

Variable-Valent Re≡NAr Species. A Family of Re^{VI}NAr Amide Complexes and Their Re^VNAr Imine Precursors Related by Oxygen Atom Transfer

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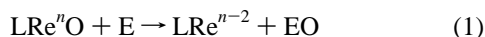
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Imide complexes of type Re^VCl₃(X-SB)(NC₆H₄Y(*p*)), with X, Y = H, Me, OMe, Cl have been synthesized where X-SB is the Schiff base of pyridine-2-carboxaldehyde (the corresponding complex is **4**), 2-acetylpyridine (**5**), 2-benzoylpyridine (**6**), and anilines, *p*-XC₆H₄NH₂. Treatment of **4** or **5** (but not **6**) with aqueous nitric acid in acetonitrile afforded Re^{VI}Cl₃(X-PA)(NC₆H₄Y(*p*)), **7**, via oxygen atom transfer (X-PA = monoanionic picolinamide). In the structures of **5**(X=Cl,Y=Cl), **6**(OMe,OMe), and **7**(Me,Me), the chlorine atoms are meridionally disposed in a ReCl₃N₃ coordination sphere. The *trans* influence of the imide nitrogen considerably lengthens the Re–N(pyridine) bond. The ReNC₆H₄Y(*p*) group has the triple-bonded linear moiety, Re≡N–C. The amide group in **7**(Me,Me) is planar. In **6**(OMe,OMe) the two aryl rings on the imine function block water attack and hence amide formation. The rhenium(VI)–rhenium(V) *E*_{1/2} values for **4–6** (0.7–1.0 V *vs* SCE) are much higher than that for **7** (*E*_{1/2} ~ 0.15 V), which displays the rhenium(VII)–rhenium(VI) couple near 1.6 V. Six EPR hyperfine lines are observed for solutions of **7** at room temperature (*g*_{iso} ~ 1.91; *A*_{av} ~ 490 G). Crystal data for the complexes are as follows: **5**(Cl,Cl), empirical formula C₁₉H₁₅Cl₅N₃Re, crystal system monoclinic, space group *P*2₁/*c*, *a* = 13.360(6) Å, *b* = 12.110(3) Å, *c* = 14.954(9) Å, β = 111.41(4)°, *V* = 2252.4(1.7) Å³, *Z* = 4; **6**(OMe,OMe), empirical formula C₂₆H₂₃Cl₃N₃O₂Re, crystal system orthorhombic, space group *Pbca*, *a* = 12.079(5) Å, *b* = 17.083(9) Å, *c* = 26.049(9) Å, *V* = 5375.4(4.0) Å³, *Z* = 8; **7**(Me,Me), empirical formula C₂₀H₁₈Cl₃N₃ORe, crystal system monoclinic, space group *P*2₁/*c*, *a* = 7.071(2) Å, *b* = 17.541(6) Å, *c* = 16.857(8) Å, β = 100.59(3)°, *V* = 2055.3(1.3) Å³, *Z* = 4.

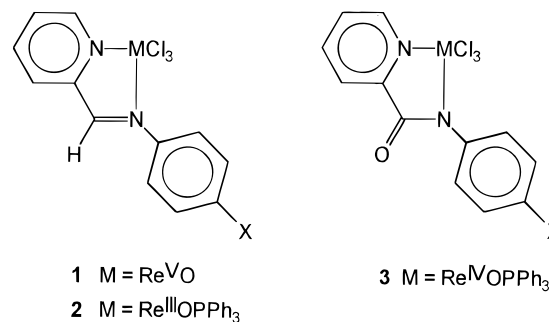
Introduction

Mediation of facile oxygen atom transfer reactions by rhenium complexes was first authenticated more than two decades ago.¹ Noteworthy progress in this area has been discernible in recent years,^{2–5} the usual transfer reaction being of the type shown in eq 1 where E is an oxophilic substrate and LRe^{*n*}O is an

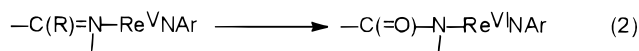


oxorhenium reagent (L = ligand; *n* = metal valence). We have been interested in developing new instances of rhenium-promoted oxygen atom transfer reactions and in using them for synthesis. It was recently shown that pyridine-2-carboxaldimine complexes of type **1** react as in eq 1 (E = PPh₃), affording **2**, which in turn is subject to a second and unusual oxygen atom transfer from a water molecule to the imine function, leading to the amide complex **3**.⁶

The scope of the imine → amide transformation is under scrutiny especially as a synthetic tool. Herein we report its successful utilization for assembling the first family of picoli-



namide complexes incorporating the rare arylimide motif of hexavalent rhenium, Re^{VI}NAr. The hitherto unknown pyridine-2-carboxaldimine chelates of Re^VNAr have been used as precursors. The relevant imine → amide reaction outlined in eq 2 is found to be facile in the case of aldimines, R = H, and



ketimines with R = Me, but it fails for ketimines with R = Ph. The origin of this R-discrimination is probed. The syntheses, structures, spectra, and metal redox reactions of selected imine and amide complexes are reported.

Results and Discussion

Synthesis. In the reaction **2** → **3**, the metal oxidation state increases by 1 unit, the amide ligand stabilizing the higher

- (6) (a) Dirghangi, B. K.; Menon, M.; Pramanik, A.; Chakravorty, A. *Inorg. Chem.* **1997**, *36*, 1095. (b) Menon, M.; Choudhury, S.; Pramanik, A.; Deb, A. K.; Chandra, S. K.; Bag, N.; Goswami, S.; Chakravorty, A. *J. Chem. Soc., Chem. Commun.* **1994**, 57. (c) Menon, M.; Pramanik, A.; Bag, N.; Chakravorty, A. *Inorg. Chem.* **1994**, *33*, 403.

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- (1) (a) Rouschias, G.; Wilkinson, G. *J. Chem. Soc. A* **1967**, 993. (b) Rowbottom, J. F.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1972**, 826.
 (2) (a) Mayer, J. M.; Tulip, T. H. *J. Am. Chem. Soc.* **1984**, *106*, 3878. (b) Bryan, J. C.; Stenkamp, R. E.; Tulip, T. H.; Mayer, J. M. *Inorg. Chem.* **1987**, *26*, 2283.
 (3) Fontaine, X. L. R.; Fowles, E. H.; Layzell, T. P.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1991**, 1519.
 (4) (a) Abu-Omar, M. M.; Espenson, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 272. (b) Herrmann, W. A.; Kühn, F. E.; Rauch, F. E.; Carreira J. D. G.; Artus, G. *Inorg. Chem.* **1995**, *34*, 2914. (c) Du Mez, D. D.; Mayer, J. M. *Inorg. Chem.* **1995**, *34*, 6396. (d) Zhu, Z.; Al-Ajlouni, A. M.; Espenson, J. H. *Inorg. Chem.* **1996**, *35*, 1408.
 (5) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401 and references therein.

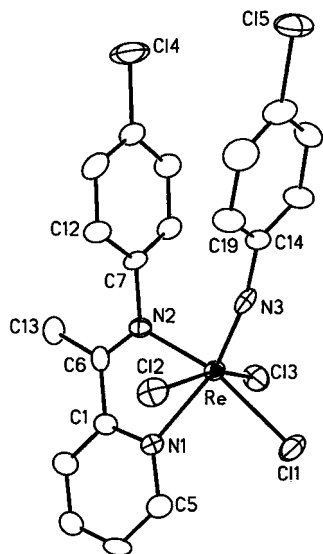


Figure 1. ORTEP plot and atom-labeling scheme for **5(Cl,Cl)**. All non-hydrogen atoms are represented by their 30% probability ellipsoids.

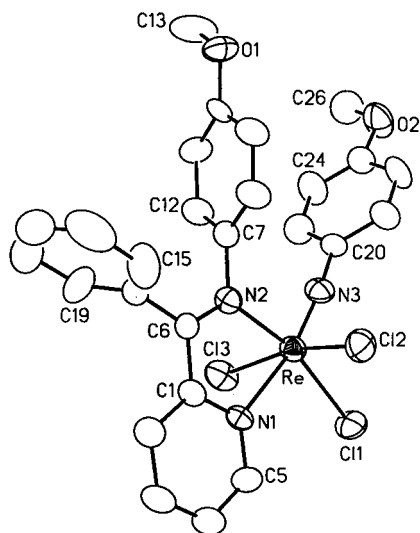


Figure 2. ORTEP plot and atom-labeling scheme for **6(OMe,OMe)**. All non-hydrogen atoms are represented by their 30% probability ellipsoids.

7(Me,Me) is expectedly much longer (by ~ 0.08 Å) than the imine bond, C(6)–N(2) in **5(Cl,Cl)** and **6(OMe,OMe)**.

Radial contraction between rhenium(V) and rhenium(VI) is relatively small, and the corresponding bond lengths in **7(Me,Me)** are not particularly short compared to those of **5(Cl,Cl)** and **6(OMe,OMe)**. In general, the Re–N(1) length is ~ 0.2 Å higher than the Re–N(2) length due to the *trans* influence of the imide nitrogen. In the Re^VNAr motif the Re–N distances and Re–N–C angle are 1.691(7) Å and 167.2(8)° for **5(Cl,Cl)** and 1.712(10) Å and 173.1(10)° for **6(OMe,OMe)**. Among hexacoordinated Re^VNQ (Q = alkyl or aryl) structures,^{8,12–18} the Re–N length spans the range 1.67–1.74 Å and the ReNQ

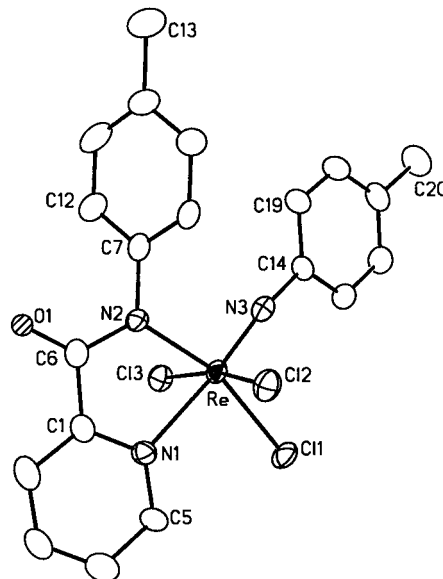


Figure 3. ORTEP plot and atom-labeling scheme for **7(Me,Me)**. All non-hydrogen atoms are represented by their 30% probability ellipsoids.

Table 2. Selected Bond Distances (Å) and Their Estimated Standard Deviations for **5(Cl,Cl)**, **6(OMe,OMe)**, and **7(Me,Me)**

	5(Cl,Cl)	6(OMe,OMe)	7(Me,Me)
Re–N(1)	2.209(7)	2.236(9)	2.231(7)
Re–N(2)	2.060(7)	2.052(10)	2.026(6)
Re–N(3)	1.691(7)	1.712(10)	1.699(6)
Re–Cl(1)	2.370(3)	2.347(4)	2.339(3)
Re–Cl(2)	2.393(3)	2.360(4)	2.336(3)
Re–Cl(3)	2.350(3)	2.377(4)	2.362(3)
C(6)–O(1)			1.213(10)
N(2)–C(6)	1.299(12)	1.287(15)	1.368(10)

Table 3. Selected Bond Angles (deg) and Their Estimated Standard Deviations for **5(Cl,Cl)**, **6(OMe,OMe)**, and **7(Me,Me)**

	5(Cl,Cl)	6(OMe,OMe)	7(Me,Me)
Cl(1)–Re–Cl(2)	88.3(1)	88.7(1)	88.4(1)
Cl(1)–Re–Cl(3)	87.8(1)	86.8(1)	88.7(1)
Cl(2)–Re–Cl(3)	163.4(1)	164.3(1)	168.4(1)
Cl(1)–Re–N(1)	91.2(2)	89.8(3)	86.8(2)
Cl(2)–Re–N(1)	80.3(2)	84.5(2)	85.3(2)
Cl(3)–Re–N(1)	83.6(2)	80.5(2)	83.3(2)
Cl(1)–Re–N(2)	164.1(2)	163.3(3)	162.6(2)
Cl(2)–Re–N(2)	92.4(2)	89.1(3)	90.5(2)
Cl(3)–Re–N(2)	87.0(2)	90.9(3)	89.0(2)
N(1)–Re–N(2)	73.3(3)	73.5(4)	75.8(3)
Cl(1)–Re–N(3)	102.5(3)	100.5(3)	96.7(2)
Cl(2)–Re–N(3)	93.2(3)	99.5(4)	99.4(2)
Cl(3)–Re–N(3)	103.4(3)	96.2(4)	92.1(2)
N(1)–Re–N(3)	164.7(3)	169.0(4)	174.1(2)
N(2)–Re–N(3)	99.3(3)	96.2(4)	100.6(3)
Re–N(3)–C(i) ^a	167.2(8)	173.1(10)	168.9(6)

^a C(i) = C(14) for **5(Cl,Cl)** and **7(Me,Me)** and C(20) in the case of **6(OMe,OMe)**.

moiety is more or less linear (Re–N–C angle 167–180°) in most cases. Bending of Re–N–C angles to below 160° (“semibent”¹⁵) is rare.^{14,15}

The idealized Re–N, Re=N, and Re≡N bond lengths in Re^V–NQ are 2.14, 1.84, and 1.69 Å, respectively.¹⁴ The distances in **5(Cl,Cl)** and **6(OMe,OMe)** are consistent with the triple-bond description, Re≡NAr. A qualitative description of the bonding¹⁵

- (12) (a) Bakir, M.; Paulson, S.; Goodson, P.; Sullivan, B. P. *Inorg. Chem.* **1992**, *31*, 1127. (b) Masood, M. A.; Hodgson, D. J. *Inorg. Chem.* **1994**, *33*, 2488. (c) Masood, M. A.; Sullivan, B. P.; Hodgson, D. J. *Inorg. Chem.* **1994**, *33*, 5360. (d) Bakir, M.; Sullivan, B. P. *J. Chem. Soc., Dalton Trans.* **1995**, 2189.
- (13) (a) Wang, W. P.; Che, C.-M.; Wong, K.-Y.; Peng, S.-M. *Inorg. Chem.* **1993**, *32*, 5827. (b) Che, C.-M. *Polyhedron* **1995**, *14*, 1791. (c) Yan, U. W. W.; Tam, K. K.; Cheung, K. K. *J. Chem. Soc., Dalton Trans.* **1995**, 2779.
- (14) (a) Goeden, G. V.; Haymore, B. L. *Inorg. Chem.* **1983**, *22*, 157 (b) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.

- (15) Lahiri, G. K.; Goswami, S.; Falvello, L. R.; Chakravorty, A. *Inorg. Chem.* **1987**, *26*, 3365.
- (16) Rossi, R.; Marchi, A.; Marvelli, L.; Magon, L.; Peruzzini, M.; Casellato, U.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1993**, 723.
- (17) Shandless, R. S.; Murmann, R. K.; Schlemper, E. O. *Inorg. Chem.* **1974**, *13*, 1373.
- (18) Bright, D.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 703.

suggests that the $5d_{xy}$ orbital can back-bond with the empty $p\pi^*$ orbital of the imine function. If the positions of pyridine and imine nitrogen atoms were interchanged in **4–6**, the advantage of the Re→imine back-bonding interaction would be diminished, and this may be a reason for the observed relative geometrical disposition of the imide and imine ligands. Significantly the imine N(2)–C(6) lengths in **5**(Cl,Cl) and **6**(OMe,OMe) are ~ 0.05 Å longer than those¹⁹ in pyridine-2-carboxaldimine complexes of bivalent cobalt and zinc, where no back-bonding is expected.

In the $\text{Re}^{\text{VI}}\text{NAr}$ amide complex **7**(Me,Me), the Re–N(3) distance, 1.699(6) Å, and Re–N(3)–C(14) angle, 168.9(6)°, are similar to those in **5**(Cl,Cl) and **6**(OMe,OMe), again reflecting the marginal effect of metal valence change on bond parameters. It is logical to assign a bond order of 3 to the Re–N(3) bond here as well. To our knowledge, only one other hexacoordinated complex incorporating a $\text{Re}^{\text{VI}}\text{NQ}$ motif, viz. $\text{Re}(\text{NC}_2\text{Cl}_5)\text{Cl}_4(\text{POCl}_3)$, having a perhalogenated Q group, has been structurally characterized (Re–N 1.69(1) Å, Re–N–C 169(1)°).¹⁰ The structures of two tetrahedral $\text{Re}^{\text{VI}}\text{NQ}$ species having a very bulky Q group (Bu^t) are known.¹¹ In **7**(Me,Me), we have the first structural characterization of a $\text{Re}^{\text{VI}}\text{NQ}$ motif in which the Q group is a simple aryl function unencumbered by special electronic/steric features.

Magnetism. The type **4–6** complexes are diamagnetic corresponding to the $5d_{xy}^2$ configuration. The type **7** compounds behave as one-electron paramagnets ($5d_{xy}^1$) although the bulk magnetic moments are significantly lower than the spin-only value due to strong orbital coupling as in other rhenium(VI) complexes.^{20,21} Representative room-temperature values: **7**(Me,Cl), 1.48 μ_B ; **7**(H,Cl), 1.41 μ_B .

The type **7** complexes are EPR-active in fluid solution at room temperature; see Figure 4a and Table 4. Six well-resolved hyperfine lines due to the $I = 5/2$ nuclei (¹⁸⁵Re, 37.07%; ¹⁸⁷Re, 62.93%) are observed—the isotopic fine structure is not resolved due to the small difference (1%) in the two nuclear moments. Well-resolved EPR spectra of the present type in fluid solution at room temperature are relatively rare^{15,21} for rhenium(VI) species—only broad signals are usually observed.²² The separations between adjacent hyperfine lines of **7** are unequal, increasing systematically from the low-field to the high-field side. The range of this variable separation, arising from second-order effects,²³ is 310–660 G. Center-field g values and the average hyperfine splittings for the complexes are listed in Table 4. When solutions of **7** are frozen (77 K), rhombic spectra with partial overlap of the unequally spaced lines of the three components are observed.²⁴

Metal Redox. All the complexes are electroactive in acetonitrile solution at platinum electrodes. Quasireversible one-electron cyclic voltammetric responses with peak-to-peak separations of ~ 80 mV are observed. Reduction potential data

- (19) Wentworth, R. A. D.; Dahl, P. S.; Huffman, C. J.; Gillum, W. O.; Streib, W. E.; Huffman, J. C. *Inorg. Chem.* **1982**, *21*, 3060.
 (20) Gardner, J. K.; Paryadath, N.; Corbin, J. L.; Stiefel, E. I. *Inorg. Chem.* **1978**, *17*, 897.
 (21) de Learie, L. A.; Haltiwanger, R. C.; Pierpont, C. G. *Inorg. Chem.* **1987**, *26*, 817.
 (22) (a) AlMowali, A. H.; Porte, A. L. *J. Chem. Soc., Dalton Trans.* **1975**, 250. (b) Holloway, J. H.; Raynor, J. B. *J. Chem. Soc., Dalton Trans.* **1975**, 737. (c) Baldas, J.; Boas, J. F.; Bonnyman, J.; Pilbrow, J. R.; Williams, G. A. *J. Am. Chem. Soc.* **1985**, *107*, 1886. (d) Kirmse, R.; Stach, J. *Inorg. Chim. Acta* **1980**, *45*, L251 (e) Gibson, J. F.; Mertis, K.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1975**, 1093. (f) Al Mowali, A. H.; Porte, A. L. *J. Chem. Soc., Dalton Trans.* **1975**, 50.
 (23) Abragam, A.; Bleaney, B. *Electron Paramagnetic Resonance of Transition Ions*; Clarendon: Oxford, England, 1970; p 163.
 (24) Dirghangi, B. K.; Menon, M.; Banerjee, S.; Chakravorty, A. Unpublished results.

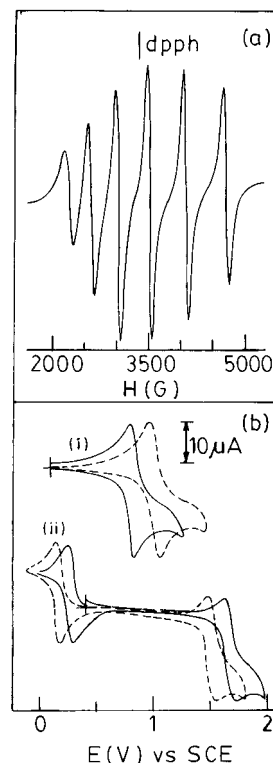


Figure 4. (a) X-band EPR spectrum of **7**(H,Cl) in dichloromethane–toluene (1:1). Instrument settings: power, 28 dB; modulation, 100 kHz; sweep center, 3000 G; sweep time, 250 s, at 298 K. (b) Cyclic voltammograms of a $\sim 10^{-3}$ M solution of (i) **4**(H,Cl) (---) and **5**(Cl,Cl) (—) and (ii) **7**(OMe,OMe) (---) and **7**(Cl,Cl) (—) in acetonitrile (0.1 M TEAP) at a platinum electrode (scan rate 50 mV s^{-1}).

Table 4. EPR Spectral Data at 298 K in Dichloromethane–Toluene (1:1)

compd	g^a	A^b	compd	g^a	A^b
7 (H,H)	1.915	490	7 (Cl,H)	1.928	493
7 (H,Me)	1.906	484	7 (Cl,Me)	1.923	488
7 (H,Cl)	1.912	488	7 (Cl,Cl)	1.917	492
7 (Me,Me)	1.917	492	7 (OMe,OMe)	1.908	486

^a At center field. ^b Average values.

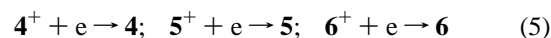
Table 5. Cyclic Voltammetric Formal Potentials at 298 K in Acetonitrile (0.1 M Et_4NClO_4) at a Platinum Electrode^{a–e}

compd	$E_{1/2}, \text{V}$ ($\Delta E_p, \text{mV}$)	compd	$E_{1/2}, \text{V}$ ($\Delta E_p, \text{mV}$)
4 (H,H)	0.92(80)	7 (H,H)	0.14 (80) 1.56 (80)
4 (H,Cl)	1.07(80)	7 (H,Me)	0.07 (80) 1.51 (80)
5 (Me,Me)	0.72(80)	7 (H,Cl)	0.16 (80) 1.58 (80)
5 (Cl,Cl)	0.76(100)	7 (Me,Me)	0.13 (80) 1.50 (80)
6 (Cl,Cl)	0.83(80)	7 (Cl,H)	0.16 (80) 1.58 (80)
6 (OMe,OMe)	0.75(80)	7 (Cl,Me)	0.18 (80) 1.56 (80)
		7 (Cl,Cl)	0.23 (80) 1.63 (80)
		7 (OMe,OMe)	0.11 (80) 1.50 (80)

^a The couples are **4**⁺/**4**($\text{Re}^{\text{VI}}/\text{Re}^{\text{V}}$), **5**⁺/**5**($\text{Re}^{\text{VI}}/\text{Re}^{\text{V}}$), **6**⁺/**6**($\text{Re}^{\text{VI}}/\text{Re}^{\text{V}}$), **7**⁺/**7**($\text{Re}^{\text{VI}}/\text{Re}^{\text{V}}$), and **7**⁺/**7**($\text{Re}^{\text{VI}}/\text{Re}^{\text{V}}$). ^b Scan rate 50 mV s^{-1} . ^c $E_{1/2} = 1/2(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively. ^d $\Delta E_p = E_{pc} - E_{pa}$. ^e Reference electrode SCE.

are collected in Table 5, and representative voltammograms are displayed in Figure 4b.

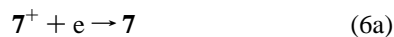
The response in the type **4–6** complexes corresponds to the couple of eq 5 where **4**⁺/**5**⁺/**6**⁺ is the rhenium(VI) congener of **4**/**5**/**6**. The reduction potentials of the couples of eq 5 are



subject to the usual Hammett effect of X and Y substituents

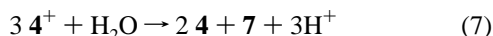
(Table 5, Figure 4b). The result of going from **4** to **5** or **6** (variation of imine carbon substituent) is more dominant, with $E_{1/2}$ shifting to lower potentials by ~ 0.2 V. The $E_{1/2}$ values of the couples of eq 5 (0.7–1.0 V *vs* SCE) are much lower than that (~ 1.7 V) of the corresponding couple for oxo complexes of type **1**. The arylimide ligands impart much superior redox stabilization to rhenium(VI) compared to the oxo ligand.

The amide complexes exhibit two successive one-electron couples, eq 6, where the metal oxidation states in 7^+ and 7^-

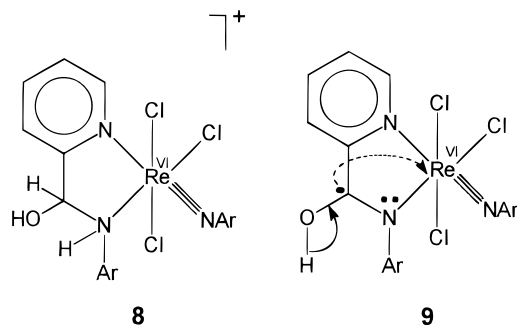


are $+7$ and $+5$, respectively. The potentials are again subject to the usual X, Y substituent effects. The $E_{1/2}$ values (~ 0.15 V) of the rhenium(VI)–rhenium(V) couple of eq 6b are lower than those of eq 5 by 0.6–0.8 V. The redox stabilization of the hexavalent state by the deprotonated amide function is quite remarkable, and consequently, the rhenium(VII)–rhenium(VI) couple (eq 6a) becomes accessible near 1.6 V.

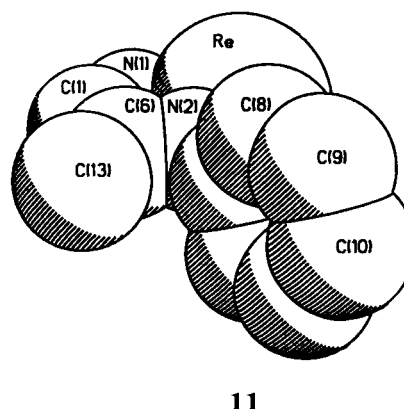
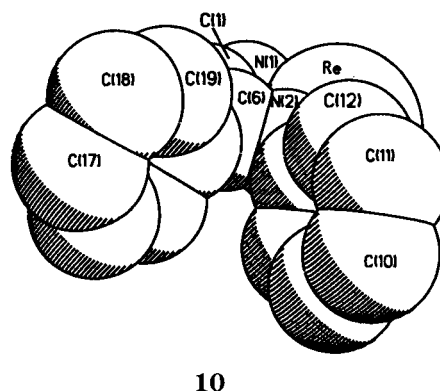
Blockade of the Reaction Path in 6. The conversion of **4** and **5** to **7** is logically expected to proceed via the same induced electron transfer route²⁵ proposed in the case of the reaction **2** \rightarrow **3** on the basis of rate studies.^{6a,26} In this scheme, the essential steps would be **4**(**5**) \rightarrow **4**⁺(**5**⁺) (metal oxidation), **4**⁺(**5**⁺) \rightarrow **8** (water addition), **8** \rightarrow **9** (radical formation), **9** \rightarrow **7**⁻ (internal redox), and **7**⁻ \rightarrow **7** (metal oxidation). Electrochemically generated **4**⁺ is rapidly converted to a mixture of **4** and **7** in moist solvents as in eq 7. Here, **4** in the product arises from



4⁺ partly utilized as the external oxidant. In the practical synthesis of **7**, nitric acid is used as the external oxidant and the whole of **4** is converted to **7** via **4**⁺ originating from oxidation of **4** by nitric acid.



We now consider the failure of **6** in affording **7**. Metal oxidation, **6** \rightarrow **6**⁺ (eq 5), is as facile as it is for complexes of type **5** (similar $E_{1/2}$ values, Table 5). Electrogenerated **6**⁺ is reconverted to **6** under wet conditions, and no **7** is formed. The structures of **5**(Cl,Cl) and **6**(OMe,OMe) provide a possible clue. In **6**(OMe,OMe) the two aryl rings pendent from C(6) and N(2) are both configured nearly perpendicular to the plane of the chelate ring, the respective dihedral angles being 93.2 and 84.1°. It can be seen in the space-filling drawing **10** that approach of reagents to the imine function C(6)–N(2) in **6**(OMe,OMe) is subject to a large steric hindrance by aryl crowding. In contrast, the function in **5**(Cl,Cl) shown in **11** is well-exposed especially



at the C(6) site. The crucial and rate-determining water addition step leading to **8** is initiated by nucleophilic attack by H₂O oxygen at the carbon C(6) site of the π^* aldimine orbital.^{6a} If the logical assumption is made that upon metal oxidation the steric situation remains grossly the same as in **10** and **11**, the approach of the water molecule to **6**⁺ would be strongly disfavored due to the steric factor—thus blocking amide formation.²⁷

Concluding Remarks

The present work has notably augmented the scope of the recently discovered oxygen atom transfer process involving a rhenium-coordinated diimine⁶ in aqueous oxidizing media as a synthetic tool. A family of picolinamide complexes of type **7** incorporating the rare Re^{VI}NAr motif has been conveniently assembled by treating pyridine-2-carboxaldehyde chelates of Re^{VI}NAr (**4** and **5**) with aqueous nitric acid.

The first structural characterization of an Re^{VI}NAr complex, **7**(Me,Me), has been achieved. The ReNAr motif is found to be nearly linear and triple-bonded, Re≡NAr, irrespective of the oxidation state. The effective metal radius contracts only slightly in going from the pentavalent (**4**–**6**) to the hexavalent (**7**) state of the metal.

The imine \rightarrow amide transformation is facile in the case of **4** and **5**, but it fails in the case of **6**. A plausible reason for this deactivation of the imine function to attack by water is steric crowding of the phenyl substituents lying perpendicular to the chelate ring as revealed in the structural work on **6**(OMe,OMe).

The picolinamide ligand imparts notable redox stability to the rhenium(VI) state in **7**, wherein the rhenium(VI)–rhenium(V) reduction potential is lower than those of the pyridine-2-

(25) (a) Chum, H. L.; Krumholtz, P. *Inorg. Chem.* **1974**, *13*, 519. (b) Taube, H. *Electron Transfer Reactions of Complex Ions in Solution*; Academic Press: New York, 1973; p 73.

(26) Menon, M.; Pramanik, A.; Chakravorty, A. *Inorg. Chem.* **1995**, *34*, 3310.

(27) If a water adduct of type **8** is formed from **6**⁺, it will be less prone to undergo the subsequent radical formation step (type **8** \rightarrow **9**) than the adduct of **5**⁺ because the C(6)–Ar bond (sp^3-sp^2) is stronger than the C(6)–Me bond (sp^3-sp^3). This electronic effect acts in the same direction as the steric factor hindering amide formation in the case of **6**.

carboxaldimine chelated **4–6** by ~ 0.7 V. The upshot of this is that the stable oxidation states of the imine and amide complexes as isolated are +5 and +6, respectively. The amide complexes of type **7** display well-resolved EPR spectra ($5d_{xy}^1$) in solution even at room temperature, the six metal hyperfine lines being unequally spaced due to second-order effects.

Experimental Section

Materials. The complexes $\text{ReOCl}_3(\text{PPh}_3)_2$,²⁸ **1(X)**,^{6a} **2(X)**,^{6a} and pyridine-2-carboxaldimines²⁹ were prepared by reported methods. The purification and drying of dichloromethane and acetonitrile for synthesis as well as electrochemical and spectral work were done as described in an earlier work.³⁰ Toluene was distilled over sodium before use. All other chemicals and solvents were of reagent grade and were used as received.

Physical Measurements. Spectra were recorded with the following equipment: electronic spectra, Hitachi 330 spectrophotometer; infrared spectra (KBr disk, 4000–300 cm^{-1}), Perkin-Elmer 783 spectrophotometer; X-band EPR spectra, Varian E-109C spectrometer (calibrant DPPH, $g = 2.0037$). Electrochemical measurements were performed by using a PAR model 370-4 electrochemistry system as described elsewhere.³¹ All experiments were performed at a platinum working electrode under dinitrogen atmosphere, the supporting electrolyte being tetraethylammonium perchlorate (TEAP). The potentials are referred to the saturated calomel electrode (SCE) and are uncorrected for junction contribution. Magnetic susceptibilities were measured on a PAR-155 vibrating-sample magnetometer. Microanalyses were performed using a Perkin-Elmer 240C elemental analyzer. All compounds afforded satisfactory elemental analyses, and only some representative instances will be cited.

Synthesis of 4(X,Y). The complexes could be prepared from **1(X)** or **2(X)** in 70–75% yields. The route from **2(X)** is more convenient. Details are given for one representative case.

(Trichlorophenylimido)(N-phenylpyridine-2-carboxaldimine)rhenium(V), 4(H,H). **a. From 1(X).** To a solution of **1(X=H)** (50 mg, 0.10 mmol) suspended in 10 mL of toluene was added an excess of aniline (150 mg, 1.61 mmol), and the mixture was refluxed for 1.5 h. Evaporation of the solvent under reduced pressure gave a dark product, and this was dissolved in a minimum volume of dichloromethane and subjected to chromatographic workup. The violet band obtained by a using benzene–acetonitrile (10:1) mixture as eluent was separated from the mixture, and the required complex was obtained in $\sim 80\%$ yield by slow evaporation of the eluate.

b. From 2(X). A 100 mg (0.13 mmol) sample of **2(X=H)** was suspended in 10 mL of toluene, and the suspension was warmed to 60 °C. To it was added 160 mg (1.72 mmol) of aniline, and the mixture was refluxed for 2 h. The resulting violet solution was evaporated to dryness under reduced pressure. The solid mass thus obtained was dissolved in 5 mL of dichloromethane and the solution subjected to chromatography on a silica gel column (20 \times 1 cm; 60–120 mesh, BDH). Upon elution with benzene, a small yellow band separated out which was rejected. The violet band that followed was eluted with a benzene–acetonitrile (10:1) mixture. The required complex was obtained from the eluate as dark shining microcrystals by slow evaporation. Yield: 58 mg, 72%. Anal. Calcd for **4(H,H)**, $\text{ReC}_{18}\text{H}_{15}\text{N}_3\text{Cl}_3$: C, 38.19; H, 2.65; N, 7.43. Found: C, 37.90; H, 2.60; N, 7.51.

Synthesis of 5(X,X). The complexes were prepared by the same general method. Details are given for one representative case. Yields were in the range 70–75%.

Trichloro(p-chlorophenyl)imido(2-acetylpyridine (p-chlorophenyl)imine)rhenium(V), 5(Cl,Cl). A mixture of 2-acetylpyridine (21 mg, 0.17 mmol) and *p*-chloroaniline (22 mg, 0.17 mmol) was heated in the absence of any solvent for 10 min. This mixture was then added to a suspension of $\text{ReOCl}_3(\text{PPh}_3)_2$ (100 mg, 0.12 mmol) in 20 mL of

Table 6. Crystallographic Data for **5(Cl,Cl)**, **6(OMe,OMe)**, and **7(Me,Me)**

	5(Cl,Cl)	6(OMe,OMe)	7(Me,Me)
empirical formula	$\text{C}_{19}\text{H}_{15}\text{Cl}_3\text{N}_3\text{Re}$	$\text{C}_{26}\text{H}_{23}\text{Cl}_3\text{N}_3\text{O}_2\text{Re}$	$\text{C}_{20}\text{H}_{18}\text{Cl}_3\text{N}_3\text{ORe}$
fw	648.8	702.0	608.9
space group	<i>P2₁/c</i>	<i>Pbca</i>	<i>P2₁/c</i>
<i>a</i> , Å	13.360(6)	12.079(5)	7.071(2)
<i>b</i> , Å	12.110(3)	17.083(9)	17.541(6)
<i>c</i> , Å	14.954(9)	26.049(9)	16.857(8)
β , deg	111.41(4)		100.59(3)
<i>V</i> , Å ³	2252.4(1.7)	5375.4(4.0)	2055.3(1.3)
<i>Z</i>	4	8	4
<i>T</i> , °C	22	22	22
λ , Å	0.710 73	0.710 73	0.710 73
ρ_{obsd} , g cm ⁻³	1.919	1.730	1.960
ρ_{calcd} , g cm ⁻³	1.913	1.735	1.968
μ , cm ⁻¹	59.98	48.47	63.19
<i>R</i> , %	2.90	3.63	2.86
<i>R_w</i> , %	3.15	3.81	3.00

^a $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2(|F_o|) + g|F_o|^2$; $g = 0.0002$ for **5(Cl,Cl)**, 0.0001 for **6(OMe,OMe)**, and 0.0001 for **7(Me,Me)**.

toluene, along with an excess of *p*-chloroaniline (150 mg, 1.18 mmol), and the solution was refluxed for 2 h. The resulting violet solution was evaporated to dryness under reduced pressure, the solid mass dissolved in 5 mL dichloromethane, and the solution subjected to chromatography on a silica gel column (20 \times 1 cm; 60–120 mesh, BDH). A violet band eluted with a benzene–acetonitrile (10:1) mixture was collected. Solvent evaporation afforded 56 mg (72%) of dark crystalline **5(Cl,Cl)**. Anal. Calcd for **5(Cl,Cl)**, $\text{ReC}_{19}\text{H}_{15}\text{N}_3\text{Cl}_3$: C, 35.16; H, 2.31; N, 6.48. Found: C, 35.60; H, 2.39; N, 6.40.

Synthesis of 6(X,X). The complexes were prepared by the same general procedure. Details are given for one representative case. Yields were in the range 75–80%.

Trichloro-(p-methoxyphenyl)imido(2-benzoylpyridine (p-methoxyphenyl)imine)rhenium(V), 6(OMe,OMe). A mixture of 2-benzoylpyridine (35 mg, 0.19 mmol) and *p*-anisidine (23 mg, 0.19 mmol) was heated in the absence of any solvent for 10 min. The yellow oil thus obtained was added to a suspension of $\text{ReOCl}_3(\text{PPh}_3)_2$ (100 mg, 0.12 mmol) in 20 mL of toluene, along with an excess of *p*-anisidine (150 mg, 1.22 mmol), and the solution was refluxed for 2 h. Chromatographic workup of the resulting violet solution (as described in the case of **5(X,X)**) afforded dark crystalline **6(OMe,OMe)** in 78% (66 mg) yield. Anal. Calcd for **6(OMe,OMe)**, $\text{ReC}_{26}\text{H}_{23}\text{N}_3\text{O}_2\text{Cl}_3$: C, 44.47; H, 3.28; N, 5.99. Found: C, 44.53; H, 3.35; N, 5.89.

Synthesis of 7(X,Y). The same general method was used to synthesize the above complexes from **4(X,Y)** as well as from **5(X,X)**. Details are given for one representative case. Yields varied in the range 80–85%.

Trichloro-(p-tolylimido)(N-p-tolyl-2-picolinamido)rhenium(VI), 7(Me,Me). A 100 mg (0.16 mmol) sample of **5(Me,Me)** was dissolved in 20 mL of acetonitrile, and 0.2 mL of 0.5 N nitric acid was added. The solution was stirred for 1 h, during which the color turned brown. Solvent evaporation afforded a dark product, which was repeatedly washed with water and dried in vacuo over P_4O_{10} . Yield: 85 mg (85%). Anal. Calcd for **7(Me,Me)**, $\text{ReC}_{20}\text{H}_{18}\text{N}_3\text{OCl}_3$: C, 39.44; H, 2.96; N, 6.90. Found: C, 39.50; H, 2.88; N, 6.99.

X-ray Structure Determination. Dimensions of the parallelepiped crystals were 0.14 \times 0.16 \times 0.22 mm³ for **5(Cl,Cl)**, 0.54 \times 0.46 \times 0.40 mm³ for **6(OMe,OMe)**, and 0.40 \times 0.18 \times 0.40 mm³ for **7(Me,Me)**. All three crystals were dark, and similar procedures were used for all of them. Single crystals of complexes **5(Cl,Cl)**, **6(OMe,OMe)**, and **7(Me,Me)** were grown by slow diffusion of hexane into dichloromethane solutions of the complexes.

Cell parameters were determined by a least-squares fit of 30 machine-centered reflections ($2\theta = 15\text{--}30^\circ$). Data were collected by the ω scan technique in the range $3^\circ \leq 2\theta \leq 45^\circ$ on a Siemens R3m/V four-circle diffractometer with graphite-monochromated Mo K α radiation. Two check reflections after each 198 reflections showed no intensity reduction. All data were corrected for Lorentz–polarization effects

(28) Chatt, J.; Rowe, G. A. *J. Chem. Soc.* **1962**, 4019.

(29) Bahr, G.; Thamlitz, H. *Z. Anorg. Allg. Chem.* **1955**, 282, 3.

(30) Basu, P.; Bhanja Choudhury, S.; Chakravorty, A. *Inorg. Chem.* **1989**, 28, 2680.

(31) Pramanik, A.; Bag, N.; Lahiri, G. K.; Chakravorty, A. *Inorg. Chem.* **1991**, 30, 410.

and absorption.³² Totals of 3388 (**5**(Cl,Cl)), 4026 (**6**(OMe,OMe)), and 3139 (**7**(Me,Me)) reflections were collected, of which 2964, 3499, and 2701 were respectively unique; of these, 1998, 2013, and 2149 were respectively taken as observed ($I > 3\sigma(I)$) for structure solution and refinement. The metal atoms were located from Patterson maps, and the rest of the non-hydrogen atoms emerged from successive Fourier syntheses. The structures were then refined by full-matrix least-squares procedures. All hydrogen atoms were included in calculated positions with fixed $U = 0.08 \text{ \AA}^2$. Calculations were done on a Micro VAX II computer using the SHELXTL-PLUS Program Package;³³ significant crystal data are listed in Table 6.

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Supporting Information Available: Listings of crystal data (Table S1), complete atomic coordinates (Tables S2, S7, and S12), bond lengths (Tables S3, S8, and S13), bond angles (Tables S4, S9, and S14), anisotropic thermal parameters (Tables S5, S10, and S15), and hydrogen atom positional parameters (Tables S6, S11, and S16) for **5**(Cl,Cl), **6**(OMe,OMe), and **7**(Me,Me) (17 pages). Ordering information is given on any current masthead page.

IC9701322

(32) North, A. C. T.; Philips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

(33) Sheldrick, G. M. *SHELXTL-PLUS 88, Structure Determination Software Programs*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1990.