of a well-characterized μ-hydroxo- and μ-oxo-bridged indium(III) complex.

Safety Note. Perchlorate salts containing organic ligands are potentially explosive, especially when heated. Only small quantities should be prepared.

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

Registry No. $LInCl_3$, 101652-41-9; $L'InCl_3$, 101652-42-0; $L''InCl_3$, 101652-43-1; $LInBr_3$, 101652-44-2; $[L_2In](ClO_4)_3$, 101652-46-4; $[L_4In_4(\mu\text{-OH})_6](ClO_4)_6$, 101670-87-5; $[L_4In_4(\mu\text{-OH})_6](S_2O_6)_3{\cdot}4H_2O$, 101670-89-7; $[L_4In_4(\mu\text{-OH})_6]I_6$, 101652-47-5; $[L_4In_4(\mu\text{-OH})_6](PF_6)_6$, 101652-49-7; $[(LIn(CH_3CO_2)_2)_2O]{\cdot}2NaClO_4$, 101652-51-1; $[L_2In_2(SH)_3]Br_3$, 101670-90-0; $[L_2In_2(SH)_3](ClO_4)_3$, 101652-53-3.

Supplementary Material Available: Tables containing thermal parameters (isotropic and anisotropic) and calculated positional parameters of hydrogen atoms for both structures (6 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (66 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

Contribution from the Lehrstuhl für Anorganische Chemie I der Ruhr-Universität, D-4630 Bochum, FRG, and Anorganisch-Chemisches Institut der Universität, D-6900 Heidelberg, FRG

Syntheses of $[LRe(CO)_3]^+$ and $[LRe(NO)(CO)_2]^{2+}$ and Their Oxidative Decarbonylation Product $[LReO_3]^+$. Crystal Structure of $[LReO_3]Cl$ (L = 1,4,7-Triazacyclononane)

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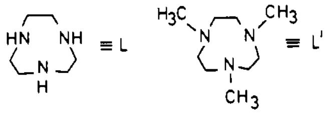
Received October 23, 1985

The reaction of $Re(CO)_5Br$ with 1,4,7-triazacyclononane ($C_6H_{15}N_3$; L) in dimethylformamide afforded air-stable, colorless $[LRe(CO)_3]Br$, which reacted with $NOBF_4$ to give yellow $[LRe(NO)(CO)_2](BF_4)_2$. Oxidative decarbonylation of $[LRe(CO)_3]Br$ with nitric acid yielded colorless $[LReO_3]ReO_4$, whereas $[LRe(NO)(CO)_2](BF_4)_2$ reacted in 35% H_2O_2 to give $[LReO_3]BF_4$. The structure of colorless $[LReO_3]Cl$ has been determined. It crystallized in the hexagonal system, space group $P6_3$, with $a = 7.792$ (1) Å, $c = 10.857$ (2) Å, and $Z = 2$. The structure was refined to a final R value of 0.0305 for 1092 unique reflections. The coordination sphere at the Re(VII) centers consists of three facially coordinated nitrogen atoms of the tridentate amine and three terminal oxo groups. The Re–O bond distance of 1.756 (5) Å is very short, indicating considerable multiple-bond character. The O–Re–O angles are obtuse (102.7 (4)°).

Introduction

We have recently shown in a series of papers[2-7] that the macrocyclic ligands 1,4,7-triazacyclononane (L) and 1,4,7-trimethyl-1,4,7-triazacyclononane (L′) coordinate strongly to a



variety of monomeric transition-metal carbonyl complexes, affording $[LM(CO)_3]^{n+}$ and $L'M(CO)_3$ species (n = 0, M = Cr,[2] Mo,[2,5-7] W;[2,3] n = 1, M = Mn[3]) in excellent yields. These complexes were used to synthesize complexes containing the LM^{n+} moiety, the metal centers in higher oxidation states, via oxidative decarbonylation reactions, e.g. eq 1 and 2.

$$LM(CO)_3 + 1.5X_2 \rightarrow LMX_3 + 3CO \qquad (1)$$

$$X = Cl, Br;\ M = Cr, Mo, W$$

$$2L'M(CO)_3 \xrightarrow{HNO_3} [L'_2M_2O_5]^{2+} \qquad (2)$$

$$M = Mo, W$$

We have now extended these investigations to rhenium chemistry using $Re(CO)_5Br$ as starting material. We here report the oxidative decarbonylation reactions of $[LRe(CO)_3]^+$ and $[LRe(NO)(CO)_2]^{2+}$ yielding the monomeric cation $[LReO_3]^+$. The analogous syntheses and chemistry of the organometallic species $(\eta^5\text{-}Me_5C_5)ReO_3$ have recently been developed by Herrmann and co-workers.[8,9]

Experimental Section

The ligand 1,4,7-triazacyclononane (L) was prepared by procedures described in the literature.[10] Infrared spectra were recorded on a Beckman Acculab 10 spectrophotometer as KBr pellets.

Preparation of Complexes. $[LRe(CO)_3]Br$. To an argon-scrubbed solution of $Re(CO)_5Br$[11] (2.4 g, 5 mmol) in dimethylformamide (DMF) (10 mL) was added 1,4,7-triazacyclononane (0.8 g, 5 mmol). This solution was stirred for 24 h at room temperature. A colorless precipitate was filtered off, washed with ether, and air-dried. Addition of diethyl ether to the mother liquor initiated the precipitation of more product (yield ~65% based on Re). This material was recrystallized from a minimum amount of acetone/H_2O or acetonitrile/H_2O mixtures (2:1), yielding colorless crystals, which are air-stable in solution and in the solid state.

Anal. Calcd for $C_9H_{15}N_3O_3BrRe$: C, 22.55; H, 3.18; N, 8.77; Br, 16.67. Found: C, 23.1; H, 3.3; N, 9.0; Br, 16.4.

$[LRe(NO)(CO)_2](BF_4)_2$. A solution of $[LRe(CO)_3]Br$ (0.48 g, 1 mmol) in acetonitrile (20 mL) and $NOBF_4$ (0.36 g, 3 mmol) was refluxed for 60 min. The solution was allowed to stand at room temperature for 12 h, after which time yellow crystals were filtered off, washed with acetone and ether, and air-dried (yield 81%). The product was recrystallized from hot acetonitrile.

Anal. Calcd for $C_8H_{15}N_4O_3Re(BF_4)_2$: C, 16.71; H, 2.63; N, 9.74. Found: C, 17.0; H, 2.7; N, 9.7.

$[LReO_3]ReO_4$. A solution of $[LRe(CO)_3]Br$ (0.48 g, 1 mmol) in 5 M nitric acid (10 mL) was refluxed for 24 h, after which time the volume of the solution was reduced (~5 mL) on a rotary evaporator. A microcrystalline, colorless solid precipitated at room temperature, which was filtered off, washed with ether, and air-dried. The material was re-

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Table I. Experimental Details of the X-ray Diffraction Study of $[LReO_3]Cl$

(A) Crystal Parameters at 22 °C

a, Å	7.792 (1)	cryst syst	hexagonal
c, Å	10.857 (2)	space group	$P6_3$ (C_6^6)
V, Å^3	570.9	d_{calcd}, g cm^{-3}	2.321
Z	2	cryst dimens, mm^3	0.1 × 0.15 × 0.2
mol wt	398.9		

(B) Measurement of Intensity Data

instrument	Syntex R3
radiation	Mo Kα (λ = 0.71069 Å), graphite monochromatized
2θ limits, deg	$3 < 2\theta < 80$
scan type	θ–2θ
octant	$\pm h,k,l$

(C) Treatment of Intensity Data

redn to prelim F_o and $\sigma(F_o)$	cor for bkgd, attenuators, and Lorentz–polarization effects of monochromatized X-radiation in usual manner
abs cor	
μ, cm^{-1}	104.0
transmissn coeff: max; min	1.00; 0.66
no. of obsd data with $I > 3.0\sigma(I)$	1092
no. of refined params	42

Table II. Atomic Coordinates of $[LReO_3]Cl$

atom	x	y	z
Re	0.6667	0.3333	0.5000
O1	0.4360 (8)	0.2556 (8)	0.5698 (5)
N1	0.5953 (8)	0.4894 (8)	0.3585 (5)
C1	0.455 (1)	0.359 (1)	0.2640 (7)
C2	0.353 (1)	0.138 (1)	0.3074 (8)
Cl	0.6667	0.3333	−0.0432 (3)

crystallized from a minimum amount of water (yield 43%).

Anal. Calcd for $C_6H_{15}N_3O_7Re_2$: C, 11.75; H, 2.47; N, 6.85. Found: C, 11.5; H, 2.3; N, 7.0.

$[LReO_3]Cl$. A solution of $[LRe(NO)(CO)_2](BF_4)_2$ (0.5 g) in 35% H_2O_2 (10 mL) was refluxed for 30 min. The solvent was removed by evaporation in vacuo, and the residue was dissolved in a minimum amount of water. Upon addition of a concentrated aqueous solution of sodium chloride (5 mL), colorless crystals of X-ray quality precipitated within a few hours (yield 55%).

Anal. Calcd for $C_6H_{15}N_3ClO_3Re$: C, 18.07; H, 3.79; N, 10.53; Cl, 8.89. Found: C, 18.2; H, 3.7; N, 10.3; Cl, 8.7.

X-ray Structural Determination of $[LReO_3]Cl$. A colorless, irregularly shaped crystal of $[LReO_3]Cl$ was attached to the end of a glass fiber and mounted on a Syntex R3 diffractometer. Preliminary examinations showed that the crystal belonged to the hexagonal system, space group $P6_3$ (C_6^6). The unit cell dimensions (22 °C) were obtained by a least-squares fit of 25 reflections. The data are summarized in Table I along with details of the treatment of intensity data. An empirical absorption correction was carried out.[12] The structure was solved via Patterson and Fourier syntheses. Positions of the hydrogen atoms were calculated on the basis of d(C–H) 0.96 Å and d(N–H) = 1.00 Å for sp^3-hybridized C and N atoms, respectively, and included in the final refinement cycle with isotropic thermal parameters. The function minimized during least-squares refinements was $\sum w(|F_o| - |F_c|)^2$ with final convergence to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.0305$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.0257$ ($w = 1/\sigma^2(F)$).[12] Scattering factors for all neutral atoms were taken from ref 13. The real and imaginary parts of anomalous dispersion for all non-hydrogen atoms were included.[13] The final atomic parameters are given in Table II and bond distances and angles in Table III. A list of anisotropic thermal parameters is available as supplementary material.

Results and Discussion

Preparation of Complexes. The cationic tricarbonylrhenium(I) complex $[LRe(CO)_3]^+$, where L represents the saturated N-donor 1,4,7-triazacyclononane, was prepared from the reaction of the ligand and $Re(CO)_5Br$ in dimethylformamide at room temperature as the colorless bromide salt. $[LRe(CO)_3]Br$ is an air-stable material both in solution and in the solid state. In the infrared spectrum (KBr disk) ν(C–O) stretching frequencies are observed at 2000 (s) and 1870 (s, b) cm^{-1}, indicating the expected C_{3v} symmetry of the complex cation ($A_1 + E$). This complex is completely analogous to $Re\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(CO)_3$, containing the tridentate N-donor hydrotris(3,5-dimethylpyrazolyl)borate anion,[14] $[Re(CO)_3(CH_3CN)_3]PF_6$,[15] and *fac*-$[Re(CO)_3(py)_3]ClO_4$.[16]

Table III. Selected Bond Distances (Å) and Angles (deg) of $[LReO_3]Cl$

Re–O1	1.756 (5)	N1–C1	1.473 (9)
Re–N1	2.197 (5)	N1–C2	1.480 (9)
		C1–C2	1.567 (11)
O1–Re–O1A	102.7 (4)	O1–Re–N1B	161.0 (4)
O1–Re–N1	89.6 (3)	O1–Re–N1A	88.0 (3)
N1A–Re–N1B	76.5 (3)	N1–Re–N1B	76.4 (2)
Re–N1–C1	144.4 (4)	Re–N–C2A	107.3 (5)
C1–N1–C2A	113.7 (8)	N1–C1–C2	110.0 (6)
N1A–C2–C1	106.9 (6)		

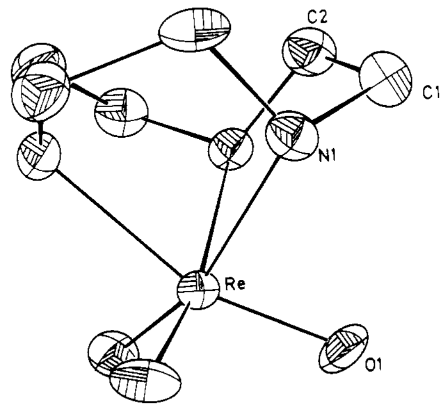

Figure 1. Perspective view of $[LReO_3]^+$ and atomic labeling scheme.

$[LRe(CO)_3]Br$ reacted smoothly in acetonitrile with $NOBF_4$, affording yellow $[LRe(NO)(CO)_2](BF_4)_2$. This nitrosyl complex is also air-stable in solution and in the solid state. The infrared spectrum exhibits a ν(NO) band at 1800 (s) cm^{-1} and two ν(CO) frequencies at 2080 (s) and 2040 (s) cm^{-1}. It is noted that the reaction of $(\eta^5\text{-}C_5H_5)Re(CO)_3$ with $NOBF_4$ yields $[(\eta^5\text{-}C_5H_5)Re(NO)(CO)_2]BF_4$.[17]

Both complexes of rhenium(I) undergo exhaustive oxidative decarbonylation reactions to yield colorless $[LReO_3]^+$, an octahedral complex of rhenium(VII). Thus, when $[LRe(CO)_3]Br$ reacts with 5 M nitric acid at 105 °C for 24 h, a microcrystalline solid of the composition $[LReO_3]ReO_4$ is obtained. This salt is readily soluble in water but insoluble in all common organic solvents. In the infrared spectrum (KBr disk) broad ν(Re=O) bands are observed at 955 and 930 cm^{-1}, which are due to the Re–O group of the cation and the ReO_4^- anion.[9] $[LRe(NO)(CO)_2](BF_4)_2$ reacts in 35% hydrogen peroxide at elevated temperatures within 30 min to give upon removal of the solvent under reduced pressure a colorless solid material, which readily dissolves in water. Addition of sodium chloride intiates the precipitation of $[LReO_3]Cl$, the crystal structure of which has been determined (see below). In the infrared spectrum two ν(Re=O) stretching frequencies at 945 (s) and 920 (vs) cm^{-1} are observed. It is noted that these ν(Re=O) frequencies are shifted to higher wavenumbers as compared with values reported for the more electron-rich $(Me_5C_5)ReO_3$ species (ν(Re=O) = 909, 878 cm^{-1}).[8]

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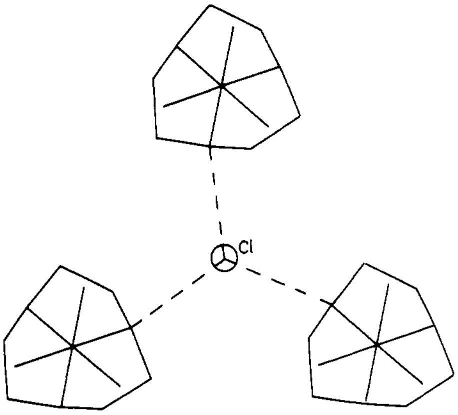

Figure 2. Packing diagram of one layer of $[LReO_3]^+$ cations and a chloride ion (viewed down the *c* axis) emphasizing the N-H···Cl hydrogen bonding (broken lines).

Description of the Crystal Structure of $[LReO_3]Cl$. Crystals of $[LReO_3]Cl$ consist of $[LReO_3]^+$ cations and uncoordinated chloride ions. Figure 1 shows a perspective view of the complex cation and the atomic labeling scheme. The cation possesses crystallographically imposed C_3 symmetry. The rhenium centers are in a highly distorted octahedral environment of three facially coordinated nitrogen atoms of the macrocyclic ligand and three facially coordinated oxygen atoms.

The Re-O bond distance of 1.756 (5) Å is rather short, indicating considerable double-bond character. Interestingly, in $Re_2O_7(OH_2)_2$, which has a dimeric molecular structure containing one distorted tetrahedral ReO_4^- and an octahedral $ReO_3(OH_2)_2^+$ unit connected by a linear oxo bridge,[18] the terminal Re=O bond distance in the octahedral part is found to be 1.75 Å. The same distance has been observed for $(\eta^5\text{-}Me_5C_5)ReO_3$[9] and for $Re_2O_7(C_5H_5N)_3$.[21]

The Re-N bond length of 2.197 (5) Å is quite long, which indicates a pronounced trans influence of the terminal oxo groups. Re-N bonds in rhenium(V) oxo complexes range from 2.11 to 2.16 Å, e.g. in $[ReO_2(4\text{-}Mepy)_4]ReO_4$ and related complexes.[19]

The N-Re-N bond angles of nitrogen atoms in cis positions with respect to each other are considerably smaller (76.5 (3)°) than the ideal octahedral angle of 90°. This is mainly due to the steric constraints of the cyclononane ring and the rather long Re-N bond lengths. On the other hand, the O-Re-O bond angles of oxygen atoms in cis positions are obtuse (102.7 (4)°). This reflects the known tendency of oxo complexes of transition metals in very high oxidation states (d^0 electronic configuration) with short M-O distances to maximize the otherwise short approaches of nonbonded oxygen atoms.

It is of interest to compare the present structure with that of $(dien)MoO_3$.[20] The geometry of the MoO_3N_3 core is remarkably similar to that found in $[LReO_3]^+$ (N-Mo-N = 75°, O-Mo-O = 106°; Mo=O = 1.736 Å, Mo-N = 2.324 Å). The structure of $[LReO_3]Cl$ consists of hexagonal-close-packed layers containing both the $[LReO_3]^+$ cations and chloride ions, stacked along the *c* axis. Each $[LReO_3]^+$ ion has a packing relationship with three chloride ions that includes hydrogen bonding between all three amine nitrogen atoms of the coordinated cyclic ligand. Each chloride ion is connected via N-H···Cl hydrogen bonds to three $[LReO_3]^+$ cations (Figure 2). The N···Cl distance is 3.167 (6) Å. The oxygen atoms of $[LReO_3]^+$ are not involved in this hydrogen-bonding scheme.

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Registry No. $[LRe(CO)_3]Br$, 101566-53-4; $Re(CO)_5Br$, 14220-21-4; $[LRe(NO)(CO)_2](BF_4)_2$, 101566-55-6; $[LReO_3]Cl$, 101566-56-7; $[LReO_3]ReO_4$, 101566-58-9.

Supplementary Material Available: Tables of anisotropic thermal parameters, calculated positional parameters of hydrogen atoms, and intraligand bond distances and angles (2 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (7 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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Contribution from the Inorganic Chemistry Laboratory,
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Theoretical Analysis of the Bonding in Octahedral Transition-Metal Clusters Containing π-Acceptor and π-Donor Bridging Ligands and Their Nido and Arachno Derivatives

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The bonding in octahedral clusters with face- and edge-bridging ligands has been studied by semiempirical molecular orbital calculations and interpreted within the framework of Stone's tensor surface harmonic theory. The function of π-acceptor and π-donor ligands in stabilizing the metal-metal bonding in clusters is discussed, and the role of the metal orbitals with δ symmetry in influencing the observed electron counts is stressed. Calculations on nido and arachno structures based on $[Mo_6Cl_{18}]^{2+}$, with edge-bridging ligands, have suggested that they behave analogously to metal carbonyl clusters, and the number of skeletal bonding molecular orbitals remains constant in the closo, nido, and arachno series. In contrast, the closo, nido, and arachno structures derived from $[Mo_6Cl_{14}]^{2-}$ with face-bridging ligands have $3n - 6$ skeletal bonding molecular orbitals where n is the number of metal atoms. The differences in electron counts in clusters with edge- and face-bridging ligands can be rationalized in terms of the complementary nature of the interactions between the metal d^δ and the ligand orbitals in the two cases.

Introduction

During the last 10 years the growth of transition-metal carbonyl cluster chemistry[1] has been assisted by the development of a simple electron-counting rules[2] that relate the total number of valence electrons to topological features of the metal polyhedra. These electron-counting rules have been underpinned theoretically by calculations on individual cluster molecules,[3] the development of

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