such as $Ln(CyDTA)^-$ (CyDTA = *trans*-1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetraacetate ion), $Ln(K22DA)^+$, and $Ln(K21DA)^+$, the acid-independent pathway involved a slow, rate-determining distortion of the complex, followed by rapid attack of a second metal ion (e.g. Cu^{2+}) or a proton.[4,5,15] The lanthanide ion in the distorted complex still binds to a portion of the ligand, presumably due to the rigid ligand structure and the relatively high formation stability. In the present case, because none of the ligands, i.e. K22MA and K22DP, form very strong complexes with lanthanide ions, the formation of the intermediate distorted complex may no longer be rate-determining. The extremes of the mechanisms may be those of alkali-metal neutral crown ether complexes, i.e. unimolecular dissociative and bimolecular cation interchange (associative),[16,17] which are beyond the scope of the present study.

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Registry No. K22MA, 82353-42-2; K22DP, 68670-15-5; K22MP, 115290-72-7.

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Contribution from the Lehrstuhl für Anorganische Chemie I, Ruhr-Universität, D-4630 Bochum, FRG,
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Synthesis and Reactivity of $[LRe(NO)(CO)(NCO)]^+$ (L = 1,4,7-Triazacyclononane). Kinetics and Mechanisms of Its Formation and Transformation to $[LRe(NO)(CO)X]^{n+}$ ($X = NH_3, Cl, HCO_2^-, CF_3SO_3^-$) and Other Species. Crystal Structure of $[LRe(NO)(CO)(NH_3)]Br_2$

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The complex $[LRe(NO)(CO)(NCO)](BF_4)$ (**1**) has been synthesized from $[LRe(NO)(CO)_2](BF_4)_2$ (L = 1,4,7-triazacyclononane, $C_6H_{15}N_3$) in methanol with a variety of nucleophiles such as $N_2H_4{\cdot}H_2O$, $H_2NNH(CH_3)$, $H_2NN(CH_3)_2$, H_2NOH, and N_3^-. The kinetics and mechanisms of the formation of **1** have been investigated. A general mechanism for these reactions is proposed: nucleophilic attack at a coordinated carbonyl produces carbazoyl intermediates when hydrazine or its N-methylated derivatives are reactants. In the rate-determining step, NH_3, $NH_2(CH_3)$, or $NH(CH_3)_2$ is then cleaved off and fast rearrangement to the N-coordinated isocyanate occurs. **1** undergoes a series of reactions at the coordinated isocyanate ligand; e.g. concentrated HBr reacts in CH_3OH with **1** to produce $[LRe(NO)(CO)(NH_3)]Br_2$ (**3**), the crystal structure of which has been determined by X-ray crystallography. Crystal data: monoclinic; space group $P2_1/c$; $a = 10.138$ (4), $b = 11.507$ (5), and $c = 12.839$ (4) Å; $\beta = 91.86$ (3)°; $V = 1497.0$ (8) Å^3; $Z = 4$. The kinetics and mechanisms of the reaction of **1** with H^+ to produce **3** and CO_2 have been investigated. **3** is electrochemically or chemically oxidized to paramagnetic $[LRe(NO)(CO)(NH_3)]Br_3$. Concentrated formic acid and trifluoromethanesulfonic acid react with **1** to produce $[LRe(NO)(CO)(HCO_2)]^+$ and $[LRe(NO)(CO)(CF_3SO_3)]^+$. In the presence of iodide anions **1** undergoes addition reactions in methanol or ethanol to form complexes containing coordinated methyl- or ethylcarbamato ligands, $[LRe(NO)(CO)\{NHCO(OR)\}]I$. The latter complexes react in methanol with $NO[BF_4]$ to yield coordinated *N*-nitrosocarbamato ligands, $[LRe(NO)(CO)\{NH(NO)CO(OCH_3)\}](BF_4)_2$. $[LRe(NO)(CO)_2](BF_4)_2$ reacts with $(CH_3)_3NO$ in stoichiometric amounts (1:1) in acetonitrile to produce $[LRe(NO)(CO)(CH_3CN)]^{2+}$ and CO_2 whereas in acetone (a weaker donor solvent) $[LRe(NO)(CO)(N(CH_3)_3)]^{2+}$ is formed. Spectroscopic properties (^1H and ^{13}C NMR, UV-vis, IR) are reported for all compounds.

Introduction

Recently we have reported the synthesis, crystal structures, and reactivity of a series of rhenium(I) tricarbonyl complexes containing tridentate macrocyclic ligands such as 1,4,7-triazacyclononane, 1,4,7-trimethyl-1,4,7-triazacyclononane and 1,4,7-trithiacyclononane.[2-4] These compounds are readily available in excellent yields. The thermodynamic and kinetic stability of the coordinated macrocycles render them good starting materials for rhenium complexes in low and high oxidation states. Thus the reaction of $[LRe(CO)_3]^+$ with $NO[BF_4]$ yields air- and water-stable $[LRe(NO)(CO)_2]^{2+}$, which reacts with $NaBH_4$ yielding $[LRe(NO)(CO)(CH_3)]^{+3}$, whereas with H_2O_2 the latter compound gives $[LReO_3]^+$ (L = 1,4,7-triazacyclononane throughout this paper).[2]

Here we wish to report the kinetics and mechanism of the reactions between $[LRe(NO)(CO)_2]^{2+}$ and hydrazine, methylhydrazine, and *N*,*N*-dimethylhydrazine, hydroxylamine, and azide, all of which yeild the N-coordinated isocyanato complex $[LRe(NO)(CO)(NCO)]^+$ (**1**) (Scheme I). N-Coordinated isocyanato complexes of rhenium have been characterized previously.[12,13] In organometallic chemistry the reaction between these nucleophiles and $M(CO)_6$ (M = Cr, Mo, W) (and other carbonyl complexes) producing $M(CO)_5(NCO)^-$ complexes is well-known.[5-10] For the reaction with azide, kinetic data have been reported.[8,11]

Nucleophilic attack at the C atom of the carbonyl ligand in **1** by nucleophiles such as N_2H_4, NH_2OH, and N_3^- is believed to produce the intermediates A, B, and C (Scheme I). In some instances coordinated carbazoyl intermediates have been isolated or were characterized by infrared spectroscopy in solution.[7,8,14-16]

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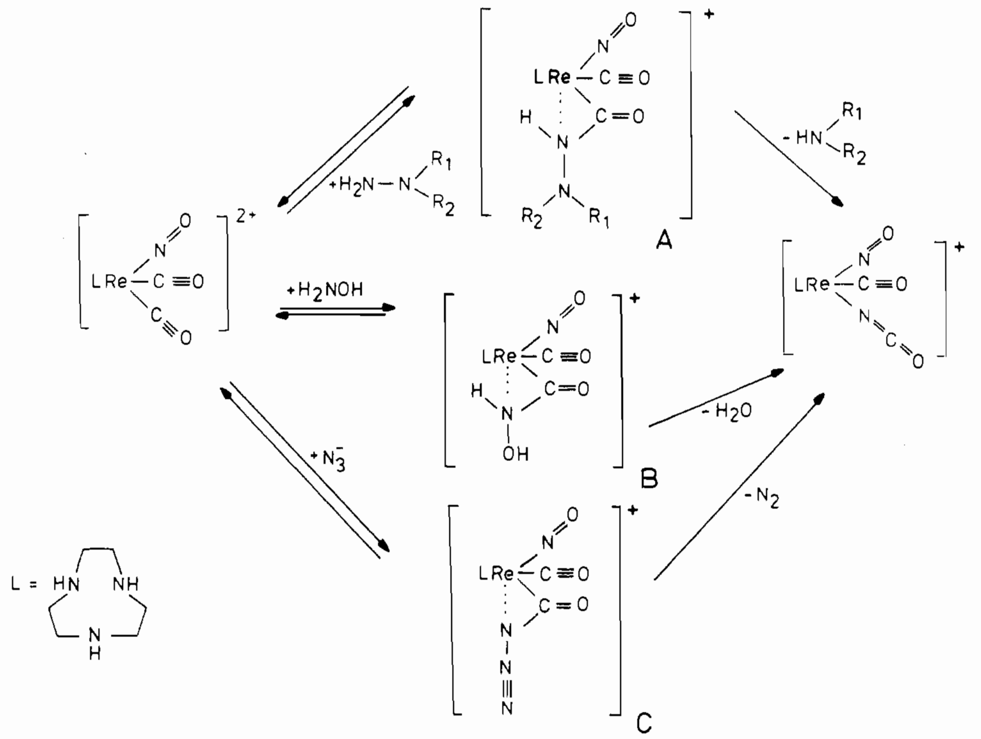
Scheme I



In the rate-determining step an N–N or N–O bond is cleaved with concomitant intramolecular rearrangement to form an N-coordinated isocyanato ligand. NH_3, $NH_2(CH_3)$, $HN(CH_3)_2$, H_2O, or N_2 are the respective leaving groups.

1 undergoes a series of reactions at the coordinated NCO^- ligand. With aqueous acids, $[LRe(NO)(CO)(NH_3)]^{2+}$ is formed. The kinetics and the mechanism of this reaction are reported here. Addition of alcohols to **1** produces N-coordinated carbamic acid esters, which further react with NO generating *N*-nitrosocarbamic acid ester ligands. Preparation and spectroscopic characterization of these complexes are described in detail here.

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.[2,17]

$[LRe(NO)(CO)(NCO)](BF_4)$ (1). Method A. To a suspension of $[LRe(NO)(CO)_2](BF_4)_2$ (0.58 g; 1 mmol) in degassed methanol (100 mL) was added 1 M methanolic hydroxylamine (10 mL), which was prepared from $NH_2OH{\cdot}HCl$ (6.95 g, 0.1 mol) dissolved in methanol (100 mL) by addition of KOH (5.6 g, 0.1 mol) and filtration. An immediate color change to red was observed. After the above solution was stirred for 24 h at room temperature and the reaction volume was reduced to 50 mL by evaporation under reduced pressure, the microcrystalline red precipitate was filtered off, washed with ether, and air-dried. Yield: 78%.

Method B. To the above suspension was added NaN_3 (0.07 g, 1 mmol). The solution was refluxed for 1 h. The workup of the resulting red solution was as described above. Yield: 87%.

Method C. To the above suspension was added hydrazine (0.04 mL; 1 mmol). The reaction mixture was heated at 60 °C for 3 h and stirred at room temperature for 20 h. The workup was as described above. Yield: 92%.

Method D. To the above suspension was added methylhydrazine (1 mmol) or, alternatively, *N,N*-dimethylhydrazine (1 mmol). The reaction mixture was heated at 60 °C for 6 h. The workup was as described above. Yield: 90%.

^{13}C NMR (D_2O, $CDCl_3$; δ): 47.05–51.98 (6 s, $-CH_2CH_2-$), 131.70 (s, –NCO), 205.97 (s, –CO). ^1H NMR (CD_3OD; V): 3.00–3.80 (m, 12 H, $-CH_2CH_2-$), 6.41, 6.92, 7.65 (3 s, 3 H, –NH). UV–vis (H_2O; λ_{max}, nm (ϵ = L mol^{-1} cm^{-1})): 378 (98); 495 (106). IR (KBr; cm^{-1}): ν(NO) 1700 (s), ν(CO) 1950 (s), ν(CN) 2220 (s), ν(CO) 1340 (m), δ(NCO) 590 (w).

Anal. Calcd for $[(C_6H_{15}N_3)Re(NO)(CO)(NCS)](BF_4)$: C, 19.14; H, 3.01; N, 13.95; F, 15.14; Re, 37.08. Found: C, 19.1; H, 3.1; N, 14.0; F, 15.4; Re, 37.0.

$[LRe(NO)(NCO)_2]$ (2). To a suspension of $[LRe(NO)(CO)_2](BF_4)_2$ (0.58 g, 1 mmol) in degassed methanol (100 mL) was added 98% hydrazine (3.2 mL, 0.1 mol). The reaction mixture was refluxed for 3 h and stirred at room temperature for a further 24 h until a clear red solution was obtained. After reduction of the reaction volume under reduced pressure to ca. 10 mL, deep red microcrystals precipitated, which were filtered off and washed with ether. Yield: 60%.

IR (KBr; cm^{-1}): ν(NO) 1620 (s), ν(CO) 1320 (m), ν(CN) 2220 (s), 2200 (s), δ(NCO) 600 (m). UV–vis (reflectance spectrum): 550 nm.

Anal. Calcd for $(C_6H_{15}N_3)Re(NO)(NCO)_2$: C, 22.38; H, 3.52; N, 19.57; Re, 43.36. Found: C, 22.2; H, 3.8; N, 19.9; Re, 42.9.

$[LRe(NO)(CO)(NH_3)]X_2$ (X = Cl, Br) (3). To a red solution of **1** (0.51 g, 1 mmol) in methanol (20 mL) was added at 20 °C dropwise 37% hydrochloric acid or 48% hydrobromic acid until a color change to yellow was achieved. When HBr was used, a yellow precipitate formed immediately. With HCl as reactant the yellow solution was allowed to stand at room temperature for a few hours during which time yellow crystals precipitated, which were filtered off, washed with ether and air-dried. Yield: 80–90%.

^1H NMR (DMSO-d_6; δ): 2.95–3.40 (m, 12 H, $-CH_2CH_2-$), 5.05 (s, 3 H, $-NH_3$), 6.85, 7.40, 8.35 (3 s, 3 H, –NH). IR (KBr; cm^{-1}): ν(NO) 1720 (s), ν(CO) 1970 (s), $\nu(NH_3)$ 3020 (m), $\delta(NH_3)$ 1625 (m), $\delta_s(NH_3)$ 1310 (m). UV–vis (H_2O; λ_{max}, mm (ϵ, L mol^{-1} cm^{-1})): 375 (158), 460 (100).

Anal. Calcd for $(C_6H_{15}N_3)Re(NO)(CO)(NH_3)Br_2$: C, 15.28; H, 3.30; N, 12.73; Br, 29.05; Re, 33.84. Found: C, 15.25; H, 3.3; N, 12.7; Br, 29.3; Re, 33.8.

$[LRe(NO)(CO)(NH_3)]Br_3$ (4). **1** (0.51 g, 1 mmol) was dissolved in an acetone/water mixture (2:1) (30 mL), and bromine (0.48 g, 3 mmol) was added. A clear green solution was immediately obtained from which green microcrystals precipitated within 30 min, which were filtered off, washed with ether, and dried under an argon atmosphere. Yield: 93%.

IR (KBr; cm^{-1}): ν(NO) 1740 (s), ν(CO) 1990 (s), $\nu(NH_3)$ 3320 (m), $\delta(NH_3)$ 1310 (m). Effective magnetic moment: $\mu_{eff}(293\ K) = 1.71\ \mu_B$. UV–vis ($H_2O$; λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})): 396 (1340), 620 (58), 690 sh.

Anal. Calcd for $(C_6H_{15}N_3)Re(NO)(CO)(NH_3)Br_3$: C, 13.34; H, 2.88; N, 11.12; Br, 38.04; Re, 29.55. Found: C, 13.3; H, 3.1; N, 11.3; Br, 37.9; Re, 29.1.

$[LRe(NO)(CO)(CF_3SO_3)](CF_3SO_3)$ (5). A solution of **1** (0.51 g, 1 mmol) in freshly distilled trifluormethanesulfonic acid (5 mL) was stirred in a sealed vessel for 24 h at room temperature. Addition of dry diethyl

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ether (30 mL) initiated the precipitation of a yellow material, which was filtered off and air-dried. Yield: 87%.

IR (KBr; cm^{-1}): ν(NO) 1760 (s), ν(CO) 1990 (s). UV–vis (CH_3CN; λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})): 370 (160), 475 (68).

$[LRe(NO)(CO)(HCO_2)]BF_4$ (6). To a solution of **1** (0.51 g, 1 mmol) in dry methanol (50 mL) was added concentrated formic acid (10 mL). The resulting solution was heated at 60 °C for 2 h and stirred for a further 24 h at room temperature, after which time the solvent was removed under reduced pressure. The resulting yellow oil was dissolved in acetone (30 mL), and a saturated solution of $NaBF_4$ in dry acetone (5 mL) was added. Upon addition of diethyl ether (50 mL) a yellow precipitate formed, which was filtered off, washed with ether and air-dried. Yield: 67%.

IR (KBr; cm^{-1}): ν(NO) 1680 (s), ν(C=O) 1950 (s), ν(C=O) 1650 (m), ν(CO) 1440 (m). UV–vis (CH_3CN; λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})): 340 (120), 452 (78). ^1H NMR (D_2O; δ): 2.80–3.50 (m, 12 H, $-CH_2CH_2-$), 6.60, 6.70, 7.80 (3 s, 3 H, –NH), 8.20 (s, 1 H, HCO_2^-). ^{13}C NMR (D_2O, $CDCl_3$; δ): 45.95–52.80 (m, $-CH_2CH_2-$), 165.84 (s, HCO_2^-), 207.67 (s, –CO).

Anal. Calcd for $[(C_6H_{15}N_3)Re(NO)(CO)(HCO_2)](BF_4)$: C, 19.02; H, 3.20; N, 11.09; Re, 36.86. Found: C, 19.2; H, 3.4; N, 11.2; Re, 36.5.

$[LRe(NO)(CO)\{NH(CO)(OCH_3)\}]I$ (7). To a solution of **1** (0.51 g, 1 mmol) in methanol (50 mL) was added sodium iodide (0.3 g, 2 mmol). The solution was heated at 50 °C for 2 h and stirred at room temperature for a further 24 h. When the solution was allowed to stand in an open vessel, a yellow precipitate formed, which was filtered off, washed with ether, and air-dried. Yield: 51%.

IR (KBr; cm^{-1}): ν(NO) 1680 (s), ν(CO) 1950 (s), ν(C=O) 1640 (m). ^1H NMR (DMSO-d_6; δ): 2.85–3.40 (m, 12 H, $-CH_2CH_2-$), 5.65, 6.49, 7.30, 7.95 (4 s, 4 H, –NH), 3.50 (s, 3 H, $-OCH_3$).

Anal. Calcd for $C_9H_{19}IN_5O_4Re$: C, 19.23; H, 3.41; N, 12.46; I, 22.57; Re, 33.11. Found: C, 19.1; H, 3.4; N, 12.5; I, 22.0; Re, 32.9.

$[LRe(NO)(CO)\{NH(CO)(OC_2H_5\}]I\cdot 3C_2H_5OH$ (8). The same procedure as described for **7** was employed by using ethanol as solvent instead of methanol, giving a yellow microcrystalline solid. Yield: 45%.

IR (KBr; cm^{-1}): ν(NO) 1680 (s), ν(CO) 1950 (s), ν(C=O) 1630 (m), ν(C—O) 1050 (m). ^1H NMR (CD_3CN; δ): 2.80–3.45 (m, 21 H, $-CH_2CH_2-$ and $HOCH_2CH_3$); 1.00–1.10 (2 t, 12 H, $-OCH_2CH_3$, $HOCH_2CH_3$), 3.50 (q, 2 H, $-OCH_2CH_3$; J = 6 Hz).

Anal. Calcd for $C_{16}H_{39}N_5O_7IRe$: C, 26.45; H, 5.41; N, 9.64; I, 17.47; Re, 25.63. Found: C, 26.1; H, 5.45; N, 9.6; I, 17.2; Re, 25.3.

$[LRe(NO)(CO)\{NH(NO)CO(OCH_3)\}](BF_4)_2$ (9). Method A. 1 (0.51 g; 1 mmol) was dissolved in degassed ethanol (50 mL). To this solution was added $NO[BF_4]$ (0.12 g, 1 mmol) under an argon atmosphere. After 2 days of stirring at room temperature, the volume of the solution was reduced by evaporation under reduced pressure to 25 mL. A yellow microcrystalline product precipitated, which was filtered off under argon, washed with ether, and dried. Yield: 48%.

Method B. The same product was obtained when a solution of **7** (0.57 g, 1 mmol) in degassed methanol (50 mL) was treated with $NO[BF_4]$ (0.24 g, 2 mmol). The workup was as described above. Yield: 51%.

IR (KBr; cm^{-1}): ν(NO) 1740 (s), ν(CO) 1970 (s), ν(C=O) 1650 (m), ν(NN=O) 1580 (m). ^1H NMR (CD_3CN; δ): 2.09–3.40 (m, 12 H, $-CH_2CH_2-$); 3.50 (s, 3 H, $-OCH_3$); 4.00, 5.31, 5.92, 6.65 (4 s, 4 H, –NH).

Anal. Calcd for $C_9H_{19}N_6O_5Re(BF_4)_2$: C, 16.61; H, 2.95; N, 12.91; F, 23.35; Re, 28.60. Found: C, 16.2; H, 3.0; N, 12.8; F, 23.1; Re, 28.2.

$[LRe(NO)(CO)(CH_3CN)](BF_4)_2$ (10). To a solution of $[LRe(NO)(CO)_2](BF_4)_2$ (0.58 g, 1 mmol) in dry acetonitrile (30 mL) was added under an argon atmosphere in small amounts of trimethylnitrogen oxide (0.08 g, 1 mmol) at room temperature. After the mixture was stirred for 24 h, the volume of the reaction solution was reduced by evaporation under reduced pressure to 15 mL. Addition of diethyl ether (50 mL) initiated the precipitation of a yellow-brown material, which was filtered off, washed with ether, and dried. Yield: 60%.

IR (KBr; cm^{-1}): ν(NO) 1740 (s); ν(CO) 1970 (s). ^1H NMR (CD_3CN; δ): 2.70 (s, 3 H, $-CH_3$), 2.90–3.51 (m, 12 H, $-CH_2CH_2-$), 5.10, 5.50, 6.80 (3 s, 3 H, –NH). ^{13}C NMR (CD_3CN; δ): 4.27 (s, CH_3), 136.91 (s, –CN), 46.08–53.34 (m, $-CH_2CH_2-$), 215.32 (s, CO).

Anal. Calcd for $[C_9H_{18}N_5O_2Re](BF_4)_2$: C, 18.38; H, 3.09; N, 11.91; F, 25.85; Re, 31.67. Found: C, 18.6; H, 3.1; N, 11.9; F, 25.65; Re, 31.3.

$[LRe(NO)(CO)(N(CH_3)_3)](BF_4)_2$ (11). This complex has been prepared by using the same procedure as was described for the preparation of **10** by using the solvent dry acetone instead of acetonitrile. Yield: 85%.

IR (KBr; cm^{-1}): ν(NO) 1740 (s), ν(CO) 1970 (s). ^1H NMR (CD_3CN; δ): 3.10 (s, 9 H, $-N(CH_3)_3$), 3.31–4.01 (m, 12 H, $-CH_2-CH_2-$), 5.50, 6.18, 7.00 (3 s, 3 H, –NH). ^{13}C NMR (CD_3CN; δ): 46.0 (s, $-N(CH_3)_3$), 48–56 (m, $-CH_2-CH_2-$), 210.0 (s, –CO).

Anal. Calcd for $[C_{10}H_{24}N_5O_2Re](BF_4)_2$: C, 19.82; H, 3.99; N, 11.56; F, 25.08; Re, 30.72. Found: C, 19.7; H, 4.0; N, 11.4; F, 24.8; Re, 30.4.

Table I. Crystallographic Data of $[LRe(NO)(CO)(NH_3)]Br_2$

formula	$[(C_6H_{15}N_3)Re(NO)(CO)(NH_3)]Br_2$
fw	640.35
cryst syst	monoclinic
space group	$P2_1/c$ (C_{2h}^5)
a, Å	10.138 (4)
b, Å	11.507 (5)
c, Å	12.839 (4)
β, deg	91.86 (3)
V, Å^3	1497.0 (8)
Z	4
ρ_{calcd}, g cm^{-3}	2.84
cryst dimens, mm	0.20 × 0.34 × 0.45
temp, °C	20
instrument	Syntex R3
radiation (mono)	Mo Kα (graphite)
scan mode	θ– 2θ
scan range, deg	$3 < 2\theta < 70$
no. of reflcns collcd	4176
no. of reflcns used in soln	3910 ($I \geq 2.5\sigma(I)$)
no. of params	157
abs coeff, cm^{-1}	138.7
transmission coeff	0.48–1.0
R^a	0.041
$R_w{}^b$	0.038
goodness of fit^c	2.6

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2(I)$. ^{c} GOF $= [\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$ where NO is the number of observations and NV is the number of variables.

Table II. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) of $[LRe(NO)(CO)(NH_3)]Br_2$

atom	x	y	z	U_{eq}
Re	1935.5 (3)	5564.0 (3)	7078.8 (2)	27.5 (1)
Br1	5191.4 (9)	8208.1 (8)	417.0 (6)	40.4 (3)
Br2	−162.3 (9)	2214.9 (7)	651.1 (6)	38.2 (2)
N1	2086 (6)	5616 (6)	8755 (4)	33 (2)
N2	4027 (6)	5234 (6)	7334 (5)	35 (2)
N3	1949 (6)	3746 (6)	7462 (5)	30 (2)
C1	3467 (9)	5597 (9)	9166 (6)	50 (3)
C2	4431 (9)	5892 (8)	8291 (7)	49 (3)
C3	4357 (8)	3972 (7)	7407 (7)	39 (3)
C4	3208 (8)	3233 (7)	7096 (6)	35 (2)
C5	1741 (8)	3513 (7)	8592 (6)	36 (2)
C6	1316 (9)	4594 (7)	9138 (6)	40 (3)
C7	92 (7)	5690 (6)	6994 (6)	31 (2)
N4	2082 (8)	7119 (7)	6862 (6)	51 (3)
N5	2137 (8)	5130 (7)	5436 (5)	42 (2)
O4	2196 (8)	8136 (5)	6755 (6)	69 (3)
O7	−1016 (6)	5728 (6)	6994 (6)	61 (3)

Crystal Structure Determination. Intensities and lattice parameters of a yellow crystal of $[LRe(NO)(CO)(NH_3)]Br_2$ were measured on a Nicolet R3 diffractometer. Crystal parameters and additional details of the data collection and reduction are given in Table I. Lattice parameters were obtained from a least-squares fit to the setting angles of 24 reflections with $6 < 2\theta < 30°$. An empirical absorption correction (ψ-scans of eight reflections with $7 < 2\theta < 50°$) was carried out. The structure was solved by standard Patterson and difference Fourier methods and refined[18] with anisotropic displacement parameters for all non-hydrogen atoms. Neutral-atom scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from ref 19 and hydrogen atom scattering factors from ref 20. Methylene and N–H hydrogen atoms were placed at calculated positions with d(C–H) and d(N–H) at 0.96 Å and isotropic thermal parameters. The function minimized during refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(I)$. Final atom coordinates are given in Table II.

Instrumentation. The apparatus used for electrochemical measurements has been described previously.[21] Cyclic voltammograms of dried

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(18) All computations were carried out on an ECLIPSE computer using the SHELXTL program package.

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samples of complexes ($\sim 10^{-3}$ M) were measured in water-free acetonitrile with 0.1 M $[n\text{-}Bu_4N]PF_6$ as supporting electrolyte at scan rates of 20–200 mV s^{-1}. The ferrocenium/ferrocene couple was monitored as internal standard. Electronic spectra were recorded on a Perkin-Elmer Lambda 9 UV/vis/near-IR spectrophotometer. The magnetic susceptibility of powdered samples of the rhenium(II) complex was measured by the Faraday method (Sartorius microbalance, Bruker 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.

The ^1H NMR spectra were recorded in the FT mode with a Bruker AM-400 spectrophotometer 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 internal standard. The following abbrevations were used: s = singlet, m = multiplet, q = quintet, t = triplet. ^{13}C NMR were recorded at a magnetic field of 100.6 MHz.

Kinetic Measurements. The kinetics of the reactions of **1** with the nucleophiles $N_2H_4{\cdot}H_2O$, $H_2NNH(CH_3)$, $H_2NN(CH_3)_2$, and NaN_3 and of the reaction of **1** with protons at 10 and 25 °C were measured by using conventional spectrophotometry (UNICAM SP-800 interfaced to a Commodore V64 computer for data acquisition and analysis). Kinetic experiments of the latter reaction at 40 and 56 °C were performed by using stopped-flow spectrophotometry. Pseudo-first-order conditions were employed with the nucleophiles (or protons) in at least 10-fold excess over complex **1**. Pseudo-first-order rate constants were calculated by use of a least-squares fitting program[22] where the absorbances 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 and Discussion

Synthesis. $[LRe(NO)(CO)_2](BF_4)_2$ was found to react with hydrazine, methylhydrazine, and *N,N*-dimethylhydrazine, hydroxylamine, and azide in anhydrous methanol to form in excellent yields the red isocyanato complex $[LRe(NO)(CO)(NCO)](BF_4)$ (**1**) and NH_3, $H_2N(CH_3)$, $HN(CH_3)_2$, H_2O, and N_2, respectively (Scheme I). The carbazoyl intermediate A has been identified following the reaction with hydrazine hydrate in the infrared. A band at 1650 cm^{-1}, which is assigned to the $\nu(C{=}O)$ stretching mode of the $ReNH(C{=}O)NH_2$ intermediate, appears and disappears again. The reaction product, gaseous NH_3, has been identified by its reaction with $[HgI_4]^{2-}$ to form the brown precipitate $[Hg_2N]I{\cdot}H_2O$.

The reaction of $[LRe(NO)(CO)_2]^{2+}$ with azide in methanol affords **1** and dinitrogen. This reaction is analogous to the Curtius degradation of organic acid azides which involves the rhenium acyl azide intermediate C. C has not been identified since loss of dinitrogen and rearrangement to **1** is fast.

The reaction of $[LRe(NO)(CO)_2]^{2+}$ with hydroxylamine most probably involves intermediate B, which corresponds to a rhenium C-coordinated hydroxamate (ReC(O)NHOH). B rearranges to **1** after a molecule of water is cleaved off. This reaction is analogous to the well-known Lossen degradation of hydroxamic acids in organic chemistry. A remarkable difference is the fact that in the case of B H_2O is a very good leaving group; the organometallic reaction affording **1** proceeds readily under comparatively mild conditions.

Diamagnetic **1** is air-stable in the solid state and in solution. It is soluble without detectable decomposition in water and polar organic solvents (CH_3CN, CH_3OH, etc.). In the infrared, typical stretching frequencies of the nitrosyl, carbonyl, and isocyanato ligand are observed at 1700 (s), 1950 (s), and 2220 (s) cm^{-1}, respectively. Two additional bands at 1340 (m) and 590 (w) cm^{-1} are due to $\nu(CO)$ and $\nu(NCO)$ of N-coordinated $(NCO)^-$.[23] The ^1H NMR spectrum (CD_3OD) of **1** exhibits a multiplet (6 H) at δ 3.00–3.80 of the methylene protons of the cyclic triamine and, interestingly, three singlets at δ 6.41, 6.92, and 7.65 of –NH protons. In the ^{13}C NMR spectrum six signals for methylene C atoms are observed, δ 47.05–51.98 and a signal of the C atom of the NCO^- ligand at δ 131.70 and of the C atom of the carbonyl ligand at δ 205.97. The cations in **1** do not have a center of symmetry or a mirror plane. Therefore, racemic **1** should in principle be resolvable into two optically active enantiomers. This has not been attempted here. Furthermore, the three five-membered chelate rings $\overline{\text{Re–N–C–C–N}}$ formed by the coordinated cyclic triamine have either the $\lambda\lambda\lambda$ or $\delta\delta\delta$ conformation. This leads to a total number of four possible isomers, since both the Λ and Δ configured $[LRe(NO)(CO)(NCO)]^+$ cations may have either $\lambda\lambda\lambda$ or $\delta\delta\delta$ ring conformations.

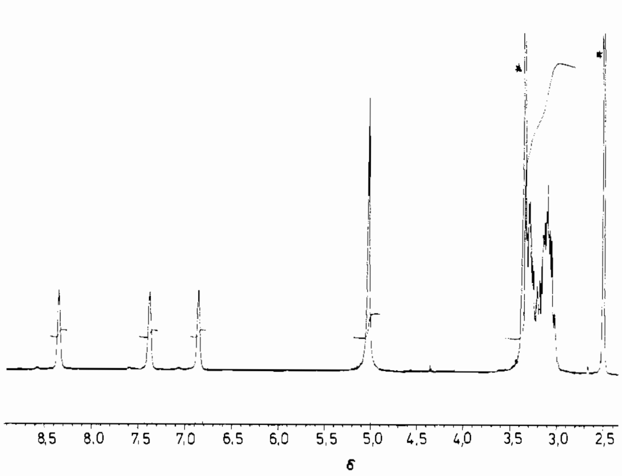

Figure 1. ^1H NMR (400.1-MHz) spectrum of $[LRe(NO)(CO)(NH_3)](BF_4)_2$ (DMSO-d_6). Signals marked with an asterisk are due to the solvent and water.

When $[LRe(NO)(CO)_2]^{2+}$ dissolved in methanol was refluxed under an argon atmosphere with a large excess of hydrazine hydrate ($\sim$100-fold), the remaining carbonyl group in **1** was also converted into a coordinated isocyanato ligand and the red neutral complex $[LRe(NO)(NCO)_2]$ (**2**) was isolated. **2** is quite unstable even under argon in the solid state and in solution; it is diamagnetic. In the infrared the $\nu(NO)$ stretching frequency is observed at 1620 cm^{-1}, which is lower by 80 cm^{-1} than that in **1**. This is due to the fact that NCO^- ligands are predominantly σ-donors compared with the carbonyl ligand in **1**, and therefore, more electron density is shifted to the Re–NO moiety in **2** than in **1**.

In the following section we will describe the chemistry of **1**, which proved to be a useful starting material for a series of complexes containing the $[LRe(NO)(CO)]^{2+}$ 16e-fragment. A well-known reaction of N-coordinated isocyanato ligands is their degradation with aqueous acids to amine ligands and CO_2.[23-28] Thus **1** reacts in methanol with concentrated aqueous hydrochloric or hydrobromic acid to yield essentially quantitatively red $[LRe(NO)(CO)(NH_3)]X_2$ (**3**) (X = Cl, Br).

$$[LRe(NO)(CO)(NCO)] \xrightarrow{+HX,\ H_2O} [LRe(NO)(CO)(NH_3)]^{2+} + CO_2 \quad (1)$$

$$X = Cl, Br$$

3 is water soluble and stable toward air. Suitable crystals for X-ray crystallography (see below) were grown from aqueous solution by addition of NaBr. In the infrared spectrum $\nu(NO)$ and $\nu(CO)$ stretching frequencies are observed at 1720 (s) and 1970 (s) cm^{-1}, respectively. $\nu(NH_3)$ and $\delta(NH_3)$ modes are observed at 3200 and 1625 cm^{-1}. The ^1H NMR spectrum of **3** (DMSO-d_6) exhibits a multiplet at δ 2.95–3.40 due to 12 methylene protons, a singlet at 5.05, which corresponds to three NH_3 protons, and three singlets of secondary amine protons of the cyclic triamine at δ 6.85, 7.40, and 8.35 (Figure 1). The latter four signals disappear if the solvent D_2O is used due to N–D exchange.

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The cyclic voltammogram of $[LRe(NO)(CO)(NH_3)]Cl_2$ dissolved in dry CH_3CN, which contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte, at a glassy-carbon working electrode exhibits a reversible one-electron wave at −0.64 V vs Fc^+/Fc in the potential range +0.8 to −0.8 V vs Ag/AgCl at 20 °C.

$$[LRe(NO)(CO)(NH_3)]^{2+} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [LRe(NO)(CO)(NH_3)]^{3+} \qquad (2)$$

Attempts to synthesize the oxidized form of **3** chemically were successful. Addition of bromine to a solution of **3** in an acetone/water (2:1) mixture initiated the precipitation of green $[LRe(NO)(CO)(NH_3)]Br_3$ (**4**). The cyclovoltammogram of **4** is identical with that observed for **3**. Reduction of green **4** dissolved in methanol with zinc amalgam afforded red **3**. In the infrared spectrum of **4** the ν(NO) and ν(CO) stretching frequencies are observed at 1740 and 1990 cm^{-1}, respectively. They are both shifted to higher wavenumbers by 20 cm^{-1} due to the increased oxidation level of the rhenium center (Re(I) → Re(II)). The effective magnetic moment of **4** of 1.71 μ_B at 293 K is in agreement with those of other octahedral complexes of Re(II)[29] of the type $\{Re–NO\}^5$ according to Enemark and Feltham's nomenclature for transition-metal nitrosyl complexes.[30]

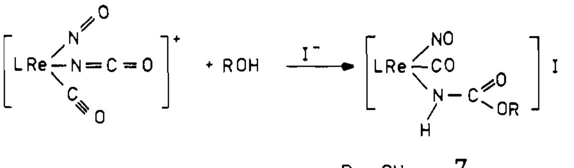
1 dissolved in anhydrous methanol reacts with anhydrous formic acid or gaseous HCl or HBr to form complexes of the type $[LRe(NO)(CO)X]^+$ where X represents a formato, chloro, or bromo ligand. [LRe(NO)(CO)Cl]Cl has been described previously.[3] $[LRe(NO)(CO)(HCO_2)]BF_4$ (**6**) exhibits ν(C=O) and ν(C—O) bands at 1650 and 1440 cm^{-1}, which are typical for a monodentate carboxylato ligand.

$$[LRe(NO)(CO)(NCO)]^+ + HX \rightarrow [LRe(NO)(CO)X]^+ + HNCO \qquad (3)$$

$$X = Cl^-,\ Br^-,\ HCO_2^-,\ CF_3SO_3^-$$

When **1** was dissolved in anhydrous, freshly distilled trifluormethanesulfonic acid, a yellow solution was obtained from which upon addition of diethyl ether a yellow solid, $[LRe(NO)(CO)(CF_3SO_3)](CF_3SO_3)$ (**5**), precipitated (eq 3).

The reactions of **1** described in the last section are formally substitution reactions of the NCO ligand. **1** also undergoes some interesting addition reactions at the coordinated Re–NCO structural unit. Thus, in the presence of iodide anions, **1** reacts with the solvent anhydrous methanol or ethanol generating N-coordinated carbamic acid esters (eq 4). These reactions do not occur in the absence of iodide anions; their function is unclear.



(4)

$R = -CH_3$; **7**

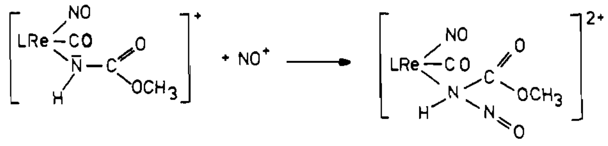
$-C_2H_5$; **8**

The iodide salts **7** and **8** have been isolated as yellow air-stable solids; they are soluble without decomposition in methanol or ethanol. Analogous reactions have been described for the clusters $Os_3H(CO)_{10}(NCO)$ and $Os_2Au(PEt_3)(CO)_{10}(NCO)$ where the NCO^- ligand is bridging between two Os atoms.[31,32] In the infrared spectrum of **7** the presence of the coordinated nitrosyl and carbonyl ligand is clearly established by two strong bands at 1680 and 1950 cm^{-1}; the carbamato ligand exhibits a ν(C=O) band at 1640 and a ν(C—O) at 1090 cm^{-1}. The ^1H NMR spectrum of **7** (DMSO-d_6) exhibits four singlets for the N–H protons, three for the cyclic amine and one for the N-coordinated carbamato ligand, at δ 5.65, 6.49, 7.30, and 7.95. The methylene protons of L and the methyl protons of the $-OCH_3$ group give rise to a complicated multiplet δ 2.85–3.40 (12 H) and a singlet (3 H) at δ 3.50, respectively. The infrared and ^1H NMR spectra of **8** also clearly establish the presence of a coordinated ethyl ester carbamato ligand.

Table III. Selected Bond Distances (Å) and Angles (deg)

Re–N1	2.154 (6)	Re–N5	2.184 (6)
Re–N2	2.169 (6)	Re–C7	1.874 (8)
Re–N3	2.149 (6)	N4–O4	1.185 (10)
Re–N4	1.818 (8)	C7–O7	1.125 (10)
N2–Re–N1	79.4 (2)	N3–Re–N2	78.2 (2)
N3–Re–N1	78.4 (2)	N5–Re–N2	89.1 (3)
N5–Re–N1	165.0 (3)	N4–Re–N2	96.4 (3)
N4–Re–N1	97.0 (3)	C7–Re–N2	172.2 (3)
C7–Re–N1	95.4 (3)	N5–Re–N3	89.9 (3)
N5–Re–N4	93.8 (3)	N4–Re–N3	173.4 (3)
N5–Re–C7	94.9 (3)	C7–Re–N3	95.0 (3)
N4–Re–C7	90.1 (3)	O4–N4–Re	177.7 (7)
O7–C7–Re	176.0 (7)		

Interestingly, **7** reacts with $NO(BF_4)$ in anhydrous methanol to yield a further addition product. NO^+ binds to the uncoordinated pair of electrons at the N atom of the carbamato ligand, generating an N-nitroso carbamic acid methyl ester ligand (eq 5). The yellow complex $[LRe(NO)(CO)\{NH(NO)CO(OCH_3)\}](BF_4)_2$ (**9**) has been isolated. The same product has been obtained via the reaction of **1** dissolved in methanol with $NO(BF_4)$. In the infrared spectrum of **9** the N-coordinated nitroso ligand exhibits a ν(NNO) stretching frequency at 1580 cm^{-1}, which is quite typical for *N*-nitroso compounds,[33] and a ν(C=O) frequency at 1650 cm^{-1}. The ^1H NMR spectrum of **9** is also in agreement with the proposed structure. In the literature, oxidative-addition reactions of square-planar complexes of the type $[(PR_3)_2M(CO)(NCO)]^+$ (M = Ir(II), Rh(II), and Pd(II)) with NO^+ have been described.[34,35] But in contrast to reaction 5 the NO^+ ligand is bound to the metal center with concomitant release of an NCO^- group and formation of $[(PR_3)_2M(CO)(NO)]^{3+}$ intermediates that undergo further reactions (disproportionation and/or formation of alkoxy carbonyl complexes). Since the compounds $[LRe(NO)(CO)Y]^+$ (Y = $-NCO$ and $-NH(CO)(OCH_3)$) possess an octahedral geometry, attack of NO^+ at the metal center is not possible and *N*-nitroso ligands are formed instead.



(5)

Finally, we have investigated the reaction between $[LRe(NO)(CO)_2]^{2+}$ and trimethylamine *N*-oxide, which is known to act as an oxygen atom transfer reagent.[36] Since its reaction with hydrazine has suggested that at least one carbonyl group is susceptible to nucleophilic attack, this is an obvious reaction to test. Stoichiometric amounts of $[LRe(NO)(CO)_2](BF_4)_2$ and $(CH_3)_3NO$ (1:1) dissolved in dry acetonitrile reacted smoothly at room temperature to afford yellow-brown $[LRe(NO)(CO)(CH_3CN)]^{2+}$, CO_2, and trimethylamine (eq 6). When a solvent

$$[LRe(NO)(CO)_2]^{2+} + (CH_3)_3NO \xrightarrow{CH_3CN} [LRe(NO)(CO)(CH_3CN)]^{2+} + N(CH_3)_3 + CO_2 \qquad (6)$$

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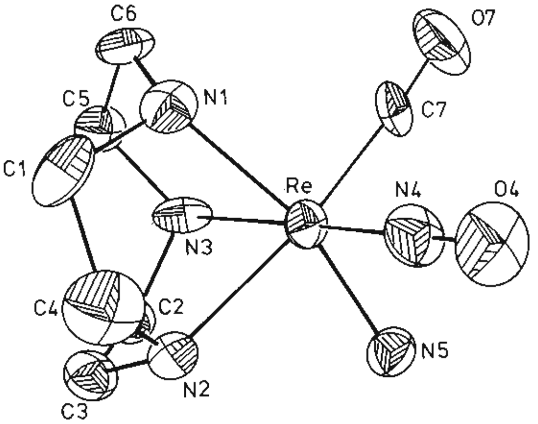

Figure 2. Perspective view of the cation in $[LRe(NO)(CO)(NH_3)]Br_2$ and the atom-labeling scheme.

with lesser σ-donor capacity such as acetone was used, $(CH_3)_3N$ was found to coordinate to the Re center and $[LRe(NO)(CO)\{(CH_3)_3N\}](BF_4)_2$ (**11**) was isolated (eq 7). **10** and to a lesser

$$[LRe(NO)(CO)_2]^{2+} + (CH_3)_3NO \rightarrow [LRe(NO)(CO)(N(CH_3)_3)]^{2+} + CO_2 \quad (7)$$

degree **11** are potentially good starting materials for the synthesis of complexes containing the 16e fragment $\{LRe(NO)(CO)\}^{2+}$, because CH_3CN is a good leaving group.

Crystal Structure of $[LRe(NO)(CO)(NH_3)]Br_2$. Crystals of the title complex consist of $[LRe(NO)(CO)(NH_3)]^{2+}$ cations and uncoordinated bromide anions. Figure 2 shows a perspective view of the dication and the atom-labeling scheme; Table III summarizes important bond distances and angles. The rhenium atom is in a pseudooctahedral environment of a face-capping 1,4,7-triazacyclononane ligand, a nitrosyl, a carbonyl, and an amine ligand. Both enantiomeric forms of the dication (Λ and Δ configuration) are present in the unit cell; the racemate crystallizes out. The Re–N bond distances of the tridentate amine are not quite equivalent; the Re–N2 bond is somewhat longer than the other two Re–N_{amine} bonds due to the trans influence of the linear Re—C≡O moiety. Re–N4 is short (1.82 (1) Å) and displays considerable double bond character (as does the Re–C7 bond), which is typical for $\{Re\text{-}NO\}^6$ complexes.[37] The N–Re–N bond angles of the triamine are much smaller than the usual octahedral angle of 90°. The maximal deviation from this angle is 11.8°. This has been observed for all coordination compounds containing the nine-membered cyclic amine ligand.[38] The structure of **3** is very similar to that of $\{LRe(NO)(CO)(CH_3)]^+$ described previously.[3]

In the crystal structure of **3** the bromide ions are hydrogen bonded to N–H amine and possibly to NH_3 protons. The closest N–H···Br contacts (<3.50 Å) are as follows: N1–Br2, 3.27 Å; N2–Br1, 3.295 Å; N3–Br2, 3.30; N5–Br2, 3.40 Å.

Kinetic Measurements. The rates of the reactions between $[LRe(NO)(CO)_2]^{2+}$ and a variety of nucleophiles ($N_2H_4\cdot H_2O$, $H_2NNH(CH_3)$, $H_2NN(CH_3)_2$, and N_3^-) in methanolic solution (Scheme I) were monitored by following changes in the electronic absorption spectra at 520 nm with time. Spectral changes for a typical reaction with hydrazine are shown in Figure 3. The observation of three well-defined isosbestic points (372, 430, and 463 nm) indicates a good stoichiometric reaction yielding **1**. The kinetics were measured at 25 °C by using pseudo-first-order conditions with the respective nucleophile in large excess over the [complex]; the ionic strength was adjusted with *n*-tetrabutylammonium hexafluorophosphate to 0.1 M. Pseudo-first-order rate constants are summarized in Table IV.

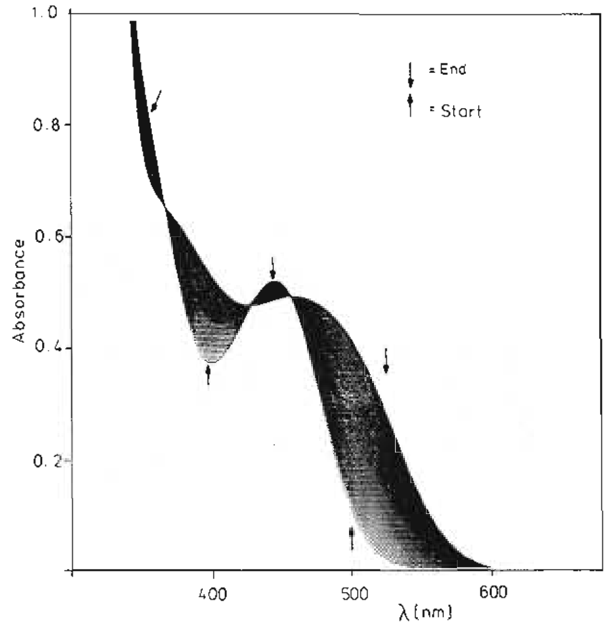

Figure 3. Scan spectrum of the reaction between $[LRe(NO)(CO)_2]^{2+}$ and $N_2H_4\cdot H_2O$ in methanol at 22 °C ([Re] = 2 × 10^{-3} M, $[N_2H_4]$ = 4 × 10^{-3} M; one scan every 2 min was recorded).

Table IV. Kinetic Data for the Reaction of $[LRe(NO)(CO)_2](BF_4)_2$ with $N_2H_4\cdot H_2O$, $H_2NNH(CH_3)$, $H_2NN(CH_3)_2$, and N_3^- at 25 °C (I = 0.1 M $[TBA]PF_6$) in Methanol[a]

	[nucl], M	10^4k_{obsd}, s^{-1}	K_1, M^{-1}	k_2, s^{-1}
(a) $N_2H_4\cdot H_2O$	0.10	1.40 (1)	2.66 (6)	6.9 (3) × 10^{-4}
	0.125	1.76 (1)		
	0.20	2.46 (2)		
	0.25	3.00 (3)		
	0.50	3.86 (3)		
	0.80	4.54 (4)		
	1.00	4.61 (4)		
(b) $H_2NNH(CH_3)$	0.10	2.23 (1)	1.70 (5)	1.6 (3) × 10^{-3}
	0.20	3.90 (1)		
	0.30	5.83 (2)		
	0.50	7.56 (2)		
	0.70	8.75 (2)		
	1.00	9.21 (3)		
(c) $H_2NN(CH_3)_2$	0.10	3.21 (3)	0.61 (6)	5.65 (31) × 10^{-3}
	0.20	5.61 (2)		
	0.25	7.64 (2)		
	0.35	10.7 (2)		
	0.40	12.6 (2)		
	0.50	14.8 (3)		
	0.80	17.8 (2)		
	1.30	21.6 (3)		
	2.00	23.4 (4)		
(d) N_3^-	0.01	1.6 (2)		1.5 (2) × 10^{-3}
	0.02	1.7 (3)		
	0.03	1.7 (3)		
	0.06	1.2 (2)		
	0.08	1.1 (2)		

[a] [complex] = 2.0 × 10^{-3} M.

When hydrazine and its two N-methylated derivatives were the nucleophiles, the experimental rate law is of the form shown in eq 8 (nucl = nucleophile). If the mechanism is assumed to be

$$-\frac{d[LRe(NO)(CO)_2{}^{2+}]}{dt} = \frac{k[\text{nucl}]}{1 + k'[\text{nucl}]}[\text{complex}] \quad (8)$$

that depicted in Scheme I, k represents the product k_2K_1 and k' is K_1. K_1 represents an equilibrium constant for the rapid formation and dissociation of the intermediate A, and k_2 is the first-order rate constant for the rate-determining cleavage of the N–N bond in A to form in a subsequent, rapid intramolecular

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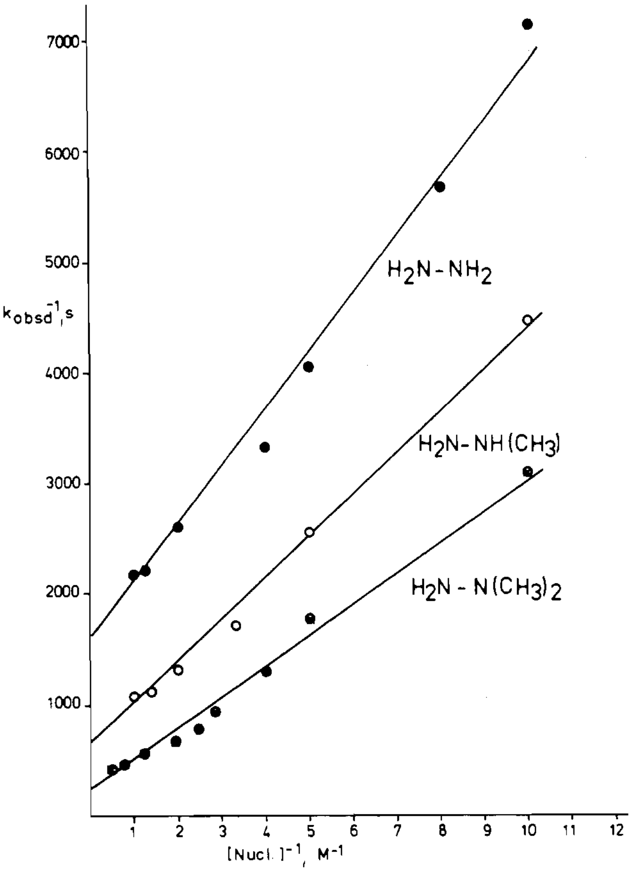


Figure 4. Plot of k_{obsd}^{-1} (s) vs $[nucl]^{-1}$ for the reaction of $[LRe(NO)(CO)_2]^{2+}$ with hydrazine and its N-methylated derivatives in methanol at 25 °C (I = 1.0 M, $[TBA]PF_6$).

rearrangement the isocyanato complex **1**.

Thus plots of k_{obsd}^{-1} vs $[nucl]^{-1}$ were reasonably linear (Figure 4), and from the intercepts and slopes, numerical values of K_1 and k_2 were calculated by using a least-squares fitting procedure (Table IV). For the reaction of $[LRe(NO)(CO)_2]^{2+}$ with N_3^- the rates were found to be independent of $[N_3^-]$ in the range 0.01–0.08 M. This reaction involves a dication and an anion, in contrast to the other reactions studied where the nucleophile is a neutral molecule. Therefore, the preequilibrium constant K_1 is substantially larger and the product $K_1[nucl]$ is greater than 1 under our experimental conditions. The rate law, eq 8, simplifies then to $k_{obsd} = k_2$. Due to experimental difficulties it has not been possible to follow the reaction as a function of time for smaller $[N_3^-]$.

Kinetic measurements of the reaction between the neutral hexacarbonyl complexes $M(CO)_6$ (Cr, Mo, W) and azide had revealed a first-order dependence on $[N_3^-]$ and [complex], respectively; the product $K_1[nucl]$ is $\ll 1$ in agreement with the fact that neutral complexes are involved in this reaction.[8]

A closer inspection of the numerical values of K_1 and k_2 for the reaction of $[LRe(NO)(CO)_2]^{2+}$ with $N_2H_4 \cdot H_2O$, and its two N-methylated derivatives reveals that the preequilibrium constant K_1 increases in the order $H_2NN(CH_3)_2 < H_2NNH(CH_3) < N_2H_4 \cdot H_2O$ whereas the values for the rate constant of the rate-determining step, k_2 (N–N bond cleavage), exhibit the reverse order. Obviously, the preequilibrium constant is influenced by a steric factor that is induced by the increasing bulkiness of the nucleophile with an increasing degree of methylation of one nitrogen atom of hydrazine. It is interesting in this respect that *N,N*-diphenylhydrazine, $H_2NN(C_6H_5)_2$, does not react at all with $[LRe(NO)(CO)_2]^{2+}$—even at elevated temperatures and prolonged reaction times. The N–N bond cleavage in intermediate A (Scheme I), on the other hand, is facilitated on going from unsubstituted hydrazine to *N,N*-dimethylhydrazine. This may be due to an electronic factor.

The rates of the acid-dependent reaction of **1** generating the ammine complex **3** have been monitored by following the decrease in absorbance of **1** at 500 nm spectrophotometrically as a function of time. Typical spectral changes during the reaction are shown in Figure 5; four clean isosbestic points at 572, 452, 423, and 395 nm were observed. Kinetic experiments were performed under pseudo-first-order conditions with $[H^+]$ (0.05–1.00 M) in large excess over [complex] (5×10^{-3} M). The ionic strength was adjusted to 1.0 M (NaCl). Plots of log $(A_t - A_\infty)$ vs time, t, where A_t is the absorption at a time t and A_∞ is that at the end of an experiment, were linear for at least 4 half-lives of the reaction. A simple second-order rate law was established (eq 9).

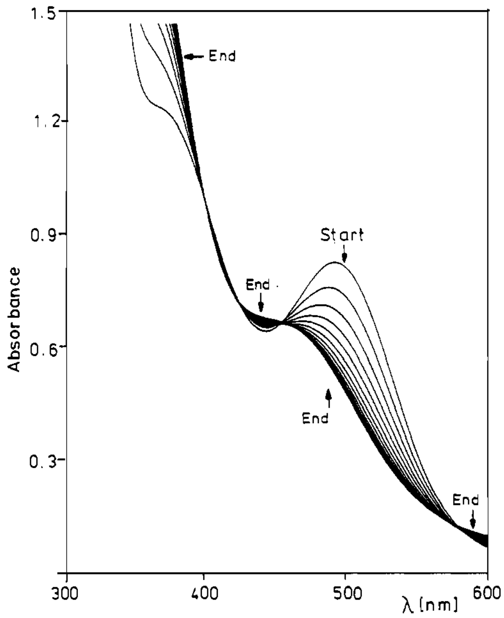


Figure 5. Scan spectrum of the hydrolysis reaction of **1** in aqueous HCl at 22 °C ([**1**] = 4.9×10^{-3}, $[H^+]$ = 0.01 M; every 3 min one scan was recorded).

Table V. Kinetic Data for the Reaction of **1** with Hydrochloric Acid

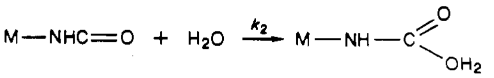
T, °C	$[H^+]$, M	$10^2 k_{obsd}$, s^{-1}	k, M^{-1} s^{-1} [a]
25	0.05	0.47 (2)	
	0.20	1.58 (3)	
	0.25	1.91 (3)	
	0.35	2.59 (4)	
	0.40	3.06 (2)	
	0.50	3.35 (3)	
	0.75	5.70 (2)	0.074 (3)
	1.00	7.45 (2)	
10	0.20	0.0055 (6)	0.0275 (2)
30	0.20	0.045 (1)	0.225 (2)
46	0.20	0.141 (1)	0.705 (2)

[a] $\Delta H^{\ddagger}$ = 12.5 ± 0.3 kcal mol^{-1}; $\Delta S^{\ddagger}$ = −25 ± 1 kcal K^{-1} mol^{-1}.

$$-d[\mathbf{1}]/dt = k[H^+][\mathbf{1}] \qquad (9)$$

Table V summarizes kinetic data and activation parameters. Acid-catalyzed hydrolysis reactions of Werner-type isocyanato complexes have been previously studied[24-27] and a general mechanism has been proposed (eq 10–12).

$$M{-}N{=}C{=}O \ + \ H^+ \ \overset{K_1}{\rightleftharpoons} \ M{-}NH{=}C{=}O \qquad (10)$$



$$M{-}NHC{=}O \ + \ H_2O \ \xrightarrow{k_2} \ M{-}NH{-}C(=O)OH_2 \qquad (11)$$

$$M{-}NH{-}C(=O)OH_2 \ \xrightarrow{fast} \ M{-}NH_3 \ + \ CO_2 \qquad (12)$$

A rapid protonation–deprotonation preequilibrium and nucleophilic attack of water at the protonated species in the rate-determining step forming a coordinated carbamato intermediate and, finally, rapid scission of a N–C bond generating the ammine ligand and CO_2 lead to a rate law as in eq 8 ([nucl] has to be

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

complex	k, $M^{-1}\ s^{-1}$	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, 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.

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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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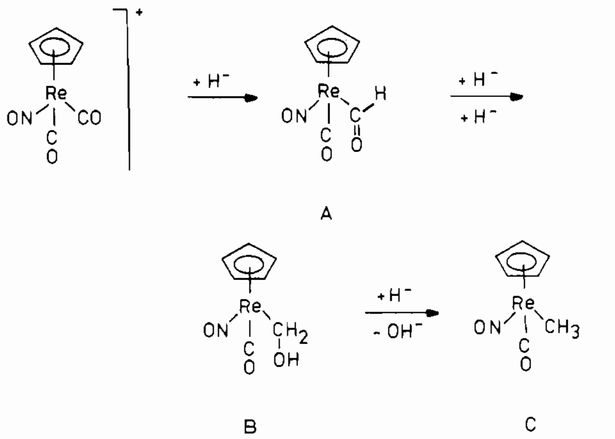
The reaction of $[LRe(NO)(CO)_2]BF_4$ in aqueous solution with $NaBH_4$ affords red, racemic $[LRe(NO)(CO)(CH_3)]BF_4$ (**1**), which has been resolved into its enantiomerically pure form as the (1*S*)-3-bromocamphorsulfonate salt (L = 1,4,7-triazacyclononane, $C_6H_{15}N_3$). **1** reacts in aqueous 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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