed for all complexes presumably due to azo reduction.[2e]

In order to confirm that $\mathbf{2}^+$ contains oxidized metal (rhenium(VI)) as opposed to oxidized ligand, the X-band EPR spectra of fresh solutions (produced coulometrically at ~1.5 V) of $\mathbf{2}^+$ were examined. The spectrum of $\mathbf{2c}^+$ is shown in Figure 3. The six-line

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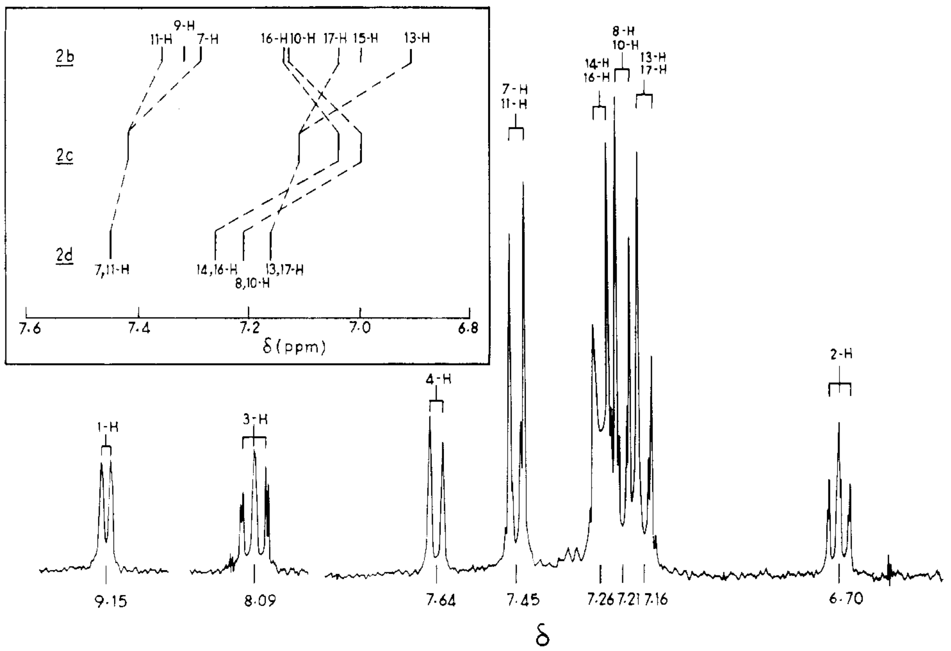

Figure 2. ^1H NMR spectrum of **2d** in $CDCl_3$ at 270 MHz. The inset shows a schematic representation of chemical shifts for the aromatic protons ($-C_6H_4Y$) of **2b–d**.

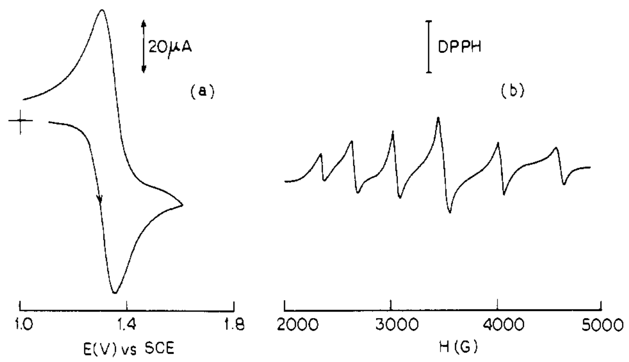

Figure 3. (a) Cyclic voltammogram of **2c** in acetonitrile (0.1 M TEAP) at a platinum electrode. Solute concentration and scan rate are $\sim 10^{-3}$ M and 50 mV s^{-1}, respectively. (b) X-Band EPR spectrum of $\mathbf{2c}^+$ in acetonitrile at room temperature.

spectrum is characteristic of hyperfine splitting by the rhenium(VI) nucleus (^{185}Re, abundance 37%, and ^{187}Re, 63%; $I = {}^5/_2$ for both). The unequal separation of the hyperfine lines is assignable to second-order effects.[17] The center-field g value and average hyperfine splitting are 1.96 and 450 G, respectively. Superhyperfine splittings due to coordinated nitrogen nuclei are not resolved.

E. Concluding Remarks. The present work further demonstrates that the (arylazo)pyridine ligands **1** are susceptible to fascinating metal-mediated reactions. In an earlier work[5] it was shown that the aromatic $-C_6H_4R$ moiety of **1** can be regiospecifically oxidized to $-C_6H_3(OH)R$ (hydroxyl group cis to the azo function) in palladium complexes. We now have the unusual reductive azo cleavage reaction mediated by rhenium leading to complexes (**2**) containing the very rare semibent organoimide function $Re^VNC_6H_4R$. These are nearly reversibly electrooxidized in solution to EPR-active congeners of the hexavalent metal.

Experimental Section

Materials. Potassium perrhenate received from Aldrich was reacted with KCl, concentrated HCl, and hypophosphorous acid to afford K_2ReCl_6.[18] Silica gel (60–120 mesh) used for chromatography was of BDH make. For spectroscopic/electrochemical studies commercial solvents were purified as follows. Acetonitrile was treated with CaH_2 (overnight) followed by successive distillations over $LiCO_3$–$KMnO_4$ and P_4O_{10}.[19,20] The solvent was stored over molecular sieves (4A). Commercial tetraethylammonium bromide was converted to the perchlorate salt (TEAP) by following an available procedure.[19] 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 spectra were recorded by using a Hitachi 330 spectrophotometer fitted with a thermostated cell compartment. Infrared (4000–250 cm^{-1}) spectra were taken on a Perkin-Elmer 783 spectrophotometer. Diamagnetism was checked with the help of a PAR 155 vibrating-sample magnatometer fitted with a Walker Scientific L75FBAL magnet. Molecular weights were determined in chloroform solution by using a Knauer vapor pressure osmometer with benzil as calibrant. ^1H NMR data were collected in $CDCl_3$ solvent, and tetramethylsilane was used as internal standard with the help of a Varian XL200 or Bruker 270-MHz FT spectrometer. 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 39273 platinum-inlay working electrode, a platinum-wire auxiliary electrode, and an aqueous saturated calomel reference electrode (SCE) were used in these electrode configurations. A platinum-wire-gauze working electrode was used in coulometric experiments. All cyclic voltammetric data were collected at 298 K and are uncorrected for junction potentials. EPR measurements were made with a Varian 109C E-line X-band spectrometer fitted with a flat cell. 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.

Synthesis of Compounds. 2-(Arylazo)pyridines. The 2-(arylazo)pyridines **1a–d** were synthesized by condensing 2-aminopyridine with the appropriate nitrosobenzene according to the reported procedure.[21]

Complexes. The syntheses of complexes **2a–d** were achieved by using the same general method. Specific details are given below for one complex, viz. **2a**.

Trichloro(phenylimido)(2-(arylazo)pyridine)rhenium(V) (2a). K_2ReCl_6 (100 mg, 0.21 mmol) was suspended in 30 mL of 2-methoxyethanol, and a stream of nitrogen was passed through the solution for 15

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Table II. Characterization Data

compd	IR[a] ν_{max}, cm^{-1} N=N	IR[a] ν_{max}, cm^{-1} Re—Cl	electronic spectral data[b] λ_{max}, nm (ϵ, M^{-1} cm^{-1})	anal. data[c] % C	anal. data[c] % H	anal. data[c] % N	M_r[d]
2a	1320	360, 340, 320	660 (2600), 495 (7800), 335 (14 250), 270 (12 500), 235 (17 450)	36.09 (36.00)	2.38 (2.47)	10.05 (9.88)	554 (566.7)
2b	1325	350, 340, 310	660 (2700), 500 (8000), 340 (14 500), 270 (12 600), 230 (21 000)	38.70 (38.34)	2.97 (3.03)	9.53 (9.42)	596 (594.7)
2c	1300	345, 325, 305	660 (3200), 500 (10 000), 340 (20 500), 270 (14 700), 230 (25 000)	38.55 (38.34)	3.14 (3.03)	9.56 (9.42)	*e*
2d	1320	355, 345	660 (2700), 500 (9200), 340 (20 200), 275 (14 900)	32.00 (32.04)	1.83 (1.88)	9.00 (8.80)	657 (636)

[a] In KBr disks (4000–250 cm^{-1}). [b] In acetonitrile. [c] Calculated values are in parentheses. [d] Molecular weight; calculated values are in parentheses. [e] Not measured.

Table III. ^{1}H NMR Spectral Data in CDCl$_3$

compd	δ (J)[a] H(1)	H(2)	H(3)	H(4)	H(7)	H(8)	H(9)	H(10)	H(11)	H(13)	H(14)	H(15)	H(16)	H(17)
2a	9.15 (5.7)[b]	6.68 (6.7)[c]	8.07 (7.3)[c]	7.64 (6.7)[b]	*d*	*e*	7.54 (6.7)[c]	*e*	*d*	*e*	*e*	*e*	*e*	*e*
2b	9.16 (5.7)[b]	6.71 (6.6)[c]	8.08 (7.4)[c]	7.66 (8.0)[b]	7.29[f]	*g*	7.32 (7.5)[b]	7.13 (7.7)[b]	7.36 (7.5)[b]	6.91[f]	*g*	7.00 (7.9)[b]	7.14 (7.7)[c]	7.04 (9.0)[b]
2c	9.16 (6.0)[b]	6.71 (6.9)[c]	8.07 (6.8)[c]	7.66 (8.0)[b]	7.42 (8.0)[b]	7.00 (8.0)[b]	*h*	7.00 (8.0)[b]	7.42 (8.0)[b]	7.11 (7.2)[b]	7.04 (8.0)[b]	*h*	7.04 (8.0)[b]	7.11 (8.2)[b]
2d	9.15 (5.6)[b]	6.70 (6.6)[c]	8.09 (7.3)[c]	7.64 (8.0)[b]	7.45 (8.7)[b]	7.21 (8.7)[b]		7.21 (8.7)[b]	7.45 (8.7)[b]	7.16 (8.8)[b]	7.26 (8.7)[b]		7.26 (8.7)[b]	7.16 (8.8)[b]

[a] J is given in Hz; tetramethylsilane is the internal standard. [b] Doublet. [c] Triplet. [d] Complex multiplet pattern centered at δ 7.52. [e] Complex multiplet pattern centered at δ 7.22. [f] Singlet. [g] Me(8) and Me(14) at δ 2.27 and 2.17. [h] Me(9) and Me(15) at δ 2.42 and 2.25.

Table IV. Crystal Data for **2a**

formula	ReCl$_3$N$_4$C$_{17}$H$_{14}$
fw	566.89
space group	$P\bar{1}$
systematic absences	none
a, Å	9.960 (3)
b, Å	11.173 (3)
c, Å	9.535 (3)
α, deg	106.06 (3)
β, deg	91.10 (3)
γ, deg	113.35 (2)
V, Å^3	926.2 (6)
Z	2
d_{calcd}, g/cm^3	2.033
cryst size, mm	0.43 × 0.40 × 0.38
μ(Mo Kα), cm^{-1}	73.79
data collecn instrum	Syntex P$\bar{1}$
radiation (monochromated in incident beam)	Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.71073 Å)
orientation rflns: no.; range (2θ), deg	15; 22–35
temp, °C	4.8–10.0
scan method	ω–2θ
data collecn range, 2θ deg	4.0–55.0
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	4198 3926
no. of params refined	226
transmission factors: max, min	obsd 1.00, 0.48
R[a]	0.0318
R_w[b]	0.0455
quality-of-fit indicator[c]	1.140
largest shift/esd, final cycle	<0.01
largest peak, e/Å^3	1.26

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

min. To this was added **1a** (115 mg, 0.63 mmol). The whole mixture was heated to reflux for 5 h under a dinitrogen atmosphere, and the resulting violet solution was evaporated. The dark residue was extracted with dichloromethane, and the solvent was evaporated. The crude product was dissolved in a small volume of dichloromethane and was subjected to chromatography on a silica gel column (20 × 1 cm). On elution with benzene a small yellow band separated out, which was rejected. The deep violet band that followed was eluted with dichloromethane; upon evaporation of the eluate crystalline **2a** was afforded in 30% yield.

After elution of **2a** a dark band remained at the top of the chromatographic column, which could be eluted only with acetonitrile (50 mL) *acidified* with perchloric acid (0.1 mL), giving a light violet eluate. This was evaporated, and the solid mass was throughly washed with water and dried in vacuo over P$_4$O$_{10}$. The amorphous material thus obtained is insoluble or only sparingly soluble in most organic solvents. The IR spectra strong bands are observed due to (i) azo stretching (1300 cm^{-1}), (ii) Re–organoimido stretching (1240 cm^{-1}), (iii) Re–Cl stretching (305, 320 cm^{-1}), and (iv) Re=O stretching (920 cm^{-1}). The material displays no electrochemical response within the range −1.2 to +1.4 V vs. SCE in dichloromethane at a platinum electrode. It appears that one or more oxo–chloro organoimido rhenium species also containing a coordinated azo ligand are formed in the course of the reaction. However, we have not been able to settle its molecular nature (Anal. Found: C, 40.36; N, 10.53; H, 3.38). It also remains to be established if the same product is formed from preparation to preparation. Further examination is in progress.

Preparation of Crystals of 2a for X-ray Analysis. Hexane (15 mL) was layered over a solution of 20 mg of **2a** in 15 mL of pure dichloromethane. The system was allowed to evaporate very slowly. Dark crystals deposited within a few days.

X-ray Structure Determination. Geometric and intensity data were taken from a deep green, regularly shaped crystal, which was mounted at the end of a glass fiber and covered with a thin layer of epoxy. The routine procedures that were used in identifying the triclinic unit cell, refining the cell parameters, and gathering intensity data have been described previously.[22] Axial photographs were used to verify the lattice

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Table V. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) and Their Estimated Standard Deviations for **2a**[a]

atom	x	y	z	B_{eqv}
Re(1)	0.37051 (2)	0.24484 (1)	0.23156 (2)	1.984 (3)
Cl(1)	0.3776 (1)	0.4648 (1)	0.3339 (1)	2.96 (2)
Cl(2)	0.1439 (1)	0.1668 (1)	0.3243 (2)	3.42 (3)
Cl(3)	0.3043 (1)	0.0118 (1)	0.0866 (1)	3.11 (3)
N(1)	0.2642 (4)	0.2408 (4)	0.0306 (4)	2.43 (8)
N(2)	0.5077 (4)	0.3445 (4)	−0.0091 (4)	2.55 (8)
N(3)	0.5311 (4)	0.3272 (4)	0.1158 (4)	2.22 (7)
N(4)	0.4898 (4)	0.2294 (4)	0.3516 (4)	2.40 (8)
C(1)	0.1168 (6)	0.1833 (5)	−0.0183 (6)	3.1 (1)
C(2)	0.0625 (6)	0.1794 (5)	−0.1563 (6)	3.2 (1)
C(3)	0.1634 (7)	0.2371 (5)	−0.2467 (6)	3.4 (1)
C(4)	0.3142 (6)	0.2951 (5)	−0.1967 (6)	3.1 (1)
C(5)	0.3585 (5)	0.2929 (4)	−0.0590 (5)	2.53 (9)
C(6)	0.6886 (5)	0.3817 (4)	0.1682 (5)	2.43 (9)
C(7)	0.7796 (6)	0.3524 (6)	0.0708 (7)	3.5 (1)
C(8)	0.9301 (6)	0.4064 (7)	0.1203 (8)	4.6 (1)
C(9)	0.9878 (6)	0.4877 (6)	0.2662 (8)	4.2 (1)
C(10)	0.8936 (6)	0.5160 (6)	0.3628 (7)	3.5 (1)
C(11)	0.7419 (5)	0.4618 (5)	0.3133 (6)	2.8 (1)
C(12)	0.5864 (5)	0.1849 (4)	0.4025 (5)	2.50 (9)
C(13)	0.6048 (6)	0.1958 (5)	0.5520 (6)	3.1 (1)
C(14)	0.6952 (7)	0.1420 (6)	0.5988 (8)	4.5 (1)
C(15)	0.7666 (6)	0.0805 (6)	0.4990 (8)	4.3 (1)
C(16)	0.7467 (6)	0.0695 (6)	0.3494 (8)	4.3 (1)
C(17)	0.6551 (5)	0.1215 (5)	0.3018 (6)	3.1 (1)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

dimensions. During intensity data collection, three monitor reflections were rescanned after every 97 data scans, as a check on crystal and instrumental stability. These reflections did not show any significant variation in intensity during the 50 h of X-ray exposure time.

Data reduction[23] included the application of an absorption correction[24] based on azimuthal scans of nine reflections with diffractometer angle χ near 90°.

The position of the unique rhenium atom was derived from a Patterson map, and the structure was developed and refined in a sequence of alternating difference Fourier maps and least-squares refinements. The final, convergent refinement fitted positional and anisotropic displacement parameters for 25 non-hydrogen atoms, along with an overall scale factor—226 parameters in all—to 3926 data, for a data-to-parameter ratio of 17.4. These were no significant correlation effects in the final refinements, and listings of R factors as functions of $|F_o|$, $(\sin\theta)/\lambda$, and data collection order showed no anomalies.

A difference map following the last refinement had five peaks with density greater than 1 e/Å^3. These were all ghosts of the rhenium atom and were considered to be caused by series-termination and absorption effects.

Important crystal data and parameters related to data collection and structure refinement are given in Table IV.

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Registry No. **1a**, 2569-57-5; **1b**, 87014-42-4; **1c**, 110015-48-0; **1d**, 14458-12-9; **2a**, 110015-49-1; **2a**$^+$, 110015-53-7; **2b**, 110015-50-4; **2b**$^+$, 110015-54-8; **2c**, 110015-51-5; **2c**$^+$, 110015-55-9; **2d**, 110015-52-6; **2d**$^+$, 110015-56-0; K_2ReCl_6, 16940-97-9.

Supplementary Material Available: For **2a** listings of anisotropic thermal parameters (Table VI), bond distances (Table VII), bond angles (Table VIII), and least-squares planes and dihedral angles (Table IX) and a figure showing the electronic spectrum of **2b** in acetonitrile and the infrared spectrum of **2c** in a KBr disk (9 pages); a listing of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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Generation of $Re_2(CO)_9(N_2)$ from $Re_2(CO)_{10}$: Identification of Photochemical Intermediates by Matrix Isolation and Liquid-Noble-Gas Techniques

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UV photolysis of $Re_2(CO)_{10}$ in liquid xenon doped with N_2 generates $Re_2(CO)_9(N_2)$ with N_2 situated in an equatorial site. Similar results are found for $Mn_2(CO)_{10}$ and $MnRe(CO)_{10}$. The same product, *eq*-$Re_2(CO)_9(N_2)$, is obtained upon narrow-band UV photolysis (313 nm) of $Re_2(CO)_{10}$ isolated in an N_2 matrix at 20 K. The mechanism is explored by low-temperature matrix isolation studies. Short-wavelength irradiation of $Re_2(CO)_{10}$ in argon matrices yields *eq*-$Re_2(CO)_9$, which upon 546-nm irradiation isomerizes to *ax*-$Re_2(CO)_9$. When the photolysis is carried out in a N_2 matrix at 10 K, no products containing N_2 are generated, but instead the coordinatively unsaturated species $Re_2(CO)_9$ is observed. $Re_2(CO)_9$ is converted to *eq*-$Re_2(CO)_9(N_2)$ by warming the matrix to 15–20 K. Conversely, narrow-band visible photolysis (546 nm) of $Re_2(CO)_9$ at 10 K in this environment yields a second isomer of $Re_2(CO)_9(N_2)$ with N_2 occupying an axial coordination site. The relevance of these matrix results to the solution photochemistry of $Re_2(CO)_{10}$ is briefly discussed.

Introduction

There is currently considerable interest in the products and mechanisms of both the thermal and photochemical[2] reactions of dinuclear metal carbonyls. In particular, for $MM'(CO)_{10}$ species (M, M′ = Mn, Re) there is now strong evidence from conventional studies,[3] from flash photolysis with both UV–visible[4–6] and IR detection,[7] and from matrix isolation studies[8,9] that two primary photochemical steps are involved:

$$\begin{tikzcd}
 & M(CO)_5 + M'(CO)_5 & (1) \\
MM'(CO)_{10} \arrow[ur] \arrow[dr, "h\nu"'] & & \\
 & MM'(CO)_9 + CO & (2)
\end{tikzcd}$$

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