was concentrated by evaporation to 130 mL. Upon addition of 500 mL of hexane, a dark blue precipitate formed. It was collected by filtration and dried under vacuum; yield 0.15 g (~8%). Anal. Calcd for $C_{23}H_{22}N_2PtS_2$: C, 47.16; H, 3.78; N, 4.78. Found: C, 46.95; H, 3.97; N, 4.59.

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Registry No. Ni(BABA)(MNT), 42593-96-4; Pd(BABA)(MNT), 88287-58-5; Pt(BABA)(MNT), 88271-97-0; Ni(BABA)(TT), 88271-98-1; Pd(BABA)(TT), 88271-99-2; Pt(BABA)(TT), 88272-00-8.

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Alcohol Formation from *O*-Alkyl Aldoximes by Reaction with Ruthenium(II) Complexes[1]

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A potentially useful goal of transition-metal chemists is the development of processes whereby one or more metal centers can catalyze the production of alcohols from small organic or gaseous substrates.[2] We report one of the few examples in which an alcohol is produced at a Ru(II) center by a Ru(II)-promoted ligand reaction without a concomitant net redox change on the metal or ligand.[3] The reaction occurs when freshly generated $Ru(NH_3)_5H_2O^{2+}(aq)$ reacts with *O*-alkyl aldoximes and has the overall stoichiometry

$$(NH_3)_5RuH_2O^{2+}(aq) + RON{=}C(H)R' \rightarrow (NH_3)_5RuN{\equiv}CR'^{2+} + ROH \quad (1)$$

where $R = CH_3$ or C_2H_5 and $R' = CH_3$ or C_6H_5.

One feature of potential importance in this system is that both the *O*-alkyl group and the activated hydrogen needed for alcohol production are poised on the same ligand.

Experimental Section

Deionized water (Continental Water) was distilled from alkaline permanganate before use. $[Ru(NH_3)_5Cl]Cl_2$ was prepared according to literature procedures[4] from $RuCl_3{\cdot}3H_2O$ (Engelhard Industries). O-alkylated aldoximes were prepared by reacting the corresponding aldehydes with either methoxyamine hydrochloride (Aldrich Chemical Co.) or ethoxyamine hydrochloride (Eastman Kodak).[5,6] The aldoximes were vacuum distilled and were analyzed for purity by gas chromatography;[7] their identity was verified by mass spectrometry. All other chemicals were of reagent grade and were obtained from Aldrich Chemical Co. All manipulations were carried out under an argon atmosphere at room temperature. In a typical reaction, 100 mg (0.34 mmol) of $[Ru(NH_3)_5Cl]Cl_2$ was suspended in 5.0 mL of distilled deionized water, and the resultant mixture was degassed by bubbling Ar through the solution via a syringe needle for 15 min. The Ru^{3+} solution was converted to $Ru(NH_3)_5H_2O^{2+}(aq)$ by base hydrolysis followed by reduction over Zn amalgam for 45 min.[8] The Zn amalgam was then removed by filtration because alkylzinc reagents in tetrahydrofuran have been reported to catalyze the room-temperature conversion of benzaldehyde *O*-ethyloxime to the corresponding nitrile over the course of more than 15 h.[6a] A 4–10 molar excess of *O*-alkyl aldoxime was added to the stirred $Ru(NH_3)_5H_2O^{2+}$ solution under Ar. The reaction was allowed to continue for approximately 30 min or until an aliquot of the reaction mixture showed no further changes in the UV–visible region of the electronic spectrum. The reaction mixture was then filtered onto solid KPF_6, whereupon a yellow solid precipitated immediately. The solid was isolated by filtration; the reaction filtrate was treated separately as described below. The solid product was washed successively with ethanol and diethyl ether and was dried in vacuum at room temperature over P_2O_5 overnight. The amounts of ruthenium products isolated ranged from 65–80% of the theoretical yields. Alcohols were detected in the reaction filtrate by both gas chromatography and ^1H NMR. GC samples were obtained directly from the reaction solutions, after precipitation of the Ru(II) compounds with KPF_6, followed by filtration. No alcohol was detected when only *O*-alkyl aldoxime samples were injected into the GC. ^1H NMR samples were prepared by extraction of the reaction filtrate with CD_2Cl_2. Solid products were characterized by infrared absorption spectroscopy (Beckman 4210) and UV–visible absorption spectroscopy (Cary 210 or 219). Gas chromatograms were obtained on a Varian Series 1400 GC (thermal conductivity detector, Poropak Q column) and ^1H NMR spectra on a Varian EM 360 spectrometer (CD_2Cl_2 solvent; tetramethylsilane, internal standard). Mass spectra of the aldoximes were run on a Finnigan 4021C GC/MS. Microanalyses were provided by Robertson Laboratories, Florham Park, NJ.

Table I. Comparison of Spectral Properties of Ruthenium Products Isolated from the Reaction of $Ru(NH_3)_5H_2O^{2+}$ with RON=CHR′

		$\nu(C{\equiv}N)$, cm^{-1}		λ_{max}, nm (log ϵ)	
R[a]	R′	lit.[b]	found[c]	lit.[b]	found[d]
CH_3	CH_3	2239[e]	2246	229 (4.19)	229 (4.17)
CH_3	C_6H_5	2188[f]	2185	376 (3.93)	376 (3.93)
C_2H_5	CH_3	2239[e]	2246	229 (4.19)	229 (4.16)
C_2H_5	C_6H_5	2188[f]	2185	376 (3.93)	376 (3.93)

[a] Alcohol reaction products were detected by GC and ^1H NMR in filtrate: first two listings, CH_3OH; last two listings, C_2H_5OH. [b] From ref 9. [c] PF_6^- salt, Nujol mull; differences in $\nu(C{\equiv}N)$ are seen as in ref 9b according to the counterion used. [d] ϵ in M^{-1} cm^{-1}; average of five determinations per compound. [e] BF_4^- salt. [f] ClO_4^- salt.

Results

UV–Visible Absorption Properties. Addition of *O*-alkyl aldoximes to an aqueous solution of $Ru(NH_3)_5H_2O^{2+}$ leads to a color change that is complete within about 30 min. The UV–visible absorption spectra of the reaction solutions containing $RON{=}CHCH_3$ displayed an absorption maximum at 229 nm, while the solutions derived from the reactions containing $RON{=}CHC_6H_5$ showed an absorption maximum at 376 nm. No spectral intermediates were detected during the course of the reactions. The electronic spectra of 10^{-4}–10^{-5} M aqueous solutions of the isolated solids displayed peaks corresponding to the analogous pentaammineruthenium(II)–nitrile compounds.[9] The observed spectra were in good agreement with those of the reaction solutions prior to product isolation.

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(1) Paper presented in part at the 34th Southeast Regional American Chemical Society Meeting, Birmingham, AL, Nov 1982, and the 56th Annual Meeting of the South Carolina Academy of Sciences, Columbia, SC, Mar 1983.

(2) For some recent reviews and examples see: (a) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61. (b) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (c) Bradley, J. S. *J. Am. Chem. Soc.* **1979**, *101*, 7419.

(3) For other examples of enhanced reactivity of N-bonded ligands on Ru(II) with no accompanying redox change, see: (a) Guengerich, C. P.; Schug, K. R. *Inorg. Chem.* **1983**, *22*, 181. (b) *Ibid.* **1983**, *22*, 1401.

(4) Allen, A. D.; Bottomley, F.; Harris, R. O.; Senoff, C. V. *Inorg. Synth.* **1970**, *12*, 1.

(5) For general syntheses of *O*-methyl oximes and aldoximes see: (a) Singh, P. *J. Org. Chem.* **1979**, *44*, 84. (b) Witanowski, M.; Stefaniak, L.; Januszwesk, H.; Szymanski, S.; Webb, G. A. *Tetrahedron* **1973**, *29*, 2833. (c) Umino, N.; Iwakuma, T.; Ikezaki, M.; Itah, N. *Chem. Pharm. Bull.* **1978**, *26*, 2897.

(6) For general syntheses of *O*-ethyl aldoximes see: (a) Pornet, J.; Migimiac, L. *Bull. Soc. Chim. Fr.* **1975**, *3–4*, 841. (b) Bernhart, C.; Wermuth, C. G. *Tetrahedron Lett.* **1974**, *29*, 2493. (c) Ioffe, B. V.; Artsybasheva, Yu. P. *Zh. Org. Khim.* **1981**, *17*, 911. (d) Deem, M. L. *Org. Mass Spectrom.* **1980**, *15*, 573.

(7) *O*-Alkyl aldoximes can exist in both *E* and *Z* isomers. For our purposes in this study, the *E* and *Z* isomers were not separated.

(8) Allen, A. D.; Senoff, C. V. *Can. J. Chem.* **1967**, *45*, 1337.

(9) (a) Guengerich, C. P.; Schug, K. R. *J. Am. Chem. Soc.* **1977**, *99*, 3298. (b) Ford, P. C.; Clarke, R. E. *Inorg. Chem.* **1970**, *9*, 227.

Infrared Absorption Studies. The infrared spectra of the solids isolated from the reaction of $Ru(NH_3)_5H_2O^{2+}(aq)$ with *O*-methyl or *O*-ethyl aldoximes showed the presence of an intense absorption in the 2100–2250-cm^{-1} region, characteristic of authentic pentaammineruthenium(II)–nitrile samples.[9] A summary of the UV–visible and IR absorption spectral data of the reaction products is given in Table I.

Detection of Alcohols. GC retention times of the alcohols detected in the reaction filtrate were in excellent agreement with retention times of authentic alcohols. ^1H NMR spectra of the CD_2Cl_2 extracts from the reaction filtrate showed the presence of excess *O*-alkyl aldoxime as well as the alcohol coproduct. The alcohols detected in the reaction filtrate from each reaction are given in footnote *a* of Table I.

Discussion

In order to investigate the feasibility of producing alcohols by a ruthenium(II)-promoted ligand reaction, we have examined the reaction between $Ru(NH_3)_5H_2O^{2+}$ and *O*-methyl and *O*-ethyl aldoximes. We have found that the corresponding Ru(II) nitrile compounds, as indicated by their characteristic infrared and UV–visible absorption properties, are produced in less than 30 min at room temperature. Methanol or ethanol is produced concomitantly and can be detected by gas chromatography and ^1H NMR. Even in the case of the bulkier *O*-ethyl aldoximes, rapid production of ethanol and the corresponding pentaammineruthenium(II)–nitrile compound ensues. *O*-Alkyl aldoximes do not normally lose alcohol in aqueous solution at room temperature, but rather require stringent experimental conditions ($SOCl_2$, refluxing sulfuric acid) to form nitriles. Guengerich and Schug[3] have found that unsubstituted aldoximes and oximes containing α-carbonyl groups display similar reactivity to that reported here. We postulate that Ru(II) is back-bonding to the *O*-alkyl aldoxime via the nitrogen atom of the oxime.[10] The back-bonding promotes increased unsaturation on the bound nitrogen donor atom, thereby facilitating rupture of the oxime N–O bond. Further confirmation of the strong driving force provided by the Ru(II) in converting an sp^2-hybridized oxime nitrogen to an sp-hybridized nitrile nitrogen is seen from an experiment in which *cis*-$(2,2'\text{-bpy})_2RuCl(H_2O)^+$ reacts with benzaldehyde *O*-methyl aldoxime.[11] Production of the *cis*-$(bpy)_2RuCl(benzonitrile)^+$ as well as the *cis*-$(bpy)_2RuH_2O(benzonitrile)^{2+}$ adducts occur; however, the reaction requires elevated temperatures and longer reaction times than do the pentaammine systems. This slower rate of reaction presumably reflects the fact that the Ru is less capable of back-bonding to the oxime nitrogen in the bipyridine complexes. Similarly, it has been suggested that Ru may be considerably less capable of back-bonding to dinitrogen in bipyridine and 1,10-phenanthroline complexes.[12] On the basis of the *rapid* product formation observed in the pentaammine case, we propose a reaction sequence, analogous to that of Guengerich and Schug,[3] in which $Ru(NH_3)_5H_2O^{2+}$ undergoes substitution by the *O*-alkyl aldoxime ligand with binding to the metal via the nitrogen atom, followed by rapid loss of alcohol (as OR^- and H^+) to form the corresponding pentammineruthenium(II)–nitrile product:

$$(H_3N)_5RuH_2O^{2+} + RON{=}CHR' \rightarrow [(H_3N)_5RuN(OR){=}CHR']^{2+} + H_2O \quad (2)$$

$$[(H_3N)_5RuN(OR){=}CHR']^{2+} \rightarrow [(H_3N)_5RuN{\equiv}CR']^{2+} + ROH \quad (3)$$

We are currently investigating the conditions under which Ru(II) can activate, catalyze, and direct similar intramolecular ligand reactions.

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Registry No. $[(H_3N)_5RuN{\equiv}CCH_3](PF_6)_2$, 34943-71-0; $[(H_3N)_5RuN{\equiv}CC_6H_5](PF_6)_2$, 34943-73-2; $Ru(NH_3)_5H_2O^{2+}$, 21393-88-4; $[Ru(NH_3)_5Cl]Cl_2$, 18532-87-1; *cis*-$(bpy)_2RuCl(H_2O)^+$, 76739-35-0; *cis*-$(bpy)_2RuClB^+PF_6^-$ (B = benzonitrile), 88413-50-7; *cis*-$[(bpy)_2RuH_2OB](PF_6)_2$ (B = benzonitrile), 88413-52-9; $CH_3ON{=}CHCH_3$, 33581-43-0; $CH_3ON{=}CHC_6H_5$, 3376-32-7; $C_2H_5ON{=}CHCH_3$, 42101-48-4; $C_2H_5ON{=}CHC_6H_5$, 13858-87-2; CH_3OH, 67-56-1; C_2H_5OH, 64-17-5.

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[10] For examples of transition-metal oxime complexes coordinated via the oxime nitrogen, see: Chakravorty, A. *Coord. Chem. Rev.* **1974**, *13*, 1.

[11] *cis*-$(bpy)_2RuCl(H_2O)^+$ was generated in aqueous solution according to Meyer et al. (Adeyemi, S. A.; Miller, F. J.; Meyer, T. J. *Inorg. Chem.* **1972**, *11*, 994). A 4 M excess of benzaldehyde *O*-methyl aldoxime was added, and the progress of the reaction was monitored spectrophotometrically. After 1 h of refluxing under Ar, *cis*-$(bpy)_2RuCl(benzonitrile)^+$ and *cis*-$(bpy)_2RuH_2O(benzonitrile)^{2+}$ were isolated as the PF_6^- salts in a product ratio of 2:3, respectively. Anal. Calcd for (2:3 mixture): C, 41.93; H, 2.89; N, 9.05. Found: C, 41.65; H, 2.86; N, 8.68.

[12] Godwin, J. B.; Meyer, T. J. *Inorg. Chem.* **1971**, *10*, 471.

Additions and Corrections

1983, Volume 22

Hans Hartl, Peter Huppmann, Dieter Lentz, and Konrad Seppelt*: Tellurium–Nitrogen Compounds.

Page 2186. In Table I the *z* value of the N atom (0.785 (2)) is incorrect. The correct value is 0.758 (2).—Konrad Seppelt