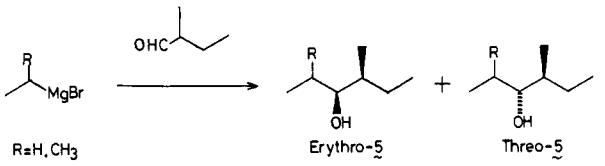
determined through NMR and GLC comparisons of their hydrogenation products (**5**) with an erythro-rich mixture independently prepared by the reaction of 2-methylbutanal with ethyl or isopropyl Grignard reagent in which the stereochemistry of the major stereoisomer can be predicted by the Cram's rule.[12-14]



The observed degree of internal asymmetric induction is particularly noteworthy since no great degree of either threo or erythro selectivity has been reported yet for different [2,3]-sigmatropic variations[10,15] except for the [2,3]-Wittig process[3b] of (*Z*)-crotyl benzyl ether exhibiting a high erythro selectivity.[16] Regardless of the origin of the regio- and stereochemical features outlined here,[17] the results of the present study anomalously expand the synthetic potential of the [2,3]-Wittig rearrangement. In particular, the high degree of diastereoselection provides the synthetic chemists with a powerful weapon with which to attack the current problem of acyclic stereocontrol.[15] Further synthetic applications of the [2,3]-Wittig rearrangements are in progress.

Supplementary Material Available: Spectral and physical properties for rearrangement products (5 pages). Ordering information is given on any current masthead page.

(12) Morrison, J. D.; Mosher, H. S. "Asymmetric Organic Reactions"; Prentice-Hall: Englewood Cliffs, NJ, 1971; Chapter 3.

(13) **5** (R = H): 77% yield; 66:34 erythro/threo (by NMR assay); GLC (PEG 20M, 100 °C), t_R 28.8 min (major) and 29.8 min (minor). **5** (R = CH_3): 79% yield; ca. 2.0 erythro/threo (by GLC and NMR assay); GLC (PEG 20M, 80 °C), t_R 47.2 min (major) and 48.7 min (minor).

(14) The stereochemical assignment for **5** (R = H) was further confirmed by NMR and GLC comparisons with an authentic threo-**5** (R = H) independently prepared via reaction of *trans*-3,4-epoxyhexane with lithium dimethylcuprate.

(15) For an excellent review on acyclic stereocontrol, see: Bartlett, P. A. *Tetrahedron* **1980**, *36*, 2. See also: Jemison, R. W.; Laird, T.: Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc., Perkin Trans 1* **1980**, 1436.

(16) In contrast, however, the *E* counterpart has exhibited a low degree of threo selectivity.[3b,4a]

(17) A detailed discussion will be reported in a full paper.

Oxidation of Isopropylamine Coordinated to Ruthenium

Peter A. Adcock and F. Richard Keene*

Department of Chemistry and Biochemistry
James Cook University of North Queensland
Townsville, Queensland 4811, Australia

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There has been much recent interest in the oxidative dehydrogenation of coordinated amines to the corresponding imines or nitriles.[1-3] Many of these studies have involved ruthenium as the metal center, and although the formation of complexes containing the α,α'-diimine moiety has been relatively common,[1] complexes containing coordinated simple monodentate imines have not been isolated.[1,2]

We have studied the oxidation of isopropylamine in the complex $[Ru(tpy)(bpy)(NH_2CHMe_2)]^{2+}$ (tpy = 2,2′:6′,2″-terpyridine; bpy = 2,2′-bipyridine). Two major processes occur: a two-electron oxidation yielding the corresponding imine complex $[Ru(tpy)(bpy)(NH{=}CMe_2)]^{2+}$, which in turn undergoes a further two-electron oxidation to yield a product characterized as $[Ru(tpy)(bpy)(NCMe_2)]^{3+}$. The nature of these two oxidation products is significant, since the two-electron oxidation product represents the first isolated monodentate imine complex of ruthenium, and the structure of the four-electron oxidation product is novel in ruthenium chemistry, as it can be formulated to contain an N-bound isopropylideneamide anion.

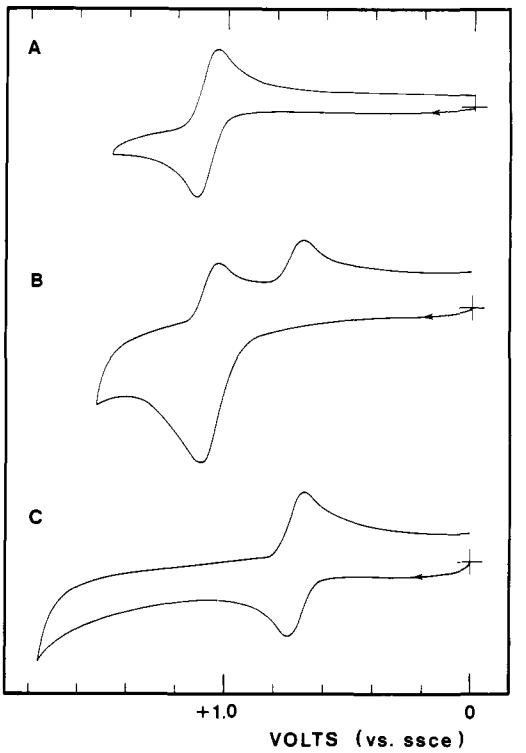

Figure 1. Cyclic voltammograms (200 mV/s) of $[Ru(tpy)(bpy)(isopropylamine)]^{2+}$ (A) and of the two-electron (B) and four-electron (C) oxidation products in acetonitrile solution.[4]

In their study of the oxidation of benzylamine in $[Ru(NH_3)_5(PhCH_2NH_2)]^{2+}$ to the benzonitrile complex, Diamond et al.[2] observed an intermediate which they assumed to be the imine species. In the same work, the oxidation of $[Ru(NH_3)_5(cyclohexylamine)]^{3+}$ yielded $[Ru(NH_3)_6]^{2+}$ and cyclohexanone, presumably by hydrolysis of the coordinated imine complex generated by dehydrogenation. Brown et al.[1] also claimed the generation in situ of nonconjugated chelated diimines in the oxidation of $[Ru(bpy)_2(tn)]^{2+}$ and $[Ru(bpy)_2(aepy)]^{2+}$ (tn = 1,3-propanediamine; aepy = 2-(aminoethyl)pyridine). In none of these cases could the imine complex be isolated.

A spectrophotometric titration of the oxidation of $[Ru(tpy)(bpy)(NH_2CHMe_2)]^{2+}$ by Ce(IV) in 2 M H_2SO_4 indicates an overall four-electron oxidation consisting of two separate two-electron processes which are consecutive. Spectra taken during exhaustive electrolyses (platinum gauze electrode) in 0.1 M HCl (at 0.90 V vs. SSCE) and acetonitrile (at 1.10 V vs. SSCE) indicate similar results. The overall spectrophotometric and coulometric *n* values were slightly less than 4.0 (viz., 3.6–3.8). The second two-electron process can be reversed electrochemically (coulometry at 0.50 V in 0.1 M HCl, 0.55 V in acetonitrile), with *n* for the reduction being exactly half the value for the overall oxidation. The two- and four-electron oxidation products were isolated by precipitation as the hexafluorophosphate salts and purified by ion-exchange chromatography on SP-Sephadex.

For the two-electron oxidation product, the visible spectrum (MLCT transitions) in 2 M H_2SO_4 has ϵ_{474}^{max} 8000 (cf. ϵ_{481}^{max} 8800 for the parent isopropylamine species). Cyclic voltammetry in acetonitrile solution[4] revealed $E_{p,a}$ = 1.10 V (compared with

(1) Brown, G. M.; Weaver, T. R.; Keene, F. R.; Meyer, T. J. *Inorg. Chem.* **1976**, *15*, 190–196 and references therein.

(2) Diamond, S. E.; Tom, G. M.; Taube, H. *J. Am. Chem. Soc.* **1975**, *97*, 2661–2664.

(3) Keene, F. R.; Salmon, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 1884–1889.

(4) Support electrolyte tetra-*n*-ethylammonium hexafluorophosphate; platinum bead working electrode; saturated sodium chloride calomel electrode (SSCE) as reference.

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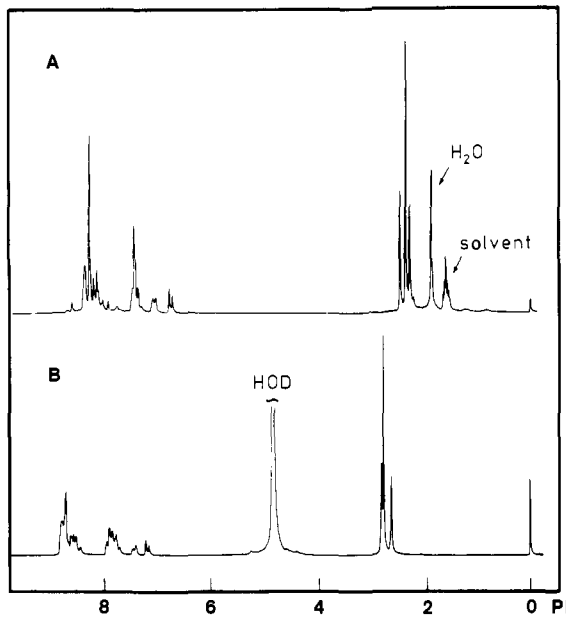

Figure 2. 100-MHz ^1H NMR spectra of $[Ru(tpy)(bpic)(C_3H_6N)]^{3+}$ in CD_3CN (A) and 0.1 M DCl (B) (Me_4Si external standard).

a reversible couple $E_{1/2}$ = 1.09 V for the amine precursor), with a peak on the reverse sweep ($E_{p,c}$ = 0.68 V) associated with the four-electron oxidation product, as shown in Figure 1. The ^1H NMR spectrum (in CD_3CN) showed two doublets in the aliphatic region centered at 1.12 and 1.62 ppm with very small coupling (0.73 and 1.56 Hz, respectively). This spectrum is consistent with the imine formulation, with both methyl groups being split by the adjacent NH=C moiety. On addition of a drop of D_2O, each doublet collapses to a singlet consistent with deuterium exchange at the imine NH group. We conclude therefore that the two-electron oxidation product is the isopropylimine complex $[Ru(tpy)(bpy)(NH{=}CMe_2)]^{2+}$ and that the small blue shift in the visible spectrum on going from the amine to imine ligand indicates there is a relatively small amount of back-bonding from Ru(II) to the isolated monodentate imine, compared with the large effect observed for the conjugated α,α'-diimine grouping.[1]

The four-electron oxidation product has the general formula $[Ru(tpy)(bpy)(C_3H_6N)]_z(PF_6)_{3z}$ by microanalysis,[5] and conductance measurements in acetonitrile using Feltham's method[6] show that the molecular complexity z = 1, so the complex is monomeric. ^1H NMR spectra of the related complex $[Ru(tpy)(bpic)(C_3H_6N)]^{3+}$ (bpic = 4,4'-dimethyl-2,2'-bipyridine) in acetonitrile-d_3 and 0.1 M DCl are shown in Figure 2. In the aliphatic region, each spectrum contains a six-proton methyl singlet due to the oxidized isopropylamine ligand, flanked by two three-proton methyl singlets arising from the dimethylbipyridine ligand. The complex shows little absorption in the visible region of the electronic spectrum, consistent with oxidation of the metal center to Ru(III)[7] or Ru(IV).[8] In dry acetonitrile solution, cyclic voltammetry shows a reversible couple, $E_{1/2}$ = 0.72 V (Figure 1).

The above evidence indicates the $NCMe_2$ skeleton remains intact in the four-electron oxidation product, which can be regarded formally as a Ru(IV) complex of the coordinated isopropylideneamide anion, $(N{=}CMe_2)^-$. Such a ligand has several possible bonding modes,[9] but the ready electrochemical interconversion of this complex with the imine species leads us to believe that it functions as an N-bound mononuclear ligand in this case. Application of the 18-electron rule for the metal center suggests the ligand should be a four-electron donor, implying Ru-N multiple bonding and a linear Ru-N-C linkage. The ^1H NMR studies are in agreement with this structure, and we are undertaking an X-ray structural analysis to confirm the assignment.

The electrochemical interconversion of the two- and four-electron oxidation products of coordinated isopropylamine occurs since on oxidation of the isopropylimine species (presumably at the metal center), the acidity of the proton on the ligating imine nitrogen would be markedly increased[10] and deprotonation gives rise to the coordinated isopropylideneamide anion. It is apparent from the cyclic voltammetric behavior of the isopropylimine and isopropylideneamide complexes (Figure 1B,C) that the oxidation of the former to the latter is more rapid than the reverse process. The cathodic shift in potential for the $E_{p,a}$ of the complex of the isopropylideneamide anion relative to the isopropylimine species reflects the unusual nature of the Ru-ligand interaction in the former complex. The concept of assignment of a formal oxidation state to the metal center is clearly inappropriate for this species, and this is further evidenced by its magnetic properties, which reveal a slight paramagnetism (μ_{eff} = 1.2 μ_B).

Details of the characterization, and chemical and electrochemical behavior of the imine and isopropylideneamide anion complexes of $Ru(tpy)(bpy)^{n+}$, will be published subsequently.

Acknowledgment. We thank Dr. T. G. Appleton (University of Queensland) for recording the 100-MHz ^1H NMR spectra. This research was supported by the Australian Research Grants Committee.

(5) Anal. Calcd. for $[Ru(tpy)(bpy)(C_3H_6N)]_z(PF_6)_{3z}$: C, 34.3; H, 2.6; N, 8.6; P, 9.4; F, 34.8. Found: C, 34.0, H, 2.7; N, 8.4; P, 9.1; F, 34.8.

(6) Feltham, R. D.; Hayter, R. G. *J. Chem. Soc.* **1964**, 4587-4591. Comparisons of equivalent conductances and slopes of Feltham plots were made with this complex and $[Ru(tpy)(bpy)(NO)](PF_6)_3$.

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(8) Moyer, B. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3601-3603.

(9) Chatt, J.; Dosser, R. J.; King, F.; Leigh, G. J. *J. Chem. Soc.*, Dalton *Trans.* **1976**, 2435-2440.

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Ru(bpy)$_3^{2+}$-Mediated Photoreduction of Olefins with 1-Benzyl-1,4-dihydronicotinamide: A Mechanistic Probe for Electron-Transfer Reactions of NAD(P)H-Model Compounds[1]

Chyongjin Pac,* Mikio Ihama, Masahide Yasuda, Yoji Miyauchi, and Hiroshi Sakurai

Department of Chemical Process Engineering
Faculty of Engineering, Osaka University
Suita, Osaka 565, Japan

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Nonenzymatic reductions of various substrates with 1,4-dihydropyridines are of interest as models for biological oxidation-reduction reactions involving the pyridine nucleotide coenzymes.[2] The reduction of carbon-carbon double bond is limited to the reactions of electron-deficient olefins with Hantzsch compounds at elevated temperatures[3] and to the reduction of very electron-poor olefins by 1-alkyl-1,4-dihydronicotinamides.[4] Although the mechanism still remains uncertain, it was demonstrated that direct hydrogen transfer from the reductants to olefins is involved.[3b,4,5] In this communication we wish to report that

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