Volume 33

Number 3

February 2, 1994

Inorganic Chemistry

Communications

Facile Aldimine → Amide Oxidation in a Rhenium Complex[†]

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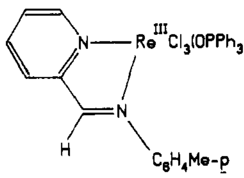
Received August 2, 1993

The common aldehyde → amide conversion route is outlined in eq 1. The route of eq 2 with a reverse sequence of reagent

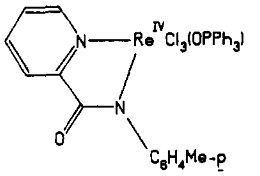
$$-CHO \xrightarrow{[O]} -COOH \xrightarrow{RNH_2} -CONHR \qquad (1)$$

$$-CHO \xrightarrow{RNH_2} -CHNR \xrightarrow{[O]} -CONHR \qquad (2)$$

application is conceivable but the difficulty lies in realization of the second step: azomethine → amide. In this work we report an authentic example of this transformation in which the azomethine function is activated via metal binding. The reaction is **1** → **2** wherein a chelated pyridine-2-aldimine (L) is quantitatively oxidized (chemically/electrochemically) to the corresponding deprotonated 2-picolinamide with concomitant metal oxidation.



1



2

The ligand[1] L prepared from pyridine-2-aldehyde and *p*-toluidine reacts smoothly with $ReOCl_3(PPh_3)_2$[2] in warm (323 K) benzene under nitrogen affording red crystals of the new solvated complex **1**·C_6H_6 in excellent yields.[3] Oxo-transfer from oxo–rhenium moieties to PPh_3 is well-documented.[4–9] Instances where PPh_3 in the reactant and $OPPh_3$ in the product occur in the coordinated states are, however, rare. Upon treating a stirred solution of **1**·C_6H_6 (20 mg) in MeCN (20 mL) with aqueous H_2O_2 (30%, 0.1 mL) under ambient conditions, the color changed from red to brownish yellow. After 1 h of reaction, the solvent was removed in vacuo and upon recrystallization of the residue from benzene the oxidized complex was afforded in virtually quantitative yield in the form of the benzene adduct[10] **2**·$^1/_2C_6H_6$. The same results were obtained when H_2O_2 was replaced by aqueous Ce(IV) (here a filtration before removal of solvent was necessary).

The X-ray structures[11,12] of **1** and **2** in their benzene adducts

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[†] This work is dedicated to Professor C. N. R. Rao on the occasion of his 60th birthday.

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(3) Anal. Calcd for **1**·C_6H_6, $C_{37}H_{33}N_2OPCl_3Re$: C, 52.53; H, 3.94; N, 3.31. Found: C, 52.68; H, 3.86; N, 3.37. UV–vis (CH_3CN): $\lambda = 675$ nm (ϵ 2220), 475 (4100), 450 sh (2575), 425 sh (2425) (sh = shoulder). μ_{eff}: 2.84μ_B (t_2^4). IR: ν (C=N), 1591 cm^{-1}; ν (O—P), 1123 cm^{-1}.

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(10) Anal. Calcd for **2**·$^1/_2C_6H_6$, $C_{34}H_{29}N_2O_2PCl_3Re$: C, 49.68; H, 3.56; N, 3.41. Found: C, 49.58; H, 3.49; N, 3.48. UV–vis (CH_3CN): $\lambda = 725$ nm (ϵ 85), 525 sh (540), 400 sh (2260) (sh = shoulder). μ_{eff}: 3.64 μ_B (t_2^3). IR: ν (amide), 1642 and 1605 cm^{-1}; ν (O–P), 1121 cm^{-1}.

(11) X-ray quality crystals of **1**·C_6H_6 and **2**·$^1/_2C_6H_6$ were obtained by diffusion of a benzene solution of the respective complex into hexane followed by slow evaporation. X-ray parameters for **1**·C_6H_6: $C_{37}H_{33}N_2OPCl_3Re$, space group, $P\bar{1}$; $a = 11.515(5)$ Å, $b = 12.361(7)$ Å, $c = 13.288(6)$ Å, $\alpha = 88.28(4)°$, $\beta = 73.90(3)°$, $\gamma = 75.67(4)°$; $V = 1757(1)$ Å^3; $Z = 2$; $\rho_{calc} = 1.598$ g cm^{-3}; $\mu = 37.64$ cm^{-1}; $F(000) = 836$; crystal dimensions $0.24 \times 0.26 \times 0.14$ mm^3. X-ray parameters for **2**·$^1/_2C_6H_6$: $C_{34}H_{29}N_2O_2PCl_3Re$, space group, $P2_1/c$; $a = 9.799(5)$ Å, $b = 15.777(6)$ Å, $c = 21.402(11)$ Å, $\beta = 102.58(4)°$; $V = 3229(2)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.689$ gcm^{-3}; $\mu = 40.95$ cm^{-1}; $F(000) = 1616$; crystal dimensions $0.36 \times 0.42 \times 0.28$ mm^3. The intensities of 6948 unique reflections ($3 < 2\theta < 52°$) for **1**·C_6H_6 and 5632 unique reflections ($3 < 2\theta < 50°$) for **2**·$^1/_2C_6H_6$ were measured at 295 K on a Siemens R3m/V diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). These were corrected for Lorentz, polarization, and absorption effects and 4948 and 3726 reflections $[I > 3\sigma(I)]$ respectively were used for structure solution. Both the structures were solved by the Patterson heavy-atom method and difference Fourier syntheses, and subsequently refined by full-matrix least squares procedures using the SHELXTL-PLUS program package[12] on a MicroVax II computer. Non-hydrogen atoms were refined anisotropically, and hydrogens were added at their respective calculated positions. The benzene of crystallization in **2**·$^1/_2C_6H_6$ lies on a special position (centrosymmetric). Final $R = 0.0396$, $R_w = 0.0451$ for **1**·C_6H_6 and $R = 0.0387$, $R_w = 0.0443$ for **2**·$^1/_2C_6H_6$ where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. Largest residual electron density was 1.24 e Å^{-3} for **1**·C_6H_6 and 1.16 e Å^{-3} for **2**·$^1/_2C_6H_6$ near the metal atoms.

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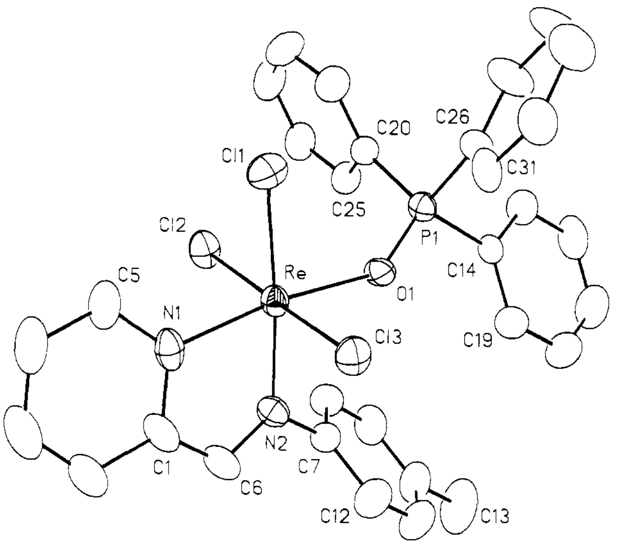

Figure 1. ORTEP plot (40% probability ellipsoids) and atom labeling scheme for **1** in **1**·C_6H_6. Selected bond distances (Å) and angles (deg): Re–Cl1, 2.372(2); Re–Cl2, 2.363(2); Re–Cl3, 2.367(2); Re–O1, 2.080(4); Re–N1, 2.030(5); Re–N2, 2.033(5); C6–N2, 1.320(9); Re–O1–P1, 143.1(3); N1–Re–N2, 76.9(3).

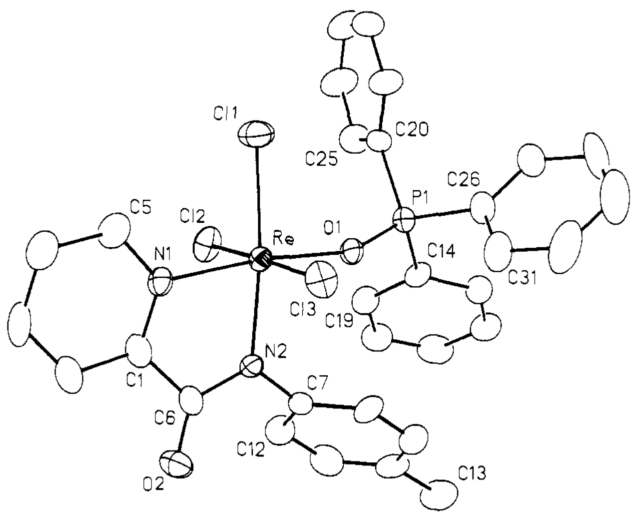

Figure 2. ORTEP plot (40% probability ellipsoids) and atom labeling scheme for **2** in **2**·$^1/_2C_6H_6$. Selected bond distances (Å) and angles (deg): Re–Cl1, 2.385(3); Re–Cl2, 2.332(3); Re–Cl3, 2.318(3); Re–O1, 2.003(6); Re–N1, 2.091(6); Re–N2, 2.070(6); C6–O2, 1.235(9); C6–N2, 1.375(10); Re–O1–P1, 157.7(3); N1–Re–N2, 77.7(3).

are shown in Figures 1 and 2 respectively. The gross geometries of the distorted octahedral $ReOCl_3N_2$ coordination spheres are very similar in the two complexes. Thus the pyridine nitrogen lies trans to $OPPh_3$ oxygen and the Cl_3 fragment is meridional in both **1** and **2** species. The Re–O and the average Re–Cl lengths correctly reflect the increase of metal oxidation state in going from **1** to **2**. The Re–N lengths are, however, longer in **2** and this is ascribed to the superior back-bonding ability of Re(III)[13] in the α-diimine chelate of **1** compared to that of Re(IV) in the amide–imine chelate of **2**. Reversal of bond length trends due to back-bonding is well-documented elsewhere.[14,15] The distances within the amide function in **2** are C–O = 1.235(9) Å and C–N = 1.375(10) Å. The azomethine C–N length in **1** is 1.320(9) Å.

In MeCN solution (0.1 M in NH_4PF_6), **1** displays a reversible cyclic voltammetric Re(IV)–Re(III) couple, $\mathbf{1}^+ + e^- \rightleftharpoons \mathbf{1}$ ($E_{1/2}$ = 0.30 V vs SCE at a platinum electrode).[16] The yellow Re(IV) complex $\mathbf{1}^+$ can be generated quantitatively by electrooxidation at 0.5 V vs SCE. It has the same voltammogram (initial scan cathodic) as **1** (initial scan anodic). Solutions of $\mathbf{1}^+$ are stable when the solvent is dry. Upon addition of H_2O, the spontaneous transformation of eq 3 occurs.[17] Exhaustive electrolysis of **1**

$$3\mathbf{1}^+ + H_2O \rightarrow 2\mathbf{1} + \mathbf{2} + 3H^+ \qquad (3)$$

in MeCN containing 5% H_2O at 0.5 V vs SCE, resulted in complete conversion to **2** as expected (since **1** formed in eq 3 is reoxidized), and from workup of the electrolyzed solution, the complex **2**·$^1/_2C_6H_6$ can be isolated in nearly quantitative yields. The conversion $\mathbf{1} \rightarrow \mathbf{2}$ by aqueous chemical oxidizing agents (H_2O_2, Ce^{4+}) may also proceed via $\mathbf{1}^+$. Preliminary studies show that the rate of reaction between $\mathbf{1}^+$ and H_2O is first order with respect to either reactant. A plausible pathway is the addition of H_2O to the azomethine function[18] of $\mathbf{1}^+$ (–CH=N– → –CH(OH)—NH–) followed by rapid oxidation of the α-hydroxyamine moiety to amide by $\mathbf{1}^+$.

Ongoing studies include generalization of the unusual metal-mediated oxidation process reported here to other systems and detailed mechanistic probing of the processes involved.

Acknowledgment. Crystallography was done at the National Single Crystal Diffractometer Facility, Department of Inorganic Chemistry, Indian Association for the Cultivation of Science. Financial supports received from the Department of Science and Technology and the Council of Scientific and Industrial Research, New Delhi, are gratefully acknowledged.

Supplementary Material Available: Listings of atomic coordinates with isotropic thermal parameters (Tables S1 and S6), complete bond distances (Tables S2 and S7) and angles (Tables S3 and S8), anisotropic thermal parameters (Tables S4 and S9), and hydrogen atom coordinates (Tables S5 and S10) for **1**·C_6H_6 and **2**·$^1/_2C_6H_6$ (12 pages). Ordering information is given on any current masthead page.

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(16) Complex **2** also displays a reversible Re(IV)–Re(III) couple in MeCN solution: $\mathbf{2} + e^- \rightleftharpoons \mathbf{2}^-$ ($E_{1/2}$ –0.41 V vs SCE). The higher oxidation state is much better stabilized by the amide ligands as compared to the aldimine ligand.

(17) The 1:2 concentration ratio of **2** and **1** in the product was established from UV–vis spectrophotometry[3,10] and cyclic voltammetric current heights of the $\mathbf{1}^+/\mathbf{1}$ and $\mathbf{2}/\mathbf{2}^-$ couples which have widely separated $E_{1/2}$ values.

(18) Some documentation on the addition of hydroxylic solvents (H_2O, EtOH) to azomethine functions and subsequent oxidation is available: (a) Busch, D. H.; Bailer, J. C., Jr. *J. Am. Chem. Soc.* **1956**, *78*, 1137. (b) Harris, C. M.; McKenzie, E. D. *Nature*, **1962**, *196*, 670. (c) Chum, H. L.; Helene, M. E. M. *Inorg. Chem.* **1980**, *19*, 876 and references therein.