Table VI. Comparison of Kinetic Data for the Reaction of Isocyanato Complexes with Acid

complex	k, M^{-1} s^{-1}	ΔH^{*}, kcal mol^{-1}	ΔS^{*}, cal K^{-1} mol^{-1}	ref
$[Ru(NH_3)_5(NCO)]^{2+}$	0.059[a]	12.2	−23	27
$[Rh(NH_3)_5(NCO)]^{2+}$	0.617[a]	10.9	−23	27
$[Co(NH_3)_5(NCO)]^{2+}$	0.162[b]	13.1	−18	25
1	0.074[b]	12.5	−25	*c*

[a] Ionic strength 0.10 M. [b] Ionic strength 1.0 M. [c] This work.

substituted by $[H^+]$), which simplifies to eq 9 if $K_1[H^+] \ll 1$. The second-order rate constant, k (eq 9), is then the product k_2K_1.

The above mechanism has been corroborated by the isolation and characterization of a carbamato species $[Rh(NH_3)_5(NH_2CO_2H)]^{3+}$ from the reaction of $[Rh(NH_3)_5(NCO)]^{2+}$ with acid.[27]

Table VI gives observed second-order rate constants k_2K_1 and activation parameters for a series of isocyanato complexes. The present data for **1** are in excellent agreement with those, and the above mechanism also appears to be operative in the present case.

Acknowledgment. We thank the Fonds der Chemischen Industrie for financial support of this research.

Supplementary Material Available: Tables containing calculated positional parameters of hydrogen atoms (S1), anisotropic thermal parameters of non-hydrogen atoms (S2), and intraligand bond distances and angles (S3) (3 pages); tables of observed and calculated structure factor amplitudes (S4) (23 pages). Ordering information is given on any current masthead page.

Contribution from the Lehrstuhl für Anorganische Chemie I,
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Synthesis and Reactivity of Air-Stable $[LRe(NO)(CO)(CH_3)]^+$ (L = 1,4,7-Triazacyclononane). Kinetics and Mechanism of Its Reactions with HX (X = Cl, Br, NO_3). Formation of $[\{LRe(NO)(CO)\}_2(\mu\text{-}CH_2OCH_2)]I_2$ Containing a Bridging 2-Oxapropane-1,3-diide

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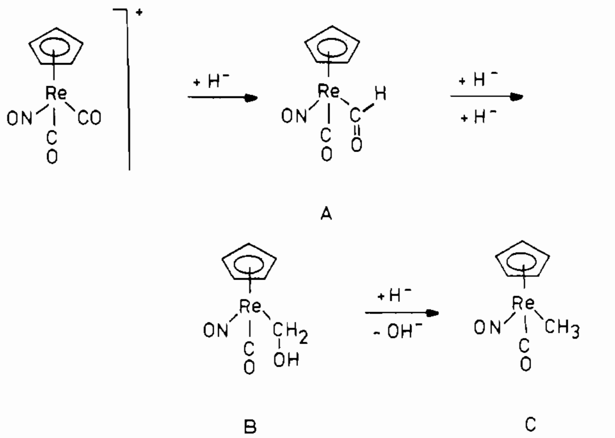
Received March 15, 1988

The reaction of $[LRe(NO)(CO)_2]BF_4$ in aqueous solution with $NaBH_4$ affords red, racemic $[LRe(NO)(CO)(CH_3)]BF_4$ (**1**), which has been resolved into its enantiomerically pure form as the (1*S*)-3-bromocamphorsulfonate salt (L = 1,4,7-triazacyclononane, $C_6H_{15}N_3$). **1** reacts in aqueous solution with HX (X = F, Cl, Br, I) to yield the compounds $[LRe(NO)(CO)X]^+$ and methane. The kinetics of the reactions have been measured. A third-order rate law, $-d[\mathbf{1}]/dt = k[\mathbf{1}][X][H^+]$, has been established. The formal substitution reaction proceeds with retention of configuration at the Re center. A mechanism is proposed that involves the acid-catalyzed cleavage of an $Re-N_{amine}$ bond, followed by nucleophilic attack of the nucleophile X^- at the 16e fragment with concomitant expulsion of CH_3^- (which is immediately protonated) and rapid re-formation of the $Re-N_{amine}$ bond. **1** reacts with I_2, forming $[LRe(NO)(CO)(CH_2I)]^+$, which dimerizes in aqueous solution generating $[\{LRe(NO)(CO)\}_2(\mu\text{-}CH_2OCH_2)]I_2$, which contains the novel bridging group 2-oxapropane-1,3-diide. $[LRe(NO)(CO)(O_2CCF_3)]^+$ (**2**) has been prepared from **1** in F_3CCO_2H. **2** reacts with bromine to form the paramagnetic Re(II) complex $[LRe(NO)(CO)Br]^{2+}$, which is reduced by BH_4^- to yield $[LRe(NO)(CH_3)Br]$; oxidation of the latter species with Br_2 yields $[LRe(NO)Br_2]^+$, which is reduced by zinc amalgam to $[LRe(NO)Br_2]$. Spectroscopic (IR, ^1H NMR, ^{13}C NMR) and magnetic properties of all new compounds are reported as well as their electrochemical behavior.

Introduction

Graham et al., Gladysz et al., and Casey et al. have in series of elegant studies shown that hydride addition reactions to $[(\eta^5\text{-}C_5H_5)Re(NO)(CO)_2]^+$ afford formyl,[3-5,8] hydroxymethyl,[6,7] and finally methyl[1-7] complexes of types A, B, and C depending on the stoichiometry and reaction conditions.



Berke et al.[9] have recently characterized such a formylrhenium complex by X-ray crystallography. Gladysz[10] et al. have prepared

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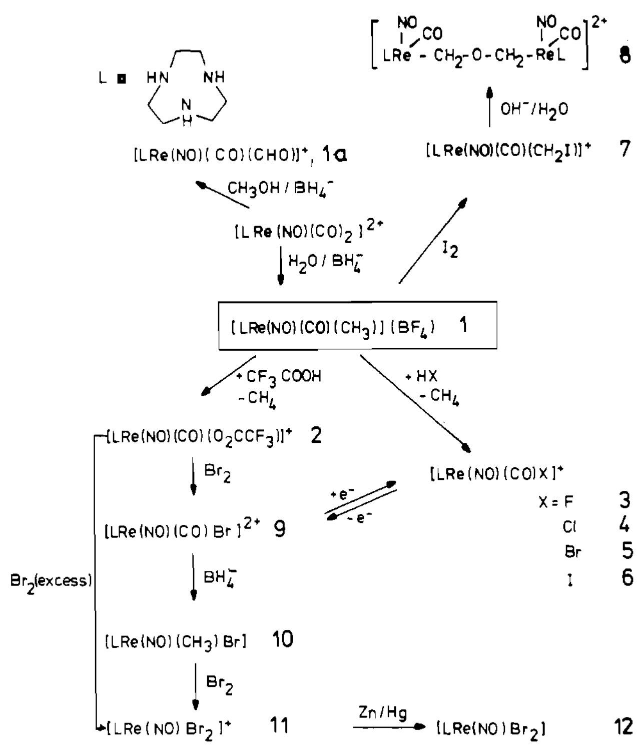
Scheme I. Summary of Reactions Studied in This Work



and structurally characterized a formaldehyde–rhenium complex containing an η^2-$H_2C{=}O$ coordinated ligand. Fenske, Milletti, and Arndt[11] have carried out a molecular orbital analysis of $[(\eta^5\text{-}C_5H_5)Re(NO)(CO)(PPh_3)]^+$ and its reduction to the corresponding formyl complex. They have concluded that the ReNO moiety is the most probable site of attack of the hydride nucleophile rather than the Re–CO group. The kinetic product thus formed, $(\eta^5\text{-}C_5H_5)Re(NHO)(CO)(PPh_3)$, is thermodynamically unstable; it rearranges to the formylrhenium product.

We have in the past few years shown that formal substitution of the six electron donor $(\eta^5\text{-}C_5H_5)^-$ in organometallic compounds by the pure σ-donor 1,4,7-triazacyclononane (L) leads to very stable octahedral complexes with a by one unit increased overall charge as compared to that of the parent organometallic species.[12] Thus the reaction of $Re(CO)_5Br$ with L yields air- and water-stable colorless $[LRe(CO)_3]^+$,[13,14] which was found to be readily nitrosylated by NO^+, affording the yellow stable complex $[LRe(NO)(CO)_2]^{2+}$, which is isoelectronic with $[(\eta^5\text{-}C_5H_5)Re(NO)(CO)_2]^+$. $[LRe(NO)(CO)_2]^{2+}$ reacts with nucleophiles such as $N_2H_4{\cdot}H_2O$, H_2NOH, or N_3^- forming $[LRe(NO)(CO)(NCO)]^+$, the chemistry of which has been described recently.[15] Oxidation of $[LRe(NO)(CO)_2]^{2+}$ with H_2O_2 yields essentially quantitatively $[LReO_3]^+$,[13] which again is isoelectronic with its organometallic counterpart $(\eta^5\text{-}Me_5C_5)ReO_3$.[16] It was therefore of interest to investigate the reactivity of $[LRe(NO)(CO)_2]^{2+}$ toward hydride ions.

We here report the synthesis and chemistry of the octahedral complex $[LRe(NO)(CO)(CH_3)]^+$ (**1**) and its optical resolution and absolute configuration. A preliminary communication of this work has been published.[17] **1** reacts with aqueous acids such as hydrochloric, hydrobromic, or nitric acids to produce methane and $[LRe(NO)(CO)X]^+$ species (X = Cl, Br, NO_3). The kinetics and mechanism of such reactions have been studied for the first time. The reactions of **1** with aqueous HX are similar to those reported for $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ in the respect that methane and $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)X$ species are formed.[18] Mechanistically differences exist. Scheme I summarizes the reactions and products studied in this work.

Experimental Section

Preparation of Complexes. The ligand 1,4,7-triazacyclononane (L) and $[LRe(NO)(CO)_2](BF_4)_2$ have been prepared according to published procedures.[13,19]

$[LRe(NO)(CO)(CH_3)](BF_4)$ (1). Solid $NaBH_4$ (0.038 g, 1 mmol) was added to a solution of $[LRe(NO)(CO)_2](BF_4)_2$ (0.58 g, 1 mmol) dissolved in H_2O (10 mL) at 20 °C with stirring. Gas evolved, and the solution turned red. Within 24 h at room temperature, red crystals of **1** formed, which were filtered off, washed with diethyl ether, and air-dried. Yield: 75%. Recrystallization of **1** was achieved from acetonitrile or an acetone/water mixture(3:1).

Anal. Calcd for $C_8H_{18}BF_4N_4O_2Re$: C, 20.22; H, 3.82; N, 11.79; F, 15.99; Re, 39.18. Found: C, 19.8; H, 3.7; N, 11.5; F, 15.8; Re, 38.9.

When $NaBD_4$ was used in the above synthesis the compound $[(C_6H_{15}N_3)Re(NO)(CO)(CD_3)]BF_4$ was obtained. ^2H NMR (CD_3CN; δ): 0.63 (s, 3 D, $-CD_3$).

$[LRe^*(NO)(CO)(CH_3)][(1S)$-3-bromocamphorsulfonate]$\cdot H_2O$. Racemic **1** (0.48 g, 1 mmol) was dissolved in water (10 mL), and a solution of (1*S*)-3-bromocamphorsulfonic acid monohydrate (0.66 g, 2 mmol) in acetone (5 mL) was added. After 3 days, needle-shaped red crystals of the title compound precipitated out, which were filtered off, washed with diethyl ether, and air-dried. Yield: 45% (based on **1**). Slow recrystallization from H_2O/acetone mixtures (1:3) produced red single crystals suitable for X-ray crystallography.

Anal. Calcd for $[C_8H_{18}N_4O_2Re][C_{10}H_{14}BrO_4S]\cdot H_2O$: C, 30.04; H, 4.77; N, 7.79; Re, 25.88. Found: C, 29.9; H, 4.9; N, 7.7; Re, 25.7. CD spectrum (H_2O): 308 ($\Delta\epsilon$ = + 2.971), 510 ($\Delta\epsilon$ = –0.036) nm.

In order to measure an unperturbated circular dichroism spectrum of one enantiomeric cation of **1**, the above (1*S*)-3-bromocamphorsulfonate salt (0.7 g, 1 mmol) was dissolved in water (10 mL) and a solution of sodium tetraphenylborate (0.65 g, 2 mmol) in acetone (10 mL) was added. Red $[LRe^*(NO)(CO)(CH_3)][BPh_4]$ precipitated immediately. CD spectrum (H_2O): 309 ($\Delta\epsilon$ = –0.042), 510 nm ($\Delta\epsilon$ = –0.015); $[\alpha]^{22}{}_{D\,589}$ –48.6 (CH_3CN).

$[LRe(NO)(CO)(CHO)]BF_4$ (1a). To a degassed suspension of **1** (0.48 g, 1 mmol) in anhydrous methanol (50 mL) was added $NaBH_4$ (0.04 g, 1 mmol) at room temperature with stirring. A clear yellow-brown solution was obtained through which a stream of argon was passed until a brown solid precipitated out. This material was filtered off under an argon atmosphere, washed with diethyl ether, and dried. Yield: 50%.

Anal. Calcd for $C_8H_{16}BF_4N_4O_3Re$: C, 19.64; H, 3.30; N, 11.45; F, 15.54; Re, 38.06. Found: C, 19.5; H, 3.5; N, 11.2; F, 15.9; Re, 37.8.

$[LRe(NO)(CO)(O_2CCF_3)]PF_6$ (2). **1** (0.48 g, 1 mmol) was dissolved in trifluoroacetic acid (10 mL) and the solution refluxed for 5 h. To the residual yellow oil acetone (10 mL) and a saturated solution of $NaPF_6$ in methanol (5 mL) were added at room temperature. Yellow microcrystals precipitated out, which were filtered off, washed with diethyl ether, and air-dried. Yield: 60%.

Anal. Calcd for $C_9H_{15}F_9N_4O_4PRe$: C, 17.12; H, 2.40; N, 8.88; F, 27.08; Re, 29.49. Found: C, 17.0; H, 2.3; N, 8.8; F, 27.0; Re, 29.2.

$[LRe(NO)(CO)F]F$ (3). **1** (0.48 g, 1 mmol) was dissolved in 40% aqueous HF and stirred at room temperature for 24 h. After this solution was allowed to stand in an open vessel for 3 days, orange crystals precipitated out, which were filtered off, washed with diethyl ether, and air-dried. Yield: 89%.

Anal. Calcd for $C_7H_{15}N_4O_2F_2Re$: C, 20.4; H, 3.68; N, 13.62; F, 9.24; Re, 45.26. Found: C, 20.1; H, 3.5; N, 13.5; F, 9.1; Re, 45.0.

$[LRe(NO)(CO)X]X$ (X = Cl (4), Br (5), (6)). **1** (0.48 g, 1 mmol) was dissolved in 40% HCl, HBr, or HI, respectively. The solutions were refluxed for 3 h. Then the reaction volume was reduced to ca. 10 mL by evaporation under reduced pressure. From these solutions red crystals

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of the respective salts precipitated upon standing at 20 °C for 2 days. Yields: 92–97%.

Anal. Calcd for $C_7H_{15}N_4O_2Cl_2Re$: C, 18.93; H, 3.41; N, 12.61; Cl, 15.96; Re, 41.91. Found: C, 19.0; H, 3.4; N, 12.8; Cl, 15.9; Re, 41.5.

Anal. Calcd for $C_7H_{15}N_4O_2Br_2Re$: C, 15.77; H, 2.84; N, 10.51; Br, 29.97; Re, 34.92. Found: C, 14.8; H, 2.7; N, 10.2; Br, 30.0; Re, 34.6.

Anal. Calcd for $C_7H_{15}N_4O_2I_2Re$: C, 13.41; H, 2.41; N, 8.94; I, 40.47; Re, 26.69. Found: C, 13.2; H, 2.4; N, 8.6; I, 40.0; Re, 27.2.

The red hexafluorophosphate salts, $[LRe(NO)(CO)X]PF_6$ (X = F, Cl, Br, I) were readily obtained from aqueous solutions (10 mL) of the above salts (1 mmol) by addition of a saturated aqueous solution of $NaPF_6$ (5 mL).

$[LRe(NO)(CO)(CH_2I)]BF_4\cdot CH_3CN$ (7). To a solution of **1** (0.48 g, 1 mmol) in anhydrous ethanol (50 mL) was added iodine (0.13 g, 1 mmol) dissolved in absolute ethanol (10 mL) under an argon atmosphere. The solution was stirred for 2 days at room temperature after which time the solvent was removed by evaporation under reduced pressure. The brown residue was washed with CCl_4 and recrystallized from a minimum amount of acetonitrile. Yield: 97%.

Anal. Calcd for $C_{10}H_{20}BF_4IN_5O_2Re$: C, 18.70; H, 3.14; N, 10.90; I, 19.76; Re, 29.00. Found: C, 18.7; H, 3.2; N, 10.7; I, 19.7; Re, 28.8.

$[\{LRe(NO)(CO)\}_2(\mu\text{-}CH_2OCH_2)]I_2$ (8). Method A. To a solution of **1** (0.48 g, 1 mmol) in an acetone/water mixture (1:1) was added a saturated aqueous solution of sodium iodide (5 mL). The solution was heated at 50 °C for 1 h. After the solution was allowed to stand in an open vessel for 10 days orange-red crystals of X-ray quality crystallized. Yield: 40% (based on **1**).

Method B. To an aqueous solution (10 mL) of **1** (0.48 g, 1 mmol) was added a solution of I_2 (0.13 g, 1 mmol) dissolved in ethanol (5 mL). After the solution was allowed to stand for 4 days in an open vessel at room temperature, orange-red crystals of **8** precipitated out. Yield: 40%.

Method C. **7** (0.65 g, 1 mmol) was dissolved in water (10 mL). From the red solution orange-red crystals of **8** precipitated within 3 days. Yield: 30%.

Anal. Calcd for $C_{16}H_{34}I_2N_8O_5Re_2$: C, 18.39; H, 3.28; N, 10.73; I, 24.30; Re, 35.65. Found: C, 18.5; H, 3.4; N, 10.7; I, 24.4; Re, 35.3.

$[LRe(NO)(CO)Br]Br_2$ (9). **1** (0.48 g, 1 mmol) was dissolved in freshly distilled trifluoroacetic acid (10 mL), and bromine (0.16 g, 1 mmol) was added. The solution was stirred at room temperature for 24 h. A green, microcrystalline precipitate was filtered off, washed with diethyl ether, and air-dried. Yield: 65%.

Anal. Calcd for $C_7H_{15}Br_3N_4O_2Re$: C, 13.72; H, 2.47; N, 9.14; Br, 39.10; Re, 30.37. Found: C, 13.7; H, 2.4; N, 9.2; Br, 38.9; Re, 30.0.

$[LRe(NO)(CH_3)Br]$ (10). To a solution of **9** (0.62 g; 1 mmol) in water (10 mL) was added $NaBH_4$ (0.08 g, 2 mmol). The color of the solution turned to pink, and a red-violet precipitate formed, which was filtered off, washed with diethyl ether, and air-dried. Yield: 55%.

Anal. Calcd for $C_7H_{18}BrN_4ORe$: C, 19.10; H, 4.12; N, 12.73; Br, 18.15; Re, 42.29. Found: C, 19.11; H, 4.0; N, 12.7; Br, 17.9; Re, 42.1.

$[LRe(NO)Br_2]Br$ (11). Method A. To a suspension of **10** (0.45 g, 1 mmol) in $CHCl_3$ (50 mL) was added Br_2 (0.8 g, 5 mmol). After the solution was refluxed for 5 h and cooled to room temperature, green crystals precipitated out, which were filtered off, washed with diethyl ether, and air-dried. Yield: 97%.

Method B. To **1** (0.48 g, 1 mmol) dissolved in CF_3CO_2H was added bromine (1.6 g, 10 mmol). The solution was stirred at room temperature for 24 h. The green precipitate was filtered off, washed, and dried as described above. Yield: 87%.

Anal. Calcd for $C_6H_{15}Br_3N_4ORe$: C, 12.32; H, 2.59; N, 9.58; Br, 40.97; Re, 31.83. Found: C, 11.9; H, 2.7; N, 9.4; Br, 40.8; Re, 31.7.

$[LRe(NO)Br_2]$ (12). To a degassed solution of **11** (0.59 g, 1 mmol) in methanol (50 mL) was added zinc amalgam (0.40 g) under an argon atmosphere. After 2 h of stirring at 20 °C, the zinc amalgam was removed. From the green solution dark green crystals precipitated slowly out, which were filtered off, washed with diethyl ether, and air-dried. Yield: 71%.

Anal. Calcd for $C_6H_{15}Br_2N_4ORe$: C, 14.27; H, 3.00; N, 11.09; Br, 31.64; Re, 36.86. Found: C, 14.2; H, 2.9; N, 11.0; Br, 31.2; Re, 36.6.

Elemental analyses (C, H, N, halogen) were performed by Microanalysis Laboratory Beller, Göttingen, FRG. Rhenium was determined spectrophotometrically according to the method described by Maloche, Martin, and Webb.[20]

Instrumentation. The apparatus used for electrochemical measurements has been described previously.[21] Cyclic voltammograms of dried samples of complexes (~10^{-3} M) were measured in water-free acetonitrile or methanol with 0.1 M $[n\text{-}Bu_4N]PF_6$ as supporting electrolyte at scan rates 20–200 mV s^{-1}. The ferrocenium/ferrocene couple was monitored as an internal standard. Electronic spectra were recorded on a Perkin-Elmer Lambda 9 UV/vis/near-IR spectrophotometer. The magnetic susceptibilities of powdered samples of the rhenium(II) complexes were measured by the Faraday method (Sartorius microbalance, Brucker B-E 1008 research magnet, and Bruker B-VT 1000 automatic temperature control) in the temperature range 98–293 K. Diamagnetic corrections were applied in the usual manner with use of tabulated Pascal's constants.

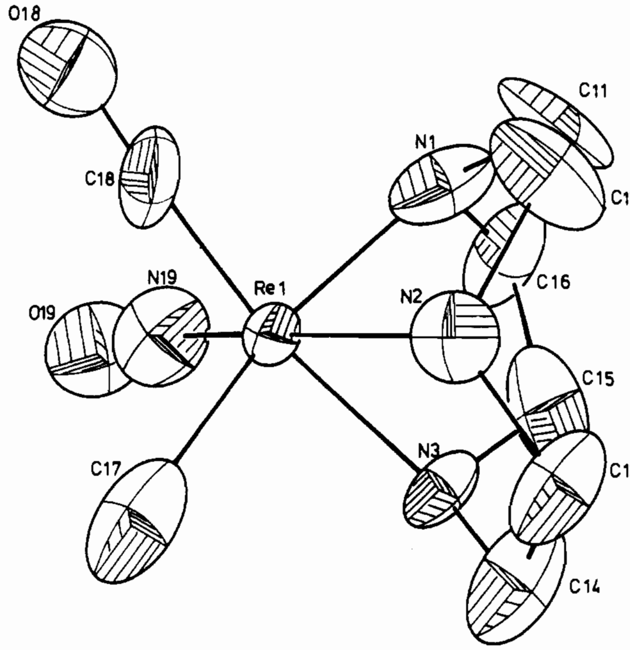

Figure 1. Structure of the cation in $[LRe(NO)(CO)(CH_3)][(1S)\text{-}3\text{-}bromocamphorsulfonate]\cdot H_2O$.[17] Selected bond lengths (Å): Re–N1, 2.14 (1); Re–N2, 2.18 (1); Re–N3, 2.19 (1); Re–C17, 2.12 (2); Re–C18, 1.82 (2); Re–N19, 1.845 (14).

The ^1H NMR spectra were recorded in the FT mode with a Bruker Am-400 spectrometer at a magnetic field of 400.1 MHz. Proton chemical shifts are reported from Me_4Si by taking the chemical shift of dimethyl-d_6 sulfoxide or CD_3CN as an internal standard. The following abbreviations are used: s = singlet, m = multiplet, q = quartet, t = triplet. ^{13}C NMR were recorded at a magnetic field of 100.6 MHz.

Infrared spectra were recorded on an Acculab 10 (Beckmann) instrument (KBr disks) in the range 4000–600 cm^{-1}. The CD spectra were recorded on a Mark III spectrograph (Jobin Yvon) interfaced to a Tandon PC computer.

Kinetic Measurements. The kinetics of the reactions between **1** and HX in aqueous solutions were measured by using conventional spectrophotometry (UNICAM SP-800 interfaced to a Commodore V64 computer for data acquisition and analysis). Kinetic experiments were performed by using pseudo-first-order conditions with $[H^+]$ *and* $[X^-]$ in at least 10-fold excess over [complex] (1.0×10^{-2} M). Pseudo-first-order rate constants were calculated by use of a least-squares fitting program[22] where the absorbance at the beginning of the reaction and after completion of the reaction were treated as variables. Measured and calculated absorbance values differed only in the last digit of the reading of the instrument.

Results

Synthesis and Characterization of Complexes. An aqueous solution of $[LRe(NO)(CO)_2](BF_4)_2$ was treated at 20 °C with solid $NaBH_4$ (ratio 1:1). Within 24 h red crystals of $[LRe(NO)(CO)(CH_3)]BF_4$ (**1**) formed in 75% yield; they are indefinitely air- and water-stable both in solution and in the solid state. Racemic **1** may be recrystallized from water/acetone mixtures. The identity of **1** was established by infrared, ^1H NMR, and ^{13}C NMR spectroscopy (Table I) as well as X-ray crystallography[17] (Figure 1). **1** is diamagnetic; strong ν(NO) and ν(CO) stretching bands occur at 1700 and 1940 cm^{-1}. They are shifted to lower

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Table I. Spectroscopic Properties of Complexes (IR, ^1H NMR, ^{13}C NMR, UV–vis)

compd	IR (KBr), cm^{-1}	^1H NMR,[h] δ	^{13}C NMR,[i] δ	UV–vis: λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})
1	$\nu(NO)$ 1700 (s) $\nu(CO)$ 1940 (s)	0.65 (s, 3 H, $-CH_3$) 2.71–3.50 (m, 12 H, $-CH_2CH_2-$) $\left.\begin{array}{l}4.76\\5.70\\6.10\end{array}\right\}$ (3 s, 3 H, $-NH$)[a]	−10.19 (s, $-CH_3$) 49.61–59.78 (6 s, $-CH_2CH_2-$) 220.02 (s, $-CO$)[a]	301 (423), 496 (52)[b]
1a	$\nu(NO)$ 1740 (s) $\nu(CO)$ 1970 (s)	2.91–3.50 (m, 12 H, $-CH_2CH_2-$) 4.75, 4.85, 5.46 (3 s, 3 H, $-NH$) 16.2 (s, 1 H, $-CHO$)[g]	47.64–54.81 (6 s, $-CH_2CH_2-$) 208.19 (s, $-CO$) 272.2 (s, $-CHO$)[g]	320 (413), 450 (71)[a]
2	$\nu(NO)$ 1700 (s) $\nu(CO)$ 1990 (s) $\nu(C{=}O)$ 1650 (m) $\nu(C{-}O)$ 1440 (w)		52.40–58.07 (6 s, $-CH_2CH_2-$) 115.42–124.46 (q, $-CF_3$, $^1J_{C-F}$ = 262.8 Hz) 166.18–167.30 (q, $-OCO$, $^2J_{C-F}$ = 32.4 Hz) 211.54 (s, $-CO$)[a]	367 (144), 473 (100)[c]
3	$\nu(NO)$ 1720 (s) $\nu(CO)$ 1970 (s)	2.71–3.49 (m, 12 H, $-CH_2CH_2-$)[d]		454 (56)[b]
4	$\nu(NO)$ 1710 (s) $\nu(CO)$ 1950 (s)	2.72–3.52 (m, 12 H, $-CH_2CH_2-$)[d]		378 (72), 484 (54)[b]
5	$\nu(NO)$ 1700 (s) $\nu(CO)$ 1940 (s)	2.73–3.45 (m, 12 H, $-CH_2CH_2-$)[d]		391 (61), 489 (76)[b]
6	$\nu(NO)$ 1700 (s) $\nu(CO)$ 1935 (s)	2.76–3.52 (m, 12 H, $-CH_2CH_2-$)[d]		389 (76), 492 (117)[b]
7	$\nu(NO)$ 1700 (s) $\nu(CO)$ 1940 (s)	2.90–3.52 (m, 12 H, $-CH_2CH_2-$) 3.70, 3.87 (2 q, 2 H, $-CH_2I$, J = 6 Hz) 5.25, 5.95, 6.95 (3 s, 3 H, $-NH$)[a]	49.83–53.47 (7 s, $-CH_2CH_2-$, $-CH_2I$)[c] 230.0 ($-CO$)	361 (98)[c]
8	$\nu(NO)$ 1680 (s) $\nu(CO)$ 1920 (s)	2.85–3.40 (m, 24 H, $-CH_2CH_2-$) 4.00, 4.30, 4.65, 5.00 (4 d, 4 H, $-CH_2OCH_2-$) 6.10, 6.41, 6.63, 6.92 (4 s, 4 H, $-NH$) 7.51 (s, 2 H, $-NH$)[e]	46.72–53.85 (10 s, $-CH_2CH_2-$) 71.72, 72.14 (2 s, $-CH_2OCH_2-$) 220.14, 220.96 (2 s, $-CO$)[e]	482 (89)[b]
9	$\nu(NO)$ 1740 (s) $\nu(CO)$ 1980 (s)			403 (1079), 660 (42), 720 sh[b]
10	$\nu(NO)$ 1600 (s)			364, 546[f]
11	$\nu(NO)$ 1740 (s)			401 (1120), 648 (44), 702 sh[b]
12	$\nu(NO)$ 1600 (s)			396 (517), 528 (204)[b]

[a] In CD_3CN. [b] In H_2O. [c] In CH_3CN. [d] In D_2O. [e] In dimethyl-d_6 sulfoxide. [f] Reflectance spectrum. [g] In CD_3OD. [h] 400.1 MHz, δ = chemical shift, m = multiplet, s = singlet, and q = quartet. [i] 100.6 MHz.

wavenumbers by 100 cm^{-1} as compared to those of $[LRe(NO)(CO)_2]^{2+}$. The ^1H NMR and ^{13}C NMR spectra (CD_3CN) are very informative; the ^1H NMR spectrum of **1** exhibits a singlet at δ 0.65 (3 H), which is assigned to the $Re-CH_3$ group. Similar values have been reported for $(\eta^5\text{-}C_5H_5)Re(NO)(CO)(CH_3)$ and $(\eta^5\text{-}C_5Me_5)Re(NO)(CO)(CH_3)$ (δ 0.92 and 0.62, respectively).[2] A further typical feature of the ^1H NMR spectra of complexes of the type [LReXYZ] is the observation of three singlets due to three inequivalent secondary amine protons of the coordinated 1,4,7-triazacyclononane ligand (δ 4.76, 5.70, 6.10) and a complicated multiplet of the amine ligand methylene protons in the range δ 2.71–3.50 (12 H). The former three singlets are not observed in D_2O solvent due to rapid N–H/N–D exchange. In the ^{13}C NMR spectrum six signals of methylene carbon atoms are observed between δ 49.61 and 59.78; a signal at δ −10.10 is assigned to the $Re-CH_3$ moiety and that at δ 220.2 to the Re–CO moiety.

When the above reaction was carried out in unlabeled water with $NaBD_4$ instead of $NaBH_4$, red $[LRe(NO)(CO)(CD_3)]BF_4$ was isolated. In the ^2H NMR spectrum (CD_3CN) only one singlet at δ 0.63 due to the $Re-CD_3$ group was observed; the corresponding ^1H NMR spectrum lacked the signal at δ 0.65 of methyl protons. This experiment corroborates the proposal that hydride transfer from BH_4^- to the $Re-C{\equiv}O$ group is the actual mechanism of CO reduction in these systems.

1 dissolved in acetonitrile with 0.10 M tetra-*n*-butylammonium hexafluorophosphate (TBA[PF_6]) as supporting electrolyte is electrochemically, reversibly oxidized at a Pt-button electrode at $E_{1/2}$ = +0.77 V vs Fc^+/Fc and irreversibly reduced at E_{red} = −2.15 V vs Fc^+/Fc. The cyclic voltammogram is shown in Figure 2. The reversibility of the one-electron oxidation of **1** is indicated by the independence of the difference $E_{p,a} - E_{p,c}$ = 68 mV and the ratio $I_{p,a}/I_{p,c}$ = 1.0 ± 0.1 from the scan rate (20–200 mV s^{-1}).

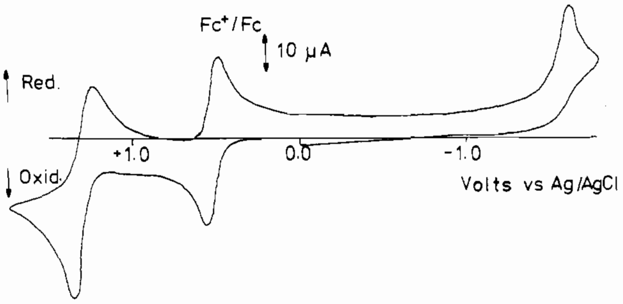

Figure 2. Cyclic voltammogram of **1** (20 °C; CH_3CN; 0.1 M TBA[PF_6]; ferrocene internal standard; scan rate 50 mV s^{-1}).

Thus the 17e complex $[LRe(NO)(CO)(CH_3)]^{2+}$ is formed (eq 1). Attempts to chemically generate this paramagnetic species

$$[LRe(NO)(CO)CH_3)]^{2+} + e^- \rightleftarrows [LRe(NO)(CO)(CH_3)]^+ \qquad (1)$$

by reaction of **1** in CH_3CN with $AgBF_4$ or TBA[S_2O_8] were unsuccessful. When the above reaction between $[LRe(NO)(CO)_2]^{2+}$ and BH_4^- was carried out under an argon atmosphere in anhydrous methanol under otherwise identical conditions, the formylrhenium complex **1a** was obtained as diamagnetic, brown tetrafluoroborate salt. In the infrared region the acyl stretching frequency is observed at 1600 cm^{-1}, which is in good agreement with the corresponding $(\eta^5\text{-}C_5H_5)Re(NO)(CO)(CHO)$ and related organometallic species.[3,6,7,9] The Re–CHO moiety in **1a** exhibits a singlet in the ^1H NMR (CD_3OD) spectrum at δ 16.2;[9] in the ^{13}C NMR spectrum the signal of the carbon atom of this group is observed at δ 272.2.[8] **1a** decomposes in the presence of water and air; the products have not been characterized, but proton-

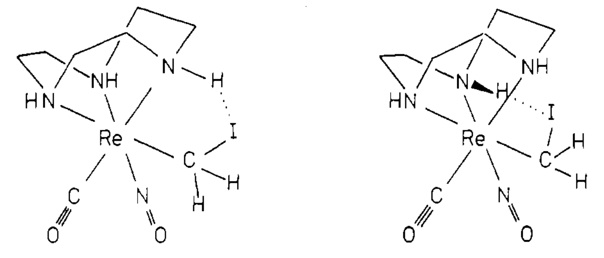

Figure 3. Possible rotamers of **7**.

induced disproportionation of the formyl ligand most probably occurs.[8]

In the following section we will describe reactions involving the cleavage of the rhenium–methyl bond of **1** by protic electrophiles. Racemic **1** reacts in anhydrous trifluoroacetic acid, yielding $[\mathrm{LRe(NO)(CO)(O_2CCF_3)}]^+$ (**2**), which was isolated as a yellow $\mathrm{PF_6}$ salt, and methane. With aqueous HX acids (X = F, Cl, Br, I) methane and complexes $[\mathrm{LRe(NO)(CO)X}]^+$ (F (**3**), Cl (**4**), Br (**5**), I (**6**)) are formed in excellent yields.

$$\mathbf{1} + \mathrm{HX} \rightarrow [\mathrm{LRe(NO)(CO)X}]^+ + \mathrm{CH_4} \qquad (2)$$

$$\mathrm{X = F, Cl, Br, I, CF_3CO_2}$$

For the reaction of **1** with 1 M HCl at 20 °C the gaseous products were analyzed by gas chromatography: 90% methane and 10% ethane and traces (<1%) of ethene were detected.

In the infrared both the $\nu(\mathrm{CO})$ and $\nu(\mathrm{NO})$ stretching frequencies shift to lower wavenumbers with decreasing electronegativity of X; thus **3** > **4** > **5** > **6**. In accord with this is the observation that the two absorption maxima in the UV–vis spectra are shifted to lower energies as the electronegativity of X decreases on going from the fluoro to the iodo complex (Table I).

Since $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Re(NO)(CO)(CH_3)}$ was shown to react with halogens $\mathrm{Cl_2}$, $\mathrm{Br_2}$, and $\mathrm{I_2}$ to produce $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Re(NO)(CO)X}$ species and $\mathrm{CH_3X}$,[18] we tested this reaction with **1** and iodine. Much to our surprise we did not observe the expected Re–$\mathrm{CH_3}$ bond cleavage and formation of **6** but rather the selective generation of a Re–$\mathrm{CH_2I}$ moiety. Thus the reaction of racemic **1** in anhydrous ethanol with iodine (1:1) at room temperature produced brown $[\mathrm{LRe(NO)(CO)(CH_2I)}]\mathrm{BF_4}$, (**7**) in 97% yield (eq 3). In the ^{1}H NMR spectrum ($\mathrm{CD_3CN}$) of **7** three singlets

$$[\mathrm{LRe(NO)(CO)(CH_3)}]^+ + \mathrm{I_2} \rightarrow [\mathrm{LRe(NO)(CO)(CH_2I)}]^+ + \mathrm{HI} \qquad (3)$$

of the N–H protons are observed at δ 5.25, 5.95, and 6.95; the 12 methylene protons of the coordinated 1,4,7-triazacyclononane ligand give rise to a complicated multiplet at δ 2.90–3.52. In addition two quadruplets corresponding to two protons are centered at δ 3.70 and 3.87 with a geminal coupling constant J = 6 Hz. It is conceivable that two rotamers of **7** exist in solution (Figure 3) where the iodine of the Re–$\mathrm{CH_2I}$ group is hydrogen bonded to either of two neighboring secondary amine groups. The ^{13}C NMR spectrum exhibits seven signals, δ 49.83–53.47, which are clearly identified as methylene carbon atoms by a DEPT experiment; six of these are due to ring–$\mathrm{CH_2}$–$\mathrm{CH_2}$ groups, and one is due to the R–$\mathrm{CH_2}$–I moiety.

The cyclic voltammogram of **7** dissolved in acetonitrile (0.1 M TBA[$\mathrm{PF_6}$] supporting electrolyte; glassy-carbon working electrode) revealed a reversible one-electron wave at $E_{1/2}$ = 0.755 V vs $\mathrm{Fc^+/Fc}$. ΔE_p = 60 mV, $I_\mathrm{p,a}/I_\mathrm{p,c}$ = 1.0 + 0.1, and the peak current functions were independent of the scan rate (20–200 mV $\mathrm{s^{-1}}$) in agreement with the diagnostic criteria for a reversible one-electron-transfer process (eq 4). The oxidized form of **7** has not been

$$[\mathrm{LRe(NO)(CO)(CH_2I)}]^{2+} + \mathrm{e^-} \rightleftarrows [\mathrm{LRe(NO)(CO)(CH_2I)}]^+ \qquad (4)$$

prepared chemically. Substitution of a $-\mathrm{CH_3}$ in **1** by $-\mathrm{CH_2I}$ in **7** does not change the redox potential significantly.

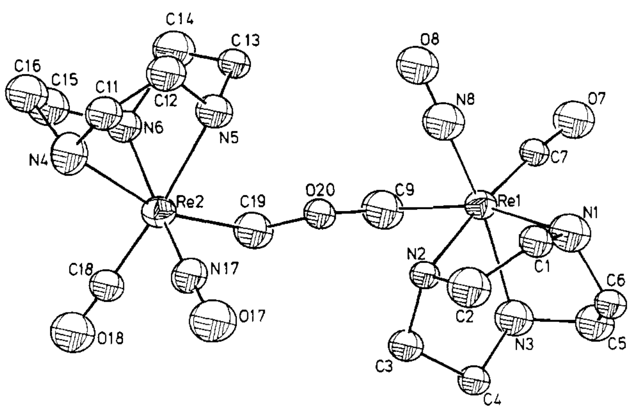

Figure 4. Structure of the dication in **8**.[17] Selected bond lengths (Å) and angles (deg): Re1–C9, 2.18 (3); Re2–C19, 2.17 (3); C19–O20, 1.49 (3); C9–O20, 1.40 (4); C19–O20–C9, 113 (2); O20–C19–Re1, 111 (2); Re2–C19–O20, 107 (2).

In an attempt to grow single crystals of the iodide salt of racemic **1** from an aqueous/acetone mixture, which contained 0.1 M sodium iodide, in an open vessel at room temperature, we obtained beautiful orange crystals within 10 days of a material that subsequently turned out to be the dimer $[\{\mathrm{Re(NO)(CO)}\}_2(\mu\text{-}\mathrm{CH_2OCH_2})]\mathrm{I_2}$ (**8**). The reaction did not work under anaerobic conditions or in the absence of iodide anions. This indicated that **7** might be the actual precursor of **8**, which dimerized slowly in aqueous solution probably via the hydroxymethylene intermediate $[\mathrm{LRe(NO)(CO)(CH_2OH)}]^+$ according to eq 5–9. When the

$$4\mathrm{I^-} + \mathrm{O_2} + 2\mathrm{H_2O} \rightarrow 2\mathrm{I_2} + 4\mathrm{OH^-} \qquad (5)$$

$$\mathbf{1} + \mathrm{I_2} \rightarrow \mathbf{7} + \mathrm{HI} \qquad (6)$$

$$\mathbf{7} + \mathrm{OH^-} \rightarrow [\mathrm{LRe(NO)(CO)(CH_2OH)}]^+ + \mathrm{I^-} \qquad (7)$$

$$[\mathrm{LRe(NO)(CO)(CH_2OH)}]^+ + \mathrm{OH^-} \rightarrow [\mathrm{LRe(NO)(CO)(CH_2O)}] + \mathrm{H_2O} \qquad (8)$$

$$[\mathrm{LRe(NO)(CO)(CH_2O^-)}] + \mathbf{7} \rightarrow \mathbf{8} + \mathrm{I^-} \qquad (9)$$

above reaction was carried out in the presence of $\mathrm{I_2}$, under otherwise identical reaction conditions, crystals of **8** precipitated within 4 days at room temperature even under anaerobic conditions. Finally, **8** was also obtained when **7** was allowed to stand in an aqueous solution for 3 days. These reactions corroborate the above mechanism of formation of **8**. The yields of all three reactions never exceeded 40% based on the starting materials **1** or **7**.

The crystal structure of **8** has been determined by X-ray crystallography. Figure 4 summarizes these results.[17] Although the complex dication does not contain any crystallographically imposed symmetry elements (it crystallizes in the acentric space group $P2_1$) the quality of the X-ray structure determination did not allow an unambiguous distinction between the coordinated nitrosyl and carbonyl groups, although it did establish the presence of the 2-oxapropane-1,3-diide bridge. In the crystal investigated, both Re centers have the same configuration R,[23] and, in each case, the conformation of the coordinated 1,4,7-triazacyclononane ring is $\lambda\lambda\lambda$. Thus, racemic resolution occurs spontaneously upon crystallization. An interesting feature of the structure of **8** is the observation of two N–H···O hydrogen bonds between the oxygen of the $\mathrm{CH_2OCH_2}$ bridge and one of the N–H groups of the two cyclic amine ligands (N5···O20 = 2.98 (2), N2···O20 = 2.95 (2) Å).

Figure 5 shows the 400.1-MHz ^{1}H NMR spectrum of **8** (DMSO-d_6) at 20 °C. In the ^{1}H and ^{13}C NMR spectra a signal is observed for each proton and carbon atom in **8** in agreement

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[23] In order to determine the configuration of [LReXYZ] complexes, the cyclic triamine L was weighted as a unit having three times the atomic number of N, resulting in the following order of priority for **1**, L > NO > CO > $\mathrm{CH_3}$, and for **8**, L > NO > CO > $\mathrm{CH_2O_{0.5}}$. For the nomenclature of configuration in octahedral complexes used here see: Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598–6599. Note: replacement of the $\mathrm{CH_3}$group in **1** by halogeno ligands F, Cl, Br, and I in **3**, **4**, **5**, and **6** results in a change in the designation of the configuration at the Re center.

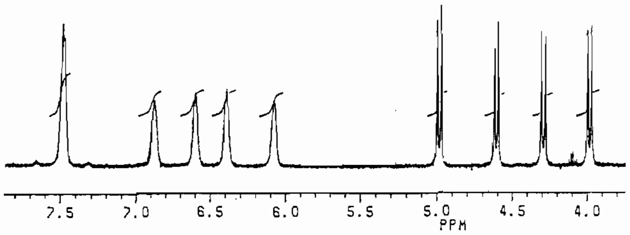
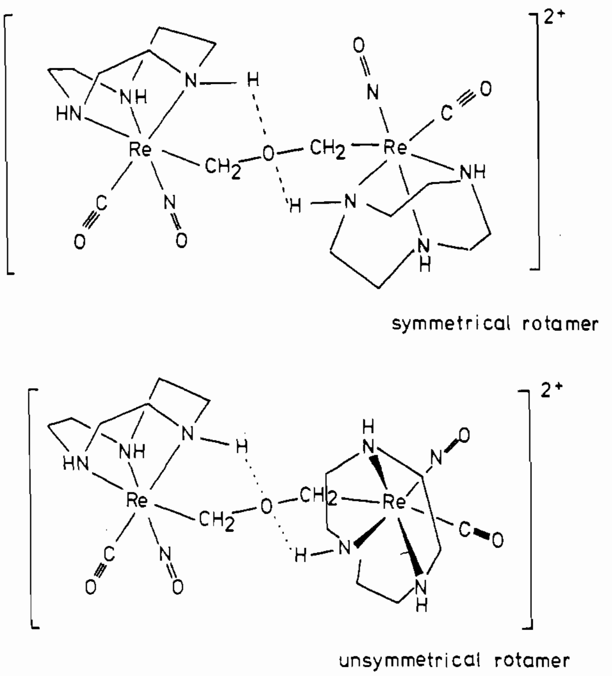


Figure 5. 400.1-MHz ^1H NMR spectrum of **8** (DMSO-d_6) at 20 °C showing the signals of NH and OCH_2 protons.

Chart I. Rotamers of **8** with Hydrogen Bonds



with the fact that the dication does not contain a mirror plane, a center of symmetry, or a proper axis of rotation (with the exception of C_1). This rules out the presence of the achiral meso form of **8** and a mixture of diastereomers. Thus crystals of **8** consist of a racemic mixture. Since the yields of solid **8** never exceeded 40%, it is likely that other diastereomers (e.g. the meso form) remain in solution.

The existence of the CH_2OCH_2 bridge between the two Re centers is established by four signals at δ 4.98, 4.62, 4.30, and 3.99, all of which display doublet character. The coupling constant J = 10–11 Hz is typical for a geminal coupling. An ^1H-^1H correlated 2D NMR experiment (Homo-COSY) indicates that the outer two and the inner two signals belong pairwise to one CH_2 group. The corresponding ^{13}C NMR signals are observed at δ 72.1 and 71.7 in the expected range of δ. The ^1H-^{13}C correlated 2D NMR spectrum (Hetero-COSY) reveals that the outer two proton signals and the carbon signal at δ 72.1 belong to the same CH_2 group, and correspondingly, the other two ^1H signals belong to the other CH_2 group. These facts rule out any other interpretation for these ^1H and ^{13}C signals.

At δ 6.08, 6.39, 6.62, 6.87, and 7.48 ^1H signals are observed that display the form of broadened singlets. The signal at δ 7.48 represents two protons whereas all other represent one proton. These signals are due to the six secondary amine –NH protons as was deduced from the existence of correlation signals with the resonances from the CH_2 groups of the triazacyclononane rings in a Homo-COSY spectrum. Furthermore, these protons are exchanged in a D_2O solution of **8**. Interestingly, this exchange is slower for the two protons resonating at δ 7.48 than for the other four protons. This together with their larger chemical shift is good NMR evidence for the presence of two N–H···O hydrogen bonds in **8** in solution.

The ^1H NMR signals of the methylene protons of **8** are observed in the δ range 2.8–3.5 as has been the case for all species containing the $\{LRe(NO)\}^{2+}$ moiety; the corresponding ^{13}C NMR signals are observed at δ 46.7–53.8 (10 different resonances with two overlapping signals for 12 C atoms).

From the crystal structure determination of **8** it follows unambiguously that in the crystal chosen the five-membered chelate rings $\overline{Re–N–C–C–N}$ have λλλ conformation at both Re centers; the configuration at Re shown in Figure 4 is *R*.[23] Note that the combination of the configuration at the Re centers and the ring conformations in **1** (see below) and **8** are identicial in both instances, i.e. *S*(δδδ) or *R*(λλλ). This implies that the *R*(δδδ) (or *S*(λλλ)) combination is relatively more unstable and is not formed. In other words, the configuration of the Re(NO)(CO)(alkane) moiety dictates the ring conformation of the coordinated triamine ligand. The differing trans influence of the NO, CO, and alkane ligands makes the three $Re–N_{amine}$ bonds inequivalent.

The fact that in solutions of **8** each proton and each carbon atom give rise to a signal rules out the possibility that the relative symmetrical N–H···O hydrogen-bonded rotamer of solid **8** depicted in Figure 4 prevails in solution. Space-filling models show that a second rotamer exists with two unsymmetrical N–H···O bonds (Chart I). Thus the solid-state and solution structure of **8** are different.

Well-characterized paramagnetic octahedral complexes of rhenium in the formal oxidation state +II (d^5) are rather scarce. Examples are $ReX_2(QAS)$ (QAS = tris(*o*-(diphenylarsino)-phenyl)arsine; X = Cl, Br)[24] and $[LRe(bpy)_2](ReO_4)_2$[25] (bpy = 2,2′-bipyridine). Next we will describe some reactions leading to such Re(II) compounds. **1** or **2** dissolved in CF_3COOH reacted with an excess bromine at room temperature to yield the green complex $[LRe(NO)(CO)Br]Br_2$ (**9**), which is the one-electron-oxidation product of **5**. **9** is soluble in water and methanol with a green color. In the infrared ν(NO) and ν(CO) stretching frequencies are observed at 1740 and 1980 cm^{-1}, which are shifted to higher wavenumbers by 40 cm^{-1} as compared to those of its reduced form **5**. An effective magnetic moment of 1.53 μ_B at 298 K is in good agreement with those for other Re(II) compounds for which values between 1.2 and 1.7 μ_B have been reported.[24-26] The cyclic voltammogram of **9** in anhydrous methanol (0.1 M TBA[PF_6] supporting electrolyte; glassy-carbon working electrode) exhibits one reversible one-electron wave in the potential range +0.8 to –0.8 V vs Ag/AgCl at $E_{1/2}$ = –0.62 vs Fc^+/Fc.

$$[LRe(CO)(NO)Br]^{2+} + e^- \rightleftarrows [LRe(NO)(CO)Br]^+ \qquad (10)$$

Interestingly, **9** can be reduced by $NaBH_4$ in aqueous solution to produce diamagnetic purple $[LRe(NO)(CH_3)Br]$ (**10**), which is rather insoluble in all common polar and unpolar solvents. In the infrared region the ν(NO) stretching band is observed at 1600 cm^{-1}. The presence of the methyl group is proven by the observation that **10** reacts in 48% HBr under anaerobic conditions to produce $[LRe(NO)Br_2]$ (**12**) and methane. If, on the other hand, **10** was treated with excess bromine in $CHCl_3$ a light yellow solid material $[LRe(NO)Br_2]Br$ (**11**) was obtained. Oxidation of **1** in CF_3CO_2H with a 100-fold excess Br_2 also gave **11**. **11** is soluble in H_2O and CH_3OH but decomposes slowly in these solvents. An effective magnetic moment of 1.70 μ_B at 293 K is in agreement with a $\{Re–NO\}^5$ moiety in **11**. **11** was reduced in methanolic solution with zinc amalgam to the dark green, diamagnetic complex $[LRe(NO)Br_2]$ (**12**). The ν(NO) stretching frequencies in **11** and **12** are observed at 1740 and 1600 cm^{-1}, respectively.

The cyclic voltammograms of **11** and **12** are identical; they show a reversible one-electron wave at $E_{1/2}$ = –0.80 V vs Fc^+/Fc in the potential range +0.8 to –0.8 V vs Ag/AgCl in methanol (0.1 M TBA[PF_6] supporting electrolyte; glassy carbon electrode).

$$\mathbf{11} + e^- \rightleftarrows \mathbf{12} \qquad (11)$$

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(24) Mawby, R. J.; Venanzi, L. M. *J. Chem. Soc.* **1962**, 4447–4454.

(25) Stebler, M.; Gutiérrez, A.; Ludi, A.; Bürgi, H.-B. *Inorg. Chem.* **1987**, *26*, 1449–1451.

(26) Lewis, J.; Nyholm, R. S.; Rodley, G. A. *J. Chem. Soc.* **1965**, 1483–1488.

Optical Resolution and Absolute Configuration of 1. Since the reaction of $[LRe(NO)(CO)_2]^{2+}$ with BH_4^- produced racemic $[LRe(NO)(CO)(CH_3)]^+$ (**1**), we made attempts to resolve this methyl complex. Cobalt(III) complexes and the resolution of the type [LCoXYZ] have been described[27] as well as that of some organometallic octahedral complexes *cis*-$(CO)_3MXYZ$ (M = Cr, Mo, W, Mn).[28] A number of $(\eta^5\text{-}C_5H_5)Re(NO)(CO)X]$ complexes have been resolved.[29] As mentioned above, the octahedral species **1** possesses in principle an *R* and *S* configuration[23] at the Re center, and in addition, the three five-membered chelate rings, Re–N–C–C–N, formed by the coordinated, tridentate amine ligand may have either the λλλ or the δδδ conformation, which gives rise to diastereomeric forms of **1** (the enantiomers are ordered pairwise):

$$R(\delta\delta\delta) \text{ and } S(\lambda\lambda\lambda)$$

$$R(\lambda\lambda\lambda) \text{ and } S(\delta\delta\delta)$$

We have added (1*S*)-3-bromocamphorsulfonic acid monohydrate dissolved in acetone to an aqueous solution of racemic **1**.[30] Within 2 days large red crystals of $[LRe(NO)(CO)(CH_3)][(1S)$-3-bromocamphorsulfonate$]\cdot H_2O$ crystallized in 45% yield based on **1**. This compound was recrystallized three times from acetone-/water mixtures. The circular dichroism (CD) spectra of aqueous solutions were recorded from each fraction. They did not change on going from the first crystalline product to the recrystallized products. Thus it is concluded that only one diastereomer containing one enantiomeric pure form of the cation in **1** crystallizes out. The CD spectrum (H_2O) exhibits a negative Cotton effect at 510 nm ($\Delta\epsilon = -0.036$) in the visible region and a positive Cotton effect at 308 nm ($\Delta\epsilon = +2.97$), which is predominantly due to the (1*S*)-3-bromocamphor sulfonate. The CD spectrum from the above mother liquor exhibited a positive Cotton effect of the same magnitude at 510 nm. These experiments clearly indicate that only one of two possible diastereomers of **1** (see above) is formed in the reaction of $[LRe(NO)(CO)_2]^{2+}$ with BH_4^-. In order to obtain a complete CD spectrum of an enantiomeric pure form of **1** that is unperturbed by the (1*S*)-3-bromocamphorsulfonate anion, we dissolved the above salt in H_2O and added $Na[BPh_4]$. The tetraphenylborate salt crystallized out immediately, and the CD spectrum of this material exhibited an additional negative Cotton effect at 309 nm ($\Delta\epsilon = -0.042$).

The crystal structure of $[LRe(NO)(CO)CH_3)][(1S)\text{-}C_{10}H_{14}BrO_4S]\cdot H_2O$ has been determined (Figure 1).[17] Since the absolute configuration of the anion is known, the absolute configuration of the cation was readily established to be *S*[23] at the Re center and the conformation of the chelate rings is δδδ. Thus the diastereomer *S*(δδδ)/*R*(λλλ) is formed exclusively.

In order to determine the stereochemical course of the reaction between **1** and HCl

$$(S)\text{-}[LRe(NO)(CO)(CH_3)]^+ + HCl \rightarrow (R)\text{-}[LRe(NO)(CO)Cl]^+ + CH_4 \quad (12)$$

we have carried out this reaction with enantiomeric pure (*S*)-$[LRe(NO)(CO)(CH_3)][(1S)\text{-}C_{10}H_{14}BrO_4S]\cdot H_2O$. After the reaction volume was reduced to half, large red crystals precipitated in 92% yield, $[LRe(NO)(CO)Cl][(1S)\text{-}C_{10}H_{14}BrO_4S]\cdot H_2O$. If the same reaction was carried out with the racemic tetrafluoroborate salt **1**, the yield of the latter salt, after addition of (1*S*)-3-bromocamphorsulfonic acid monohydrate, was only 50%. The CD spectrum (H_2O) of these materials exhibited a negative Cotton effect at 510 nm ($\Delta\epsilon = -0.054$). A crystal structure determination[31] of the above crystals proved to be severly hampered by a disorder of the cation, and the absolute configuration at the Re center could not be established unambiguously, except for the fact that the conformation of the Re–N–C–C–N chelate rings was again δδδ. This together with the observation that both the $[LRe(NO)(CO)(CH_3)]^+$ and $[LRe(NO)(CO)Cl]^+$ cations in the (1*S*)-3-bromocamphorsulfonate salts exhibit negative Cotton effects in the visible region is taken as indication that the absolute configuration at the Re centers has not changed. Therefore, we propose that reaction 12 proceeds with complete retention of configuration at the Re centers.[23]

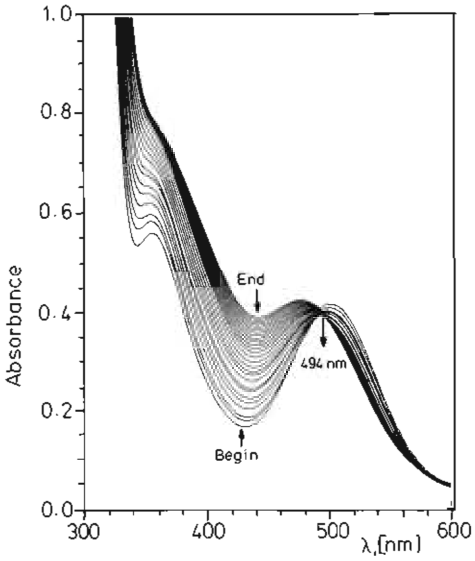
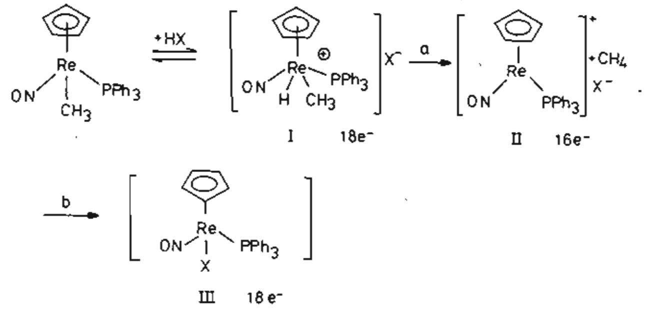


Figure 6. Scan spectrum of the reaction between **1** and HBr at 20 °C ([**1**] = 1.1×10^{-2} M; [H^+] = 1.0 M; [Br^-] = 1.0 M; *I* = 1.0 M; one scan every 10 min).

Scheme II. Proposed Mechanism for the Reaction of $(\eta^5\text{-}C_5H_5)Re(NO)(CH_3)(PPh_3)$ with HX[18]



Kinetics of the Reaction of 1 with HX. The rates of the reactions between **1** and HX (X = Cl, Br, NO_3) in aqueous solution were monitored by following changes in the electronic absorption spectra at 430 nm with time. Spectral changes for a typical reaction of **1** with HBr are shown in Figure 6. In the reactions of **1** with HCl, HBr, and HNO_3, one clear isosbestic point was observed at 486, 494, and 490 nm, respectively. In the latter reaction a

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(27) Fujinami, S.; Hosokawa, T.; Shibata, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 113–121.

(28) (a) Brunner, H.; Herrmann, W. A. *J. Organomet. Chem.* **1973**, *57*, 183–189. (b) Brunner, H.; Lappus, M. *Z. Naturforsch.* **1974**, *29B*, 363–366.

(29) Merrifield, J. H.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1204–1211.

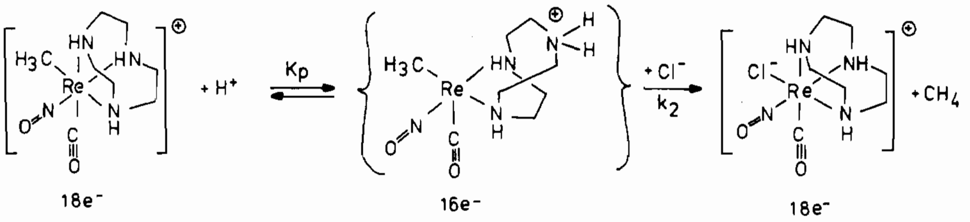
(30) When a large single crystal of $[LRe(NO)(CO)(CH_3)]BF_4$ was dissolved in H_2O, a solution (H_2O) CD spectrum was observed. A series of such solutions using single crystalline species exhibited positive or negative Cotton effects at 309 and 510 nm, respectively. Thus spontaneous resolution of the tetrafluoroborate salt is observed. (A solution containing a powdered sample of **1** did not show a CD spectrum.)

(31) Crystal data: orthorhombic, acentric space group $P2_12_12_1$; $a = 10.010$ (5), $b = 10.963$ (5), and $c = 22.683$ (9) Å; $Z = 4$; $\rho_{calcd} = 1.96$ g cm^{-3}; the space group is the same as has been reported for $[LRe(NO)(CO)(CH_3)]$ $[1\text{-}S\text{-}C_{10}H_{14}BrO_4S]\cdot H_2O$, and cell dimensions are also very similar. We thank Dr. B. Nuber and Prof. Dr. J. Weiss (Universität Heidelberg) for the crystal structure determination.

(32) (a) Chaudhuri, P.; Wieghardt, K.; Tsay, Y.-H.; Krüger, C. *Inorg. Chem.* **1984**, *23*, 427–432. (b) Schreiber, P.; Wieghardt, K.; Flörke, U.; Haupt, H.-J. *Z. Naturforsch.* **1987**, *42B*, 1391–1397.

(33) (a) La Monica, G.; Freni, M.; Cenini, S. *J. Organomet. Chem.* **1974**, *71*, 57–64. (b) Bottomley, F. *Acc. Chem. Res.* **1978**, *11*, 158–163.

Scheme III. Proposed Mechanism for the Reaction of **1** with HCl



very slow subsequent stage of the reaction has been detected in agreement with the fact that $[LRe(NO)(CO)(NO_3)]^+$ has not been isolated. The nature of this slow decomposition has not been further investigated; it did not interfere with the kinetic measurements of the first step during which methane is produced. The kinetics were measured at 35 °C for the reactions with HCl and HBr and at 30 °C for HNO_3 by using pseudo-first-order conditions with $[H^+]$ *and* $[X^-]$ in large excess over [complex]. The ionic strength was adjusted to 1.0 M (Na_2SO_4).

The experimental rate law is of the form shown in eq 13 in all three cases. Pseudo-first-order rate constants are summarized

$$-d[\mathbf{1}]/dt = k[H^+][X^-][\mathbf{1}] \tag{13}$$

in Table II. Numerical values for the third-order rate constants, k, for the reaction with HCl and HBr at 35 °C are 1.65×10^{-4} and 1.47×10^{-4} $M^{-2}\,s^{-1}$, respectively; for the reaction with HNO_3 at 30 °C a value of 1.85×10^{-2} $M^{-2}\,s^{-1}$ has been determined. Thus the reaction with HNO_3 is significantly faster than those with HCl or HBr.

It is interesting to note in this respect that **1** does not react in 1 M $HClO_4$ or 1 M H_2SO_4 or at pH 7 in the presence of 1 M Cl^-, Br^-, or NO_3^-. These experiments clearly show that the formal substitution of a methyl group in **1** by a nucleophile X^- is only feasible if both an electrophile (protons) *and* a nucleophile are present.

A mechanism that is in accord with the experimental rate law involves a rapid protonation–deprotonation preequilibrium of **1** where the protonated form reacts in the rate-determining step with the nucleophile to produce a $[LRe(NO)(CO)X]^+$ species and methane (eq 14–16). If $K_p[H^+] \ll 1$, eq 16 simplifies to eq 13.

$$\mathbf{1} + H^+ \overset{k_p}{\rightleftharpoons} \{\mathbf{1}H\}^{2+} \tag{14}$$

$$\{\mathbf{1}H\}^{2+} + X^- \xrightarrow{k_2} [LRe(NO)(CO)X]^+ + CH_4 \tag{15}$$

$$-d[\mathbf{1}]/dt = \left(\frac{k_2K_p[H^+]}{1 + K_p[H^+]}\right)[X^-][\mathbf{1}] \tag{16}$$

Discussion

The stepwise reduction of a rhenium–carbonyl unit to Re–CH_3 by hydride transfer via formyl and hydroxylmethylene intermediates has been documented for organometallic pseudotetrahedral complexes[1-11,34] such as $[(\eta^5-C_5H_5)Re(NO)(CO)(PPh_3)]$ and, in this work, for the octahedral species $[LRe(NO)(CO)_2]^{2+}$. The selective formation of a deuterium-labeled species $[LRe(NO)(CO)(CD_3)]^+$ in aqueous solution by using BD_4^- is good evidence that the protons at the Re–CH_3 group in **1** stem from the reductant.[35] No proton scrambling with the solvent H_2O has been observed.

The mechanism of the rhenium–methyl bond cleavage in **1** by HX in aqueous solution has been studied in detail here. From the kinetics of this reaction it follows that both an electrophile (protons) and a suitable nucleophile are necessary reactants. There are three conceivable sites for an electrophilic attack of protons in **1**: (i) The electron-rich Re center may be protonated with formation of a seven-coordinated $[LRe(NO)(CO)(CH_3)H]^{2+}$ 18e intermediate. Such species have been characterized; e.g. $[LM(CO)_3H]^+$ (M = Mo, W).[32] (ii) The Re-NO group is protonated to give an Re–NHO species. (iii) An Re–N_{amine} bond is dissociatively broken, and the secondary amine is protonated.

Table II. Pseudo-First-Order Rate Constants for the Reactions between **1** and Aqueous HX (X = Cl, Br, NO_3)[a]

T, °C	$[H^+]$, M	$[X^-]$, M	10^5k_{obsd}, s^{-1}
		HCl	
35	0.10	0.50	2.83
	0.34	0.50	7.28
	0.50	0.50	8.47
	0.67	0.50	14.7
	0.84	0.50	16.5
	1.00	0.50	19.8
	0.50	0.10	2.08
	0.50	0.34	6.35
	0.50	0.50	8.44
	0.50	0.67	13.3
	0.50	0.84	15.6
	0.50	1.00	19.5
		HBr	
35	0.10	0.50	3.01
	0.34	0.50	6.83
	0.50	0.50	7.90
	0.67	0.50	12.1
	0.84	0.50	14.4
	1.00	0.50	18.4
	0.50	0.10	2.03
	0.50	0.34	5.60
	0.50	0.50	7.91
	0.50	0.67	10.5
	0.50	0.84	12.7
	0.50	1.00	14.4
		HNO_3	
30	0.10	0.50	250
	0.50	0.50	853
	0.80	0.50	1610
	1.00	0.50	2130
	0.50	0.10	251
	0.50	0.50	853
	0.50	0.80	1550
	0.50	1.00	2198

[a] Ionic strength was adjusted to 1.0 M (Na_2SO_4); the concentration of **1** was 10^{-2} M in all experiments.

The nearly linear, electron-poor Re–NO group is not available for electrophilic attack.[33] In fact, Fenske et al.[11,34] have shown that this is the most likely site for nucleophilic attack by H^-. This leaves us with the two reasonable sites i and iii. In the following section we present arguments favoring site i for Gladysz's, Graham's, and Casey's compounds and site iii for our system.

Gladysz et al.[18] have proposed a mechanism for the cleavage of the Re–CH_3 bond in the pseudotetrahedral $(\eta^5-C_5H_5)Re(NO)(PPh_3)(CH_3)$ complex by protic (Scheme II) and halogen electrophiles. They have shown that the HX-induced formation of $(\eta^5-C_5H_5)Re(NO)(PPh_3)X$ species (X = Cl, Br) and methane is stereospecific; the reaction proceeds with retention of configuration at the Re center. They did not measure the kinetics of the reaction. In contrast, the reaction with X_2 (X = Cl, Br, I) yields the same but racemic complexes and CH_3X. In the present system octahedral **1** reacts with aqueous HX to produce complexes **3**–**6** and methane, also with retention of configuration at the Re center, whereas with iodine **1** was found to yield **7**; no Re–CH_3 bond cleavage is observed in this case. Gladysz's mechanism

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(34) Fenske, R. F.; Milletti, M. C. *Organometallics* **1986**, *65*, 1243–1246.
(35) Kiel, W. A.; Lin, G.-Y.; Gladysz, J. S. *J. Am. Chem. Soc.* **1980**, *102*, 3299–3301.

(Scheme III) involves attack of protic electrophiles at the Re center, generating a square-pyramidal hydride intermediate that undergoes rapid reductive elimination of methane to produce a 16e intermediate which reacts stereospecifically with X^-. These authors have argued that the lifetime of the hydride intermediate is short, i.e. reductive elimination is fast, so that no racemization by pseudorotation (or an equivalent process) occurs and retention of configuration prevails.

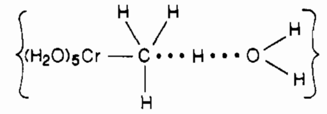
Contrary to the statement made in ref 17, a rate law as in eq 13 is in accord with this mechanism provided that (i) the reductive elimination is the rate-determining step a, which is plausible since this step involves the cleavage of covalent bonds whereas step b involves only rapid addition of X^- to a cationic 16e fragment, and (ii) steady-state conditions apply for intermediate II. There is good circumstantial evidence for an intermediate II.[18]

$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ reacts in acids with relatively nonnucleophilic counterions such as $CF_3SO_3^-$ with production of CH_4,[18] whereas **1** does not react at all in 1 M $HClO_4$ or H_2SO_4. Therefore, we feel that the chemistry of **1** with protic electrophiles HX does not support a mechanism where reductive elimination of CH_4 is the rate-determining step.

An alternative mechanism involves the protonation of **1** at a secondary amine nitrogen after one $Re–N_{amine}$ bond has been cleaved (Scheme III). The 16e intermediate IV may then react with addition of the nucleophile X^- with concomitant release of CH_3^-, which is rapidly protonated, and rapid re-formation of the $Re–N_{amine}$ bond. The $Re–N_{amine}$ bond trans to the CO ligand in **1** is the weakest; it is the bond *cis* to the $Re–CH_3$ group. The incoming Cl^- may exert a cis-labeling effect on the methyl group, which is then a good leaving group, and the rearrangement of the chloro ligand in addition to the formation of the third $Re–N_{amine}$ bond yields a formal substitution reaction with retention of configuration at the Re center and retention of the chelate ring conformations. In this context it is interesting to note that chromium(III)–alkyl complexes, e.g. $[(H_2O)_5Cr(CH_3)]^{2+}$, are hydrolyzed in acidic solutions affording $Cr(OH_2)_6^{3+}$ and methane.[36] The rate law is of the form

$$-d[Cr^{III}–CH_3]/dt = (k_{H_2O} + k_{H_3O^+}[H^+])[Cr^{III}–CH_3] \qquad (17)$$

which differs from the rate law in eq 13. A mechanism involving the transition state



$$\left\{(H_2O)_5Cr—\overset{H\ \ H}{\underset{H}{C}}\cdots H\cdots O\begin{smallmatrix}H\\H\end{smallmatrix}\right\}$$

has been proposed for the $k_{H_3O^+}$ pathways. In this instance electrophilic attack at the coordinated methyl group occurs. This mechanism cannot be operative in the reaction of **1** with HX in aqueous solution since it does not show a first-order dependence on [nucleophile] as in eq 13.

An interesting difference in reactivity between $(\eta^5\text{-}C_5H_5)Re(NO)(CH_3)(PPh_3)$ and **1** is manifested by the observation that the former reacts with I_2 affording $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)I$ and probably CH_3I, whereas the later forms **7** and HI. For the formation of the former, electrophilic attack of halogens at the Re center with a square pyramidal intermediate, $[(\eta^5\text{-}C_5H_5)Re(NO)(CO)(CH_3)X]X$, and reductive elimination of CH_3X has been proposed.[18] It is suggestive that in **1** the Re center is again not available for this kind of electrophilic attack and alternative reaction paths prevail. The origin of this reactivity difference may be steric hindrance (seven-coordinate intermediates are more crowded than "five"-coordinate $\eta^5\text{-}C_5H_5ReABCD$ species), but we feel that complexes of the type $[LRe(NO)(CO)(CH_3)]^+$ are electron poorer than their organometallic counterparts. Thus this study nicely demonstrates how the reactivity of rhenium–carbon bonds are varied by the nature of the coligands.

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Ligand Substitution Studies of Aquo(phosphine)ruthenium(II) Complexes

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Ligand substitutions for a series of complexes of the form *cis*-$[Ru^{II}(OH_2)(bpy)_2(PR_3)]^{2+}$ (where bpy = 2,2′-bipyridine and PR_3 = tertiary phosphine ligand) have been examined in nonaqueous solution. The second-order rate constants for the substitution of the water ligand by acetonitrile, 4-acetylpyridine, and chloride depend on the steric and electronic nature of the coordinated phosphine ligand. By use of tris(para-substituted phenyl)phosphines, the electronic effect of the coordinated ligand on the rate constant for substitution is investigated while a constant steric environment is maintained. The natural logarithms of the second-order rate constants for the substitution of water by acetonitrile decrease as a linear function of the Hammett parameters of the para substituents in the following order: $N(CH_3)_2 > OCH_3 > CH_3 > H > F > CF_3$. Similarly, by use of various trialkylphosphines, the steric effect of the ligand can be examined while the $E_{1/2}$ values of the Ru^{III}/Ru^{II} couples remain constant. In this case, increases in the ligand cone angles result in a linear increase in the natural logarithms of the second-order rate constants for the substitution of water by acetonitrile.

Introduction

Recently, we investigated high-valent oxometal complexes as stoichiometric oxidants, where we reported the isolation of stable oxoruthenium(IV) complexes that utilize a tertiary phosphine ligand in a position cis to the oxo ligand.[1–3] These complexes are active stoichiometric oxidants, where the coordinated phosphine ligand affects both the rate of oxidation of substrates and the resulting product distributions.[4–6] In addition, we also reported the aerobic oxidation of cyclohexene catalyzed by an aquo(phosphine)ruthenium(II) complex.[7] The first step in the catalytic

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(3) Kubow, S. A.; Marmion, M. E.; Takeuchi, K. J. *Inorg. Chem.* **1988**, *27*, 2761–2767.

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