

Rapid Communication

Aldimine→amide conversion via oxygen atom transfer from water mediated by rhenium oxidation states: Reaction model and synthetic utilization for making $\text{Re}^{\text{VI}}\text{NAr}$ species

Bimal Kumar Dirghangi, Sangeeta Banerjee, Mahua Menon & Animesh Chakravorty*

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India

Received 14 February 1997

The conversion of *N-p*-tolylpyridine-2-alimine to *N-p*-tolylpicolinamide chelated to $\text{Re}^{\text{IV}}(\text{OPPh}_3)\text{Cl}_3$ in oxidizing aqueous media is shown to proceed via initial one-electron metal oxidation followed by addition of a water molecule to the alimine function. Subsequent induced electron transfer in the adduct with concomitant proton loss affords the amide complex. The aldimine→amide reaction is utilized for the synthesis of the *N-p*-tolylpicolinamide complex of the rare $\text{Re}^{\text{VI}}\text{NAr}$ motif.

Chemical transformation brought about by transfer of oxygen, atom, mediated utilizing transition metal oxidation states, is an important theme of chemical research. It was recently shown^{1,2} that the pyridine-2-alimine complex of rhenium(III), **1** abbreviated as $\text{Re}^{\text{III}}(\text{L})(\text{OPPh}_3)\text{Cl}_3$ is spontaneously and quantitatively converted to the amide complex of rhenium(IV), **2** abbreviated as $\text{Re}^{\text{IV}}(\text{Lo})(\text{OPPh}_3)\text{Cl}_3$, in oxidizing (cerium(IV) or H_2O_2) aqueous environments. We now wish to disclose the results of mechanistic studies on this fascinating reaction. Following this lead, the aldimine→amide transformation has been utilized for the

synthesis of a stable picolinamide complex of the rare³⁻⁷ $\text{Re}^{\text{VI}}\text{NAr}$ moiety.

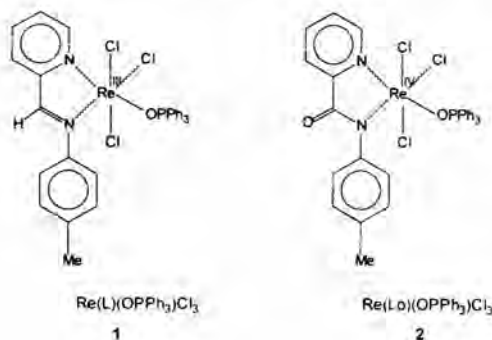
Experimental

The complexes $\text{Re}(\text{L})(\text{OPPh}_3)\text{Cl}_3$, **1**, and $\text{Re}(\text{Lo})(\text{OPPh}_3)\text{Cl}_3$, **2**, were prepared as reported^{1,2}. Electrochemical experiments were performed in pure dinitrogen atmosphere with a PAR Model 370-4 electrochemistry system⁸ with platinum working electrode. Electronic spectra were recorded on a Hitachi 330 spectrophotometer having a thermostated cell compartment. For rate measurements $\text{Re}^{\text{III}}(\text{L})(\text{OPPh}_3)\text{Cl}_3$ was first quantitatively oxidized to $\text{Re}^{\text{IV}}(\text{L})(\text{OPPh}_3)\text{Cl}_3^+$ by coulometry at 0.5V versus SCE in dry acetonitrile. Known amounts of water were added to aliquots of this solution and the reaction rate followed spectrophotometrically at 680 nm. The complex $\text{Re}^{\text{V}}(\text{L})(\text{NC}_6\text{H}_4\text{Y}(p))\text{Cl}_3$, **5**, was prepared by treating $\text{Re}(\text{L})(\text{OPPh}_3)\text{Cl}_3$ with *p*-chloroaniline in 1:5 ratio in boiling toluene. The resulting violet coloured solution afforded **5** in ~75% yield, upon chromatographic work-up. Treatment of **5** with aqueous 0.5 *N* nitric acid in acetonitrile medium afforded the brown coloured $\text{Re}^{\text{VI}}(\text{Lo})(\text{NC}_6\text{H}_4\text{Y}(p))\text{Cl}_3$, **6**, in excellent yield. Analytical data, found (calc.) are as follows: for $\text{Re}(\text{L})(\text{OPPh}_3)\text{Cl}_3$, **1**: C, 48.46 (48.52); H, 3.47 (3.52), N, 3.73 (3.65), for $\text{Re}(\text{Lo})(\text{OPPh}_3)\text{Cl}_3$, **2**: C, 47.50 (47.59); H, 3.45 (3.32); N 3.64 (3.58), for $\text{Re}(\text{L})(\text{NC}_6\text{H}_4\text{Cl})\text{Cl}_3$, **5**: C, 37.06 (37.12); H, 2.67 (2.60); N, 6.76 (6.83), for $\text{Re}(\text{Lo})(\text{NC}_6\text{H}_4\text{Cl})\text{Cl}_3$, **6**: C, (36.32); (36.23); H, 2.44 (2.38); N, 6.56 (6.67).

Results and discussion

Reaction model

The complex $\text{Re}^{\text{III}}(\text{L})(\text{OPPh}_3)\text{Cl}_3$ itself does not react with water but the rhenium(IV) congener $\text{Re}^{\text{IV}}(\text{L})(\text{OPPh}_3)\text{Cl}_3^+$ does. The reaction was followed spectrophotometrically at 680 nm corresponding to the growth of $\text{Re}^{\text{III}}(\text{L})(\text{OPPh}_3)\text{Cl}_3$. Representative time-dependent spectra at one temperature are depicted in Fig.1a. Rates were determined in the temperature range 280-300K and selected results including activation parameters are collected in Table 1. Under pseudo first-order conditions (excess H_2O) the rate is proportional to



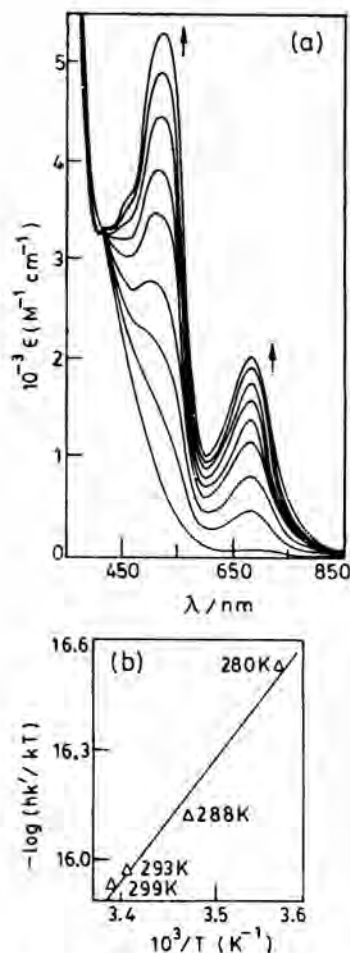


Fig. 1(a)—Time-evolution spectral changes due to the reaction of $\text{Re}(\text{L})(\text{OPPh}_3)\text{Cl}_3^+$ with water in acetonitrile solution at 298K (initial solute concentration $1.9 \times 10^{-4} \text{ M}$). (b)—Eyring plot for the reaction of $\text{Re}(\text{L})(\text{OPPh}_3)\text{Cl}_3^+$ with water

the concentration of $\text{Re}^{\text{IV}}(\text{L})(\text{OPPh}_3)\text{Cl}_3^+$ and the observed rate constant k_{obs} is proportional to the concentration of water. The rate is thus second-order as in Eq.(1). Eyring plots are shown in Fig. 1b. The entropy of activation is large and negative (Table 1) showing strong association between $\text{Re}^{\text{IV}}(\text{L})(\text{OPPh}_3)\text{Cl}_3^+$ and H_2O in the rate-determining step.

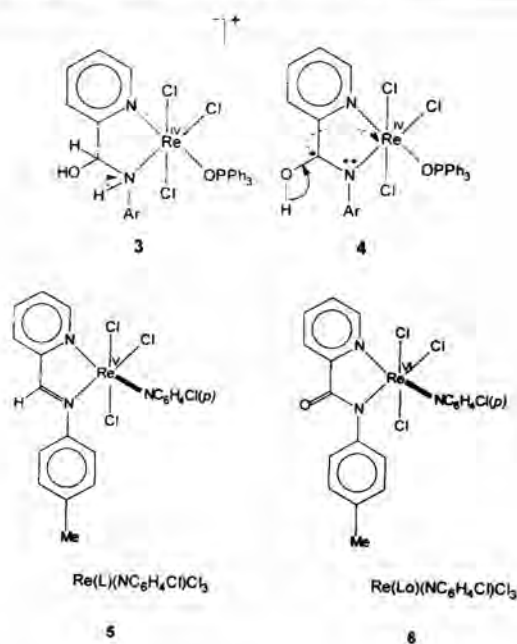
$$\text{rate} = k_{\text{obs}} [\text{Re}(\text{L})(\text{OPPh}_3)\text{Cl}_3^+] = k [\text{Re}(\text{L})(\text{OPPh}_3)\text{Cl}_3^+] [\text{H}_2\text{O}] \quad (1)$$

It is clear that the amide oxygen atom in $\text{Re}(\text{Lo})(\text{OPPh}_3)\text{Cl}_3$ originates from water and the rate is determined by the addition of water to the aldimine function, a probable adduct structure being 3. Stable aquo adducts of certain Schiff bases have actually been isolated^{9,10}. The intermediate 3 could undergo induced-electron transfer¹¹⁻¹³ involving radical formation, internal redox and proton

Table 1—Rate constants and activation parameters^a for the reaction $\text{Re}(\text{L})(\text{OPPh}_3)\text{Cl}_3^+ \rightarrow \text{Re}(\text{Lo})(\text{OPPh}_3)\text{Cl}_3$ in acetonitrile

T, K	$[\text{H}_2\text{O}], \text{M}$	$10^3 k_{\text{obs}}, \text{s}^{-1}$	$10^3 k', \text{M}^{-1} \text{s}^{-1}$	$\Delta H^\ddagger, \text{kcal mol}^{-1}$	$\Delta S^\ddagger, \text{eu mol}^{-1}$
280	1.11	0.22	0.17(0.01)		
	1.67	0.31			
	2.22	0.43			
288	1.11	0.44	0.45(0.01)	11.9(0.6)	-33.2(2.2)
	1.67	0.71			
	2.22	0.93			
293	1.11	0.52	0.65(0.04)		
	1.67	0.97			
	2.22	1.29			
299	1.11	0.85	0.69(0.02)		
	1.67	1.26			
	2.22	1.65			
		2.78	2.00		

^aLeast-squares deviations are in parentheses.



dissociation as illustrated in the transient 4 finally affording $\text{Re}^{\text{III}}(\text{Lo})(\text{OPPh}_3)\text{Cl}_3^-$ which consumes $\text{Re}^{\text{IV}}(\text{L})(\text{OPPh}_3)\text{Cl}_3^+$ giving rise to $\text{Re}^{\text{III}}(\text{L})(\text{OPPh}_3)\text{Cl}_3$ and $\text{Re}^{\text{IV}}(\text{Lo})(\text{OPPh}_3)\text{Cl}_3$. The stoichiometry of the net reaction is as given in Eq.(2).

Here $\text{Re}^{\text{IV}}(\text{L})(\text{OPPh}_3)\text{Cl}_3^+$ is acting both as a water acceptor and as an external oxidant. In the synthesis of $\text{Re}(\text{Lo})(\text{OPPh}_3)\text{Cl}_3$, an external oxidant (cerium(IV) or H_2O_2) is already present and the

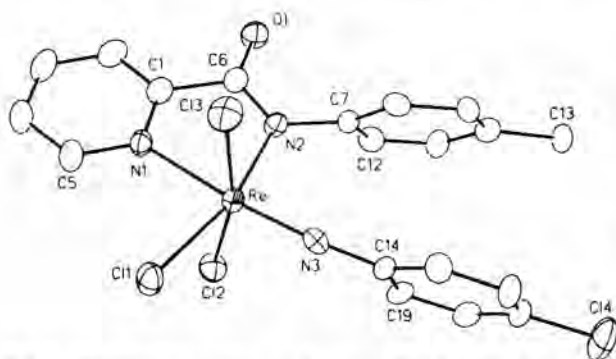
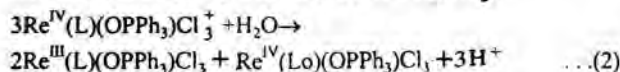


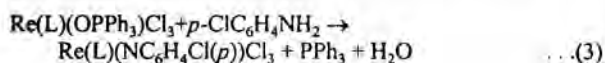
Fig.2—Perspective view and atom labelling scheme for $\text{Re}(\text{Lo})(\text{NC}_6\text{H}_4\text{Cl}(p))\text{Cl}_3$. All atoms are represented by their 30% ellipsoids.

whole of $\text{Re}(\text{L})(\text{OPPh}_3)\text{Cl}_3$ is converted to $\text{Re}(\text{Lo})(\text{OPPh}_3)\text{Cl}_3$ via $\text{Re}(\text{L})(\text{OPPh}_3)\text{Cl}_3^+$.



A $\text{Re}^{\text{VI}}\text{NAr}$ Complex

The reaction of **1** with *p*-chloroaniline afforded the imide complex **5**, Eq.(3). In this reaction the oxidation states of the metal and the phosphorus atom are interchanged. The transformation **1**→**2** encouraged us to perform a similar reaction on **5** leading to the amide complex **6** incorporating $\text{Re}^{\text{VI}}(\text{NC}_6\text{H}_4\text{Cl}(p))$. This indeed happened upon treating **5** with nitric acid in aqueous acetonitrile. The brown complex **6** has been isolated in excellent yield. Its X-ray structure (Fig.2) has been determined, and details will be published elsewhere. This is the first structure of a $\text{Re}^{\text{VI}}\text{NAr}$ complex. The known structures of the rare rhenium(VI) imide species incorporate electronically or sterically specialized ligands as in $\text{Re}^{\text{VI}}(\text{NC}_2\text{Cl}_5)^5$ and $\text{Re}^{\text{VI}}(\text{NBu}^t)^{6,7}$. Complex **6** is one-electron paramagnetic and EPR-active ($5d_{xy}^1$).



Acknowledgement

Financial support received from the Indian National Science Academy, Council of Scientific and Industrial Research and Department of Science and Technology, New Delhi is acknowledged. Affiliation with the Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore is acknowledged.

References

- Menon M, Pramanik A, Bag N & Chakravorty A, *Inorg Chem*, **33** (1994) 403.
- 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.
- Clark G R, Nielson A J & Rickard C E F, *Polyhedron*, **7** (1988) 117.
- LaMonica G & Cenini S, *J chem Soc, Dalton Trans*, (1980) 1145.
- Weiber U, Dehnicke K & Fenske D, *Z anorg allg Chem*, **457** (1979) 115.
- Danopoulos A A, Longley C J, Wilkinson G, Hussain B & Hursthouse M B, *Polyhedron*, **8** (1989) 2657.
- Danopoulos A A, Wilkinson G, Sweet T K N & Hursthouse M B, *J chem Soc Dalton Trans*, (1996) 2995.
- Pramanik A, Bag N, Lahiri G K & Chakravorty A, *Inorg Chem*, **30** (1991) 410.
- (a) Harris C M, McKenzie E D, *Nature*, **196** (1962) 670.
(b) Busch D H & Bailar (Jr) J C, *J Am chem Soc*, **78** (1956) 1137.
(c) Kotovic V, Vergez S C & Busch D H, *Inorg Chem*, **16** (1977) 1716.
- Bandoli G, Gerber T I A, Jacobs R & du Preez J G H, *Inorg Chem*, **33** (1994) 178.
- Menon M, Pramanik A & Chakravorty A, *Inorg Chem*, **34** (1995) 3310.
- Taube H, *Electron transfer reactions of complex ions in solution* (Academic Press, New York), 1973, 73.
- (a) Chum H L & Krumholz P, *Inorg Chem*, **13** (1974) 519.
(b) Chum H L & Helene M E M, *Inorg Chem*, **19** (1980) 876, and references therein.