Rapid Communication

Aldimine→amide conversion via oxygen atom transfer from water mediated by rhenium oxidation states: Reaction model and synthetic utilization for making Re VI 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

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The conversion of N-p-tolylpyridine-2-aldimine to N-p-tolylpicolinamide chelated to Re IV(OPPh3)Cl3 in oxidizing aqueous media is shown to proceed via initial one-electron metal oxidation followed by addition of a water molecule to the aldimine 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 Re VI 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 shown1,2 that the pyridine-2-aldimine complex of rhenium(III), 1 abbreviated as Re III(L)(OPPh3)Cl3 is spontaneously and quantitatively converted to the amide complex of rhenium(IV), 2 abbreviated as Re IV(LO)(OPPh3)Cl3, in oxidizing (cerium(IV) or H2O2) 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 rare Re VI NAr moiety.

Experimental

The complexes Re(L)(OPPh3)Cl3, 1, and Re(LO)(OPPh3)Cl3, 2, were prepared as reported1,2. Electrochemical experiments were performed in pure dinitrogen atmosphere with a PAR Model 370-4 electrochemistry system3 with platinum working electrode. Electronic spectra were recorded on a Hitachi 330 spectrophotometer having a thermostated cell compartment. For rate measurements Re III(L)(OPPh3)Cl3 was first quantitatively oxidized to Re IV(L)(OPPh3)Cl3+ 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 Re IV(L)(NC6H4Y(p)Cl3, 5, was prepared by treating Re(L)(OPPh3)Cl3 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 Re VI(LO)(NC6H4Y(p)Cl3, 6, in excellent yield. Analytical data, found (calc.) are as follows: for Re(L)(OPPh3)Cl3, 1: C, 48.46 (48.52); H, 3.47 (3.52); N, 3.73 (3.65), for Re(LO)(OPPh3)Cl3, 2: C, 47.50 (47.59); H, 3.45 (3.32); N, 3.64 (3.58), for Re(L)(NC6H4Cl)Cl3, 5: C, 37.06 (37.12); H, 2.67 (2.60); N, 6.76 (6.83), for Re(LO)(NC6H4Cl)Cl3, 6: C, 36.32; (36.23); H, 2.44 (2.38); N, 6.56 (6.67).

Results and discussion

Reaction model

The complex Re III(L)(OPPh3)Cl3 itself does not react with water but the rhenium(IV) congenor Re IV(L)(OPPh3)Cl3+ does. The reaction was followed spectrophotometrically at 680 nm corresponding to the growth of Re IV(L)(OPPh3)Cl3. 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 H2O) the rate is proportional to
Fig. 1(a)—Time-evolution spectral changes due to the reaction of Re(L)(OPPh₃)Cl₃ with water in acetonitrile solution at 298 K (initial solute concentration 1.9 × 10⁻⁴ M). (b)—Eyring plot for the reaction of Re(L)(OPPh₃)Cl₃ with water.

the concentration of Re⁺⁺⁺⁺(L)(OPPh₃)Cl₃ and the observed rate constant kₒbs 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 Re⁺⁺⁺⁺(L)(OPPh₃)Cl₃ and H₂O in the rate-determining step.

\[
\text{rate} = k_{\text{obs}} [\text{Re}(L)(\text{OPPh}_3)\text{Cl}_3] = k [\text{Re}(L)(\text{OPPh}_3)\text{Cl}_3] [\text{H}_2\text{O}].
\]

It is clear that the amide oxygen atom in Re(Lo)(OPPh₃)Cl₃ 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 isolated⁶⁻¹⁰. The intermediate 3 could undergo induced-electron transfer¹¹⁻¹³ involving radical formation, internal redox and proton dissociation as illustrated in the transient 4 finally affording Re⁺⁺⁺⁺(Lo)(OPPh₃)Cl₃ which consumes Re⁺⁺⁺⁺(L)(OPPh₃)Cl₃ giving rise to Re⁺⁺⁺⁺(L)(OPPh₃) Cl₂ and Re⁺⁺⁺⁺(Lo)(OPPh₃) Cl₃. The stoichiometry of the net reaction is as given in Eq. (2).

Here Re⁺⁺⁺⁺(L)(OPPh₃)Cl₃ is acting both as a water acceptor and as an external oxidant. In the synthesis of Re(Lo)(OPPh₃)Cl₃, an external oxidant (cerium(IV) or H₂O₂) is already present and the
References

(c) Kotovic V, Vergez S C & Busch D H, Inorg Chem, 16 (1977) 1716.

A Re\textsuperscript{VI}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 \(1 \rightarrow 2\) encouraged us to perform a similar reaction on 5 leading to the amide complex 6 incorporating Re\textsuperscript{V}l(\(\text{NC}_6\text{H}_4\text{Cl(p})\)). 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 Re\textsuperscript{V}NAr complex. The known structures of the rare rhenium(VI) imide species incorporate electronically or sterically specialized ligands as in Re\textsuperscript{V}(\(\text{NC}_2\text{H}_4\text{Cl(p})\))\textsuperscript{3} and Re\textsuperscript{V}(\(\text{NBu}_3\))\textsuperscript{6-7}. Complex 6 is one-electron paramagnetic and EPR-active (5\(d_{\chi\chi}\)).

\[
\text{Re(L)(OPPh}_3\text{)}\text{Cl}_3+p-\text{ClC}_6\text{H}_4\text{NH}_2 \rightarrow \text{Re(L)(NC}_6\text{H}_4\text{Cl(p})\text{)}\text{Cl}_3 + \text{PPh}_3 + \text{H}_2\text{O} \quad (3)
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