to the fact that the spin density along an equatorial bond which corresponds to the "doughnut" lobe of a z^2 type orbital is certainly smaller that along an axial bond, we can expect a reduction of the antiferromagnetic contribution in the two latter cases, i.e. for the couples Cu(201)/Cu(301), Cu(101)/Cu(201), and Cu(101)/Cu(401). As for the monoatomic bridge Cu(201)–O(202)–Cu(301), a literature survey[4,29] shows that it can only support a very weak antiferromagnetic interaction.

Those comments point out some factors that may be responsible for the lowering of the antiferromagnetic contribution. However they also underline the difficulty in analyzing, even at a qualitative level, the magnetic properties of a complex with a very distorted geometry.

Acknowledgment. R.K. is grateful to the Ella and Georg Hrnroth Foundation and the University of Granada for financial support. J.R. and E.C. are grateful to the Ministry of Education and Science for a grant and to the DGICYT for the project of investigation PB88-0482. We thank Dr. A. Mari for his contribution to the magnetic measurements.

Supplementary Material Available: Tables of ideal and observed angles for the polyhedra related to each copper atom and for the tetrahedron containing the four copper atoms, isotropic temperature factors for the O, N, C, and H atoms and anisotropic temperature factors for the copper atoms, fractional atomic coordinates for hydrogen atoms, and interatomic distances and bond angles (8 pages); structure factor tables (12 pages). Ordering information is given on any current masthead page.

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Electrochemical and Spectroscopic Studies of Rhenium(IV) Monomeric and Dimeric Chloride Complexes in the Basic Aluminum Chloride–1-Methyl-3-ethylimidazolium Chloride Room-Temperature Molten Salt

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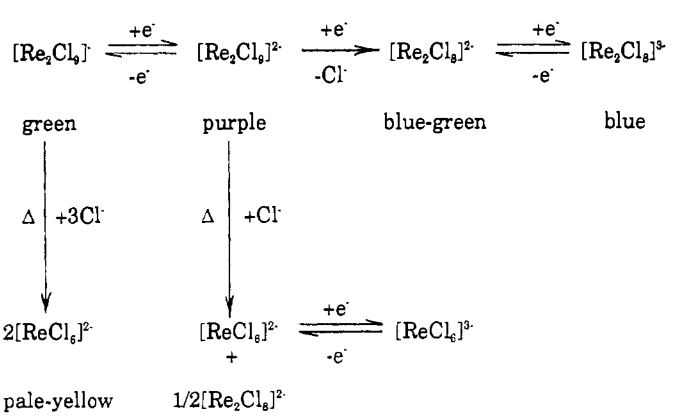
The monomeric rhenium(IV) chloride complex $[ReCl_6]^{2-}$ is stable in the basic aluminum chloride–1-methyl-3-ethylimidazolium chloride molten salt, and it can be reduced voltammetrically to $[ReCl_6]^{3-}$ at a glassy-carbon electrode in a reversible process with a half-wave potential of –0.87 V in the 49.0/51.0 mol % melt versus the Al^{3+}/Al couple in the 66.7/33.3 mol % melt. The Stokes–Einstein product for this complex is 2.3×10^{-10} g cm s^{-2} K^{-1}. The dimeric, metal–metal-bonded rhenium(IV) complex $[Re_2Cl_9]^-$ can be reduced voltammetrically to $[Re_2Cl_9]^{2-}$ in a reversible electrode reaction with a half-wave potential of approximately 0.56 V in the 49.0/51.0 mol % melt. However, $[Re_2Cl_9]^-$ exhibits only limited stability in the melt and slowly converts to $[ReCl_6]^{2-}$. The dimeric rhenium(IV,III) complex $[Re_2Cl_9]^{2-}$ can be reduced electrochemically to the dimeric rhenium(III) species $[Re_2Cl_8]^{2-}$ in an irreversible process. The Stokes–Einstein product for this complex is 1.6×10^{-10} g cm s^{-2} K^{-1}. Like $[Re_2Cl_9]^-$, $[Re_2Cl_9]^{2-}$ exhibits only limited stability in the melt; it slowly converts to a mixture of $[ReCl_6]^{2-}$ and $[Re_2Cl_8]^{2-}$. The conversion process is second order in $[Re_2Cl_9]^{2-}$ with a rate constant of 7.34×10^{-3} M^{-1} s^{-1} at 31 °C and an activation energy of approximately 92 kJ mol^{-1}. The overall chemical and electrochemical scheme for rhenium complexes in the basic $AlCl_3$–MeEtimCl molten salt is as follows:



Introduction

Room-temperature chloroaluminate molten salts or ionic liquids are obtained by combining aluminum chloride with certain quaternary ammonium chloride salts that are based on "bulky" cations like *N*-(*n*-butyl)pyridinium ($Bupy^+$) and 1-methyl-3-ethylimidazolium ($MeEtim^+$).[1] One very attractive feature of these chloroaluminate molten salts is their adjustable Lewis acidity, which can be varied over a very wide range by simply changing the relative proportion of aluminum chloride. Melts containing a molar excess of aluminum chloride are considered to be "acidic" because they contain one or more coordinately unsaturated, chloride ion acceptor species like $Al_2Cl_7^-$ and/or $Al_3Cl_{10}^-$. Conversely, melts formulated with a molar excess of the organic salt are designated as "basic" because they contain chloride ion

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(1) For reviews see: (a) Chum, H. L.; Osteryoung, R. A. In *Ionic Liquids*; Inman, D., Lovering, D. G., Eds.; Plenum: New York, 1981; pp 407–423. (b) Hussey, C. L. *Adv. Molten Salt Chem.* **1983**, *5*, 185–230. (c) Gale, R. J.; Osteryoung, R. A. In *Molten Salt Techniques*; Lovering, D. G., Gale, R. J., Eds.; Plenum: New York, 1983; Vol. 1, pp 55–78.

0020-1669/90/1329-4246$02.50/0

Table I. Electronic Spectral Data for Anionic Rhenium Chloride Complexes

solute	solvent	λ, nm (ε, M^{-1} cm^{-1})[a]	ref
K_2ReCl_6	49.0/51.0 mol % $AlCl_3$–MeEtimCl	263 (9.4 × 10^3), 283 (1.5 × 10^4), ~300^{sh}, 322^{sh} (3.2 × 10^3)	this work
K_2ReCl_6	44.4/55.6 mol % $AlCl_3$–MeEtimCl	263 (9.0 × 10^3), 283 (1.4 × 10^4), ~200^{sh}, 320^{sh} (3.0 × 10^3)	this work
K_2ReCl_6	aqueous HCl	256 (7.0 × 10^3), 281 (1.3 × 10^4), 300^{sh} (7.0 × 10^3), 320^{sh} (2.8 × 10^3), 364^{sh} (2.3 × 10^2)	16
$[Bu_4N][Re_2Cl_9]$	CH_2Cl_2	324 (2.2 × 10^4), 356 (1.4 × 10^4), 546 (3.9 × 10^2), 623 (4.7 × 10^2)	this work
$[Bu_4N][Re_2Cl_9]$	CH_2Cl_2	321 (2.3 × 10^4), 360 (1.4 × 10^4), 545 (3.8 × 10^2), 623 (4.8 × 10^2)	5
$[Bu_4N]_2[Re_2Cl_9]$	49.0/51.0 mol % $AlCl_3$–MeEtimCl	277 (1.7 × 10^4), 322 (7.9 × 10^3), 357 (4.3 × 10^3), 539 (1.1 × 10^3), 738 (1.3 × 10^3)	this work
$[Bu_4N]_2[Re_2Cl_9]$	CH_2Cl_2	277 (1.9 × 10^4), 323 (8.2 × 10^3), 357 (4.6 × 10^3), 539 (1.2 × 10^3), 740 (1.5 × 10^3)	this work
$[Bu_4N]_2[Re_2Cl_9]$	CH_2Cl_2	262, 276 (1.8 × 10^4), 322 (9.5 × 10^3), 357^{sh} (530?), 537 (1.3 × 10^3), 736 (1.4 × 10^3)	5

[a] A superscript sh denotes a shoulder.

that is not covalently bound to aluminum. Neutral melts contain exactly equal amounts of aluminum chloride and organic chloride salt. They consist principally of the organic cation and $AlCl_4^-$, and they also contain very small amounts of $Al_2Cl_7^-$ and Cl^- arising from the autosolvolysis reaction

$$2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^- \tag{1}$$

Basic room-temperature chloroaluminate melts have proven to be expedient solvents for highly charged anionic transition-metal chloride complexes because the chemical nature and low temperature of these melts precludes many of the common degradation pathways that are available to these complexes in molecular solvents and high-temperature molten salts.[2,3] A comprehensive list of the various complexes that have been studied in room-temperature chloroaluminate melts is available.[3]

In a recent paper, we reported the electrochemistry of the two known metal–metal-bonded, polynuclear rhenium(III) chloride complexes, $[Re_2Cl_8]^{2-}$ and $[Re_3Cl_{12}]^{3-}$, in the basic $AlCl_3$–MeEtimCl melt.[4] Both complexes were found to undergo one-electron, reversible reduction reactions to produce stable species, and for the first time, it was possible to stabilize the elusive $[Re_2Cl_8]^{3-}$ ion. As a continuation of this work, we have conducted electrochemical and spectroscopic studies of the related metal–metal-bonded rhenium(IV) and rhenium(IV,III) dimers, $[Re_2Cl_9]^-$ and $[Re_2Cl_9]^{2-}$, respectively, and the rhenium(IV) monomer, $[ReCl_6]^{2-}$, in this same ionic solvent.

$[Re_2Cl_9]^-$, which is produced by the chlorine oxidation of $[Re_2Cl_8]^{2-}$,[5] exhibits a metal–metal bonded structure similar to that of the isoelectronic $[W_2Cl_9]^{3-}$ ion, i.e., three bridging chloride ions and a supposed metal–metal triple bond.[6] $[Re_2Cl_9]^{2-}$ is obtained by chemical reduction of $[Re_2Cl_9]^-$, and it possesses rhenium atoms with a mean formal oxidation state of +3.5.[7] Surprisingly, the electrochemistry of these two dimeric rhenium chloride complexes does not appear to have been studied previously. On the other hand, several electrochemical studies concerned with the octahedral $[ReCl_6]^{2-}$ complex have been reported. Bailey and Nobile[8] conducted a detailed investigation of rhenium(IV) in molten LiCl–KCl at 450–550 °C, and they found that about 20% of the added K_2ReCl_6 partially decomposed upon addition to the melt to give rhenium metal and volatile $ReCl_5$. One and possibly two reduction waves at negative potentials could be attributed to the remaining rhenium(IV). Trop et al.[9] observed a voltammetric wave corresponding to the reversible, one-electron oxidation of $[ReCl_6]^{2-}$ in acetonitrile; however, a reduction wave arising from this species was ill-defined. Heath et al.[10] reported half-wave potentials for the $[ReCl_6]^{-/2-}$, $[ReCl_6]^{2-/3-}$, and $[ReCl_6]^{3-/4-}$ redox couples in dichloromethane, but they gave few details about the origin of this data. Several investigations of the $[ReCl_6]^{2-/3-}$ electrode reaction have been undertaken in aqueous solutions containing chloride ion; some notable examples are the kinetic studies reported by Gross[11] and the work by Rulfs and Elving.[12]

Experimental Section.

Apparatus. Electrochemical experiments were carried out under a highly purified nitrogen atmosphere inside a Kewaunee Scientific Equipment Corp. (KSE) glovebox. The glovebox was equipped with a KSE Model 2C2500 30 ft^3 min^{-1} inert gas purifier. The oxygen and moisture content of this system was monitored by using a procedure previously described.[13] An AMEL Model 551 potentiostat, an EG & G Princeton Applied Research Corp. Model 175 universal programmer, an EG & G Princeton Applied Research Corp. Model 379 digital coulometer, and a Pine Instruments Co. Model AFMSR electrode rotator were used to conduct cyclic voltammetry (CV), rotating disk electrode voltammetry (RDEV), and chronoamperometry (CA) experiments. Electrochemical data were recorded by using either a Houston Instruments Model 100 X-Y/Y-t recorder, a Nicolet Explorer I digital oscilloscope, or a Hewlett-Packard Model 3467A logging multimeter. Electronic resistance compensation was employed during all electrochemical experiments except bulk controlled-potential electrolysis.

The glassy carbon/Pyrex glass (GC) working electrode (area = 0.066 cm^2) that was used for CV, RDEV, and CA experiments and the electrochemical cell that was employed have been discussed previously.[14] The same cell was used to perform bulk electrolysis experiments except that the GC electrode was replaced by a large surface area platinum-gauze electrode. Aluminum wires (Alfa, m5N) isolated in 13-mm-diameter Pyrex glass tubes that were terminated with porosity E glass frits (Ace Glass) served as the counter and reference electrodes. All potentials are reported versus the Al^{3+}/Al couple in the nominal 66.7/33.3 mol % melt. The potential of this reference electrode was reproducible to within only ±10 mV; thus, the positions of the voltammetric waves often varied slightly from one experiment to another. Unless otherwise specified, all electrochemical experiments were performed at 40.0 ± 0.5 °C. A Thermolyne Corp. Model SP-10105B heater/stir plate was used to heat the solutions.

A Perkin-Elmer Model 3840 Lambda Array UV–vis spectrophotometer was used to record electronic absorption spectra. The adaptations made to the cell compartment of this instrument in order to collect spectral data at elevated temperatures have been described.[4] Fused silica cells of either 1.00 cm or 1.00 mm path length that were fitted with airtight Teflon caps were used to contain the solutions under study.

Chemicals. Potassium hexachlororhenate(IV), K_2ReCl_6, (Morton Thiokol, 99.9%) was used as received. Both tetrabutylammonium nonachlorodirhenate(IV), $[Bu_4N][Re_2Cl_9]$, and the related one-electron-reduced species, $[Bu_4N]_2[Re_2Cl_9]$, were prepared according to the procedures given by Bonati and Cotton.[5] Aluminum chloride (Fluka, puriss) was sublimed in vacuo two times with NaCl and two times in the absence of NaCl before use. MeEtimCl was synthesized and purified according to procedures described previously.[15] Methylene chloride, CH_2Cl_2

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Table II. Electrochemical Data for Anionic Rhenium Chloride Complexes in Basic $AlCl_3$–MeEtimCl

complex	mol % $AlCl_3$	E_p,[a] V	$E_{1/2}$,[b] V	$E_{1/2}$,[c] V	10^7D,[d] $cm^2\ s^{-1}$	$10^{10}\eta D/T$, $g\ cm\ s^{-2}\ K^{-1}$	$E^{\circ\prime}$,[e] V
$[ReCl_6]^{2-}$	49.0	–0.898	–0.866	–0.866	6.26	2.5 ± 0.1	
$[ReCl_6]^{2-}$	44.4	–0.921	–0.889	–0.885	3.13	2.1 ± 0.1	
$[Re_2Cl_9]^{-}$[f]	49.0	0.532	0.563	0.561	>3.75	>2.4 ± 0.1	
$[Re_2Cl_9]^{2-}$[g,f]	49.0	0.585	0.556	0.550	2.49	1.5 ± 0.2	0.565
$[Re_2Cl_9]^{-}$[f]	44.4	0.523	0.553	0.553	>2.23	>2.3 ± 0.1	
$[Re_2Cl_9]^{2-}$[g,f]	44.4	0.577	0.547	0.542	1.53	1.6 ± 0.2	0.556
$[Re_2Cl_9]^{2-}$[h,f]	49.0	–0.147		–0.118	2.44	1.5 ± 0.1	
$[Re_2Cl_9]^{2-}$[h,f]	44.4	–0.161		–0.122	1.51	1.6 ± 0.1	

[a] Average voltammetric peak potential over the range of scan rates from 0.01 to 0.20 V s^{-1}. All potentials are referenced to the Al^{3+}/Al couple in the 66.7/33.3 mol % melt. The oxidation of ferrocene was observed at approximately 0.24 V versus this reference electrode. [b] Estimated from cyclic voltammetric peak potentials by using $(E_p^c + E_p^a)/2$. [c] Average RDEV value over the range of angular velocities from 105 to 209 rad s^{-1}. [d] Average value from LSV, RDEV, and CA experiments. [e] Formal potential estimated from $E_{1/2}$, D_R, and D_O by using $E^{0\prime} = E_{1/2} + 0.027 \ln (D_O/D_R)^{2/3}$. [f] Temperature was 28 °C. [g] Oxidation. [h] Reduction.

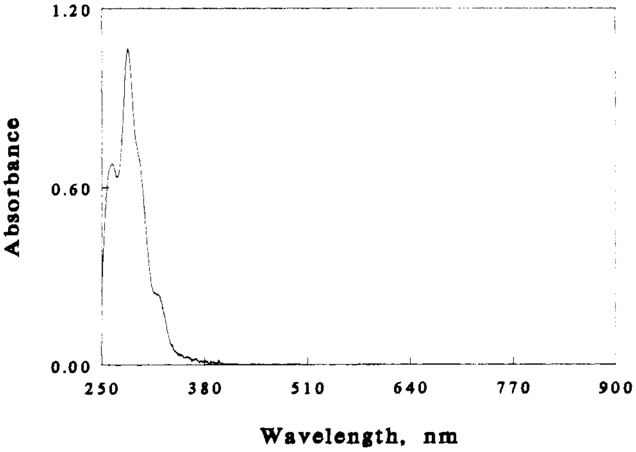

Figure 1. Electronic absorption spectrum of a 7.27 × 10^{-4} M solution of K_2ReCl_6 in the 49.0/51.0 mol % $AlCl_3$–MeEtimCl melt. The cell path length was 1.00 mm.

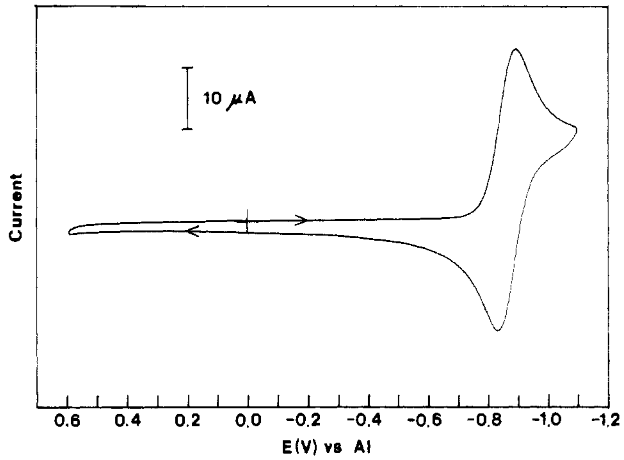

Figure 2. Cyclic voltammogram of 1.11 × 10^{-2} M K_2ReCl_6 in the 49.0/51.0 mol % $AlCl_3$–MeEtimCl melt at a glassy-carbon electrode. The scan rate was 0.050 V s^{-1}, and the temperature was 40 °C. Cathodic currents are positive.

(Aldrich, Gold Label), was used as received.

Results and Discussion

K_2ReCl_6. This salt dissolved in the basic $AlCl_3$–MeEtimCl molten salt to produce pale yellow solutions. An electronic absorption spectrum of one of these solutions, which was prepared with a 49.0/51.0 mol % melt, is shown in Figure 1. Wavelength and absorptivity data taken from this spectrum and a spectrum of a solution of K_2ReCl_6 that was prepared with 44.4/55.6 mol % melt are collected to Table I. The data in this table are in excellent agreement with the major bands appearing in the classical aqueous spectral data for $[ReCl_6]^{2-}$ reported by Jørgensen,[16] confirming that the rhenium(IV) was present in basic melt as this complex.

A cyclic voltammogram of a solution of K_2ReCl_6 in the 49.0/51.0 mol % melt at a glassy carbon electrode is shown in Figure 2. The essential features of this cyclic voltammogram are a single reduction wave with a peak potential, E_p, of ca. –0.90 V and a single oxidation wave located at ca. –0.84 V that is linked to this reduction wave; no other oxidation or reduction waves assignable to $[ReCl_6]^{2-}$ were present within the nominal electrochemical window of the melt. The average peak potential separation, ΔE_p, for this pair of waves was 0.065 V at 40 °C over the range of scan rates extending from 0.010 to 0.200 V s^{-1}. This value of ΔE_p is in good agreement with the 0.062-V theoretical separation expected for a one-electron, reversible electrode reaction at this temperature. The peak current ratio for this wave, i_p^a/i_p^c, calculated by using the empirical method described by Nicholson,[17] was 1.0, and the peak current function, $i_p^c/v^{1/2}$, was constant over this same range of scan rates. The reduction of $[ReCl_6]^{2-}$ was also investigated with RDEV; a plot of the limiting current versus the square root of the angular velocity of the GCRDE was linear over the range of angular velocities from 105 to 209 rad s^{-1}, and it passed through the origin of the plot. Similar voltammetric results were obtained in the 44.4 mol % melt, except that the reduction wave was shifted to more negative potentials by about 0.020 V.

Electrochemical parameters for the $[ReCl_6]^{2-}$ reduction process at 40 °C, which are the average values resulting from several experiments, are summarized in Table II. It is apparent that the half-wave potential, $E_{1/2}$, of the $[ReCl_6]^{2-}$ reduction wave shifts negatively with increasing chloride concentration in the melt by the amount of 0.028 V/pCl unit. However, this shift in potential is approximately the same as the shifts observed for many other transition-metal redox couples that retain the same chloride coordination after reduction,[18] and it therefore seems likely that the reduced complex also exhibits 6-fold chloride coordination. Thus, the voltammetric reduction wave proximate to –0.90 V must arise from the reversible electrode reaction

$$[ReCl_6]^{2-} + e^- \rightleftharpoons [ReCl_6]^{3-} \qquad (2)$$

in which $[ReCl_6]^{3-}$ is stable on the voltammetric time scale. Diffusion coefficients of $[ReCl_6]^{2-}$, which are the average values from several individual CV, RDEV, and CA experiments, are collected in Table II along with the calculated Stokes–Einstein product, $\eta D/T$, where D is the diffusion coefficient of the complex, η is the absolute or bulk viscosity of the melt, and T is the absolute temperature. This parameter is inversely proportional to the solvodynamic radius of the diffusing species. There is a small, but seemingly significant difference between the value of $\eta D/T$

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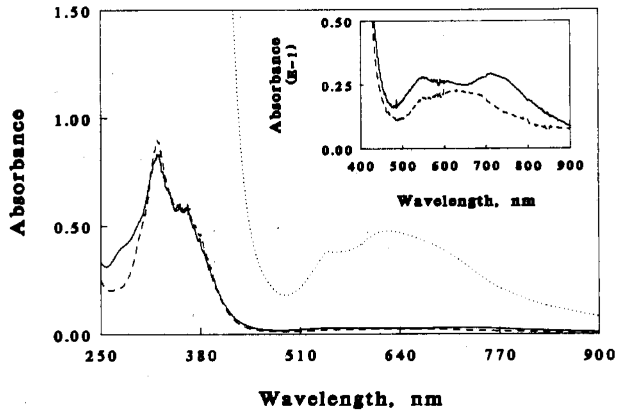

Figure 3. Electronic absorption spectra of $[Bu_4N][Re_2Cl_9]$ in various solvents: (—) 4.94 × 10^{-4} M in the 44.4/55.6 mol % $AlCl_3$–MeEtimCl melt (cell path length was 1.00 mm); (- -) 4.04 × 10^{-5} M in methylene chloride (cell path length was 1.00 cm); (⋯) 1.01 × 10^{-3} M in methylene chloride (cell path length was 1.00 cm). Inset: (—) 4.94 × 10^{-4} M in the 44.4/55.6 mol % $AlCl_3$-MeEtimCl melt (cell path length was 1.00 mm) and (- -) 4.04 × 10^{-5} M in methylene chloride (cell path length was 1.00 cm).

for $[ReCl_6]^{2-}$ in the 49.0 mol % melt and that found in the 44.4 mol % melt. However, no variation in $\eta D/T$ has been seen for any other hexachlorometalate complex in basic melt,[19] and it seems likely that the small difference seen here arises from some unaccounted for experimental error. The average value of $\eta D/T$ for $[ReCl_6]^{2-}$ is 2.3 × 10^{-10} g cm s^{-2} K^{-1}. This value falls in the upper range of values for anionic transition-metal halide complexes with the same overall charge.[19]

$[Bu_4N]Re_2Cl_9]$. An electronic spectrum of a freshly prepared solution of $[Bu_4N][Re_2Cl_9]$ in the 44.4/55.6 mol % melt is shown in Figure 3 along with the spectrum of a methylene chloride solution of this same salt. Both solutions were dark green in color. The absorptivities and band positions taken from the latter spectrum are in excellent agreement with literature data for similar solutions containing the $[Re_2Cl_9]^-$ ion (Table I). The two spectra in Figure 3 are similar in *almost* all respects, indicating that $[Re_2Cl_9]^-$ is also present in the melt. However, when these two spectra are displayed on an expanded absorbance scale (see inset), it is obvious from the bands appearing at ca. 550 and 720 nm in the melt spectrum that a very small amount (<1%) of the added $[Re_2Cl_9]^-$ has reduced to $[Re_2Cl_9]^{2-}$ (vide infra). This phenomenon was reproducible, and we were unable to prepare a solution of $[Re_2Cl_9]^-$ in the melt that did not contain at least some detectable amount of $[Re_2Cl_9]^{2-}$. This was not seen in dichloromethane solutions prepared with the same batch of $[Bu_4N][Re_2Cl_9]$. However, once the melt solution was prepared, the $[Re_2Cl_9]^-$ did not appear to reduce further. The ease with which this compound can be reduced has been observed by others; e.g., Bonati and Cotton[5] found that $[Re_2Cl_9]^-$ is reduced spontaneously to $[Re_2Cl_9]^{2-}$ in many organic solvents. The reduction seen here may be caused by a small amount of an apparently unavoidable reducing impurity in the melt.

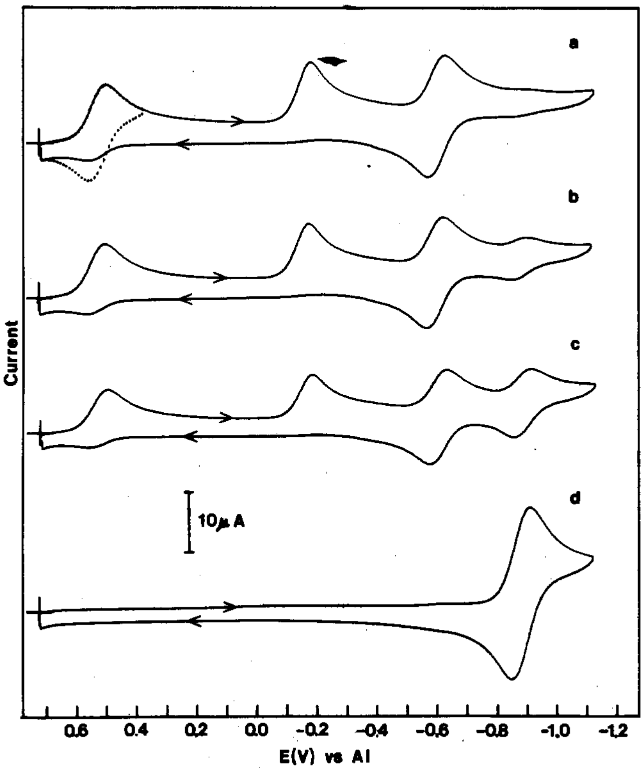

Figure 4. Cyclic voltammograms of 5.07 × 10^{-3} M $[Bu_4N][Re_2Cl_9]$ in the 44.4/55.6 mol % $AlCl_3$–MeEtimCl melt at a glassy carbon electrode: (a) fresh solution; (b) solution 70 min after preparation, (c) solution 197 min after preparation, (d) solution in part c after being heated to 90 °C for 1 h and cooled. (d) solution after the solution in part c was heated to 90 °C for 1 h and cooled. The sweep rates were 0.050 V s^{-1}, and the temperature was 28 °C. The initial potential for each scan was 0.75 V. Cathodic currents are positive.

A cyclic voltammogram of a freshly prepared solution of $[Re_2Cl_9]^-$ in the 44.4/55.6 mol % melt at 28 °C is shown in Figure 4a. Three reduction waves with approximate peak potentials of 0.52, –0.16, and –0.61 V, respectively, are apparent; the reverse scan shows that only the first and last waves are associated with an oxidation current. The latter two reduction waves are also present in solutions containing the $[Re_2Cl_9]^{2-}$ ion (vide infra). Therefore, for the sake of expediency, the electrode processes responsible for these latter two waves will be discussed in the next section. For the first electrode process at 0.52 V in Figure 4a, the average value of ΔE_p obtained over the range of scan rates from 0.010 to 0.200 V s^{-1} was 0.061 V, and it was in good agreement with the 0.060-V theoretical value expected for a one-electron reversible electrode reaction at 28 °C. In addition, i_p^a/i_p^c was 1.0, and $i_p^c/v^{1/2}$ was constant over this same range of scan rates. A plot of the RDEV limiting current for this wave varied linearly with the square root of the angular velocity of the GCRDE. As was the case for $[ReCl_6]^{2-}$, $E_{1/2}$ for the reduction of $[Re_2Cl_9]^-$ also shifted negatively with increasing chloride concentration in the melt, but this shift (0.010 V/pCl unit) was too small to suggest any change in the chloride coordination of the complex.[18] Taken together, the foregoing results indicate that the first reduction wave corresponds to the reversible electrode reaction

$$[Re_2Cl_9]^- + e^- \rightleftharpoons [Re_2Cl_9]^{2-} \qquad (3)$$

in which $[Re_2Cl_9]^{2-}$ is stable on the time scale of the experiment. Electrochemical data for the $[Re_2Cl_9]^{-/2-}$ electrode reaction are summarized in Table II. The diffusion coefficients of $[Re_2Cl_9]^-$ given in this table must be considered as the lower bound on the actual values because this species is not completely stable in the melt over an extended period of time and converts to another complex (vide infra). However, since the $[Re_2Cl_9]^-$ transformation process is relatively slow at the temperature of these experiments and the experimental data were recorded quickly with a fresh solution that exhibited no obvious electrochemical evidence of the conversion product, these diffusion coefficients are probably close to the true values. If so, then the average value of $\eta D/T$ for this dimeric complex falls somewhat below the range of values observed for monomeric complexes with the same overall charge.[19]

Voltammograms of the solution of $[Re_2Cl_9]^-$ in Figure 4a that were recorded at various intervals during a six hour time period are shown in Figure 4b–d. Inspection of these voltammograms reveals that the reduction waves at 0.52, –0.16, and –0.61 V diminish and that another reduction wave at ca. –0.90 V with an associated oxidation wave appears as time progresses. The conversion process can be accelerated greatly by moderate heating of the solution. After complete transformation of the $[Re_2Cl_9]^-$

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(19) Hussey, C. L.; Sun, I-W.; Strubinger, S. K. D.; Barnard, P. A. *J. Electrochem. Soc.* **1990**, *137*, 2515.

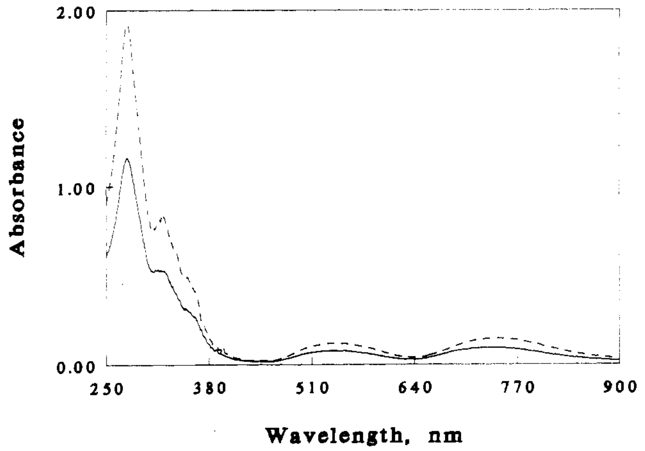

Figure 5. Electronic absorption spectra of $[Bu_4N]_2[Re_2Cl_9]$: (–) 7.02 × 10^{-4} M in the 49.0/51.0 mol % $AlCl_3$–MeEtimCl melt (cell path length was 1.00 mm); (--) 1.10 × 10^{-4} M in methylene chloride (cell path length was 1.00 cm).

has taken place, as signaled by the disappearance of the wave at 0.52 V and a change in the color of the solution from dark-green to pale yellow, only the voltammetric wave at –0.90 V is present (Figure 4d). This wave is identical with that observed for a solution containing $[ReCl_6]^{2-}$ (Figure 2), and the absorption spectrum of the solution was identical with that shown in Figure 1. Furthermore, the ratio of the peak current for the wave at –0.90 V in Figure 4d to that for the wave at 0.52 V in Figure 4a was approximately 2.0. These results indicate that $[Re_2Cl_9]^-$ is slowly converted to $[ReCl_6]^{2-}$ through the chemically irreversible process

$$[Re_2Cl_9]^- + 3Cl^- \rightarrow 2[ReCl_6]^{2-} \qquad (4)$$

The slow rate of this reaction in the relatively chloride-rich environment afforded by the basic $AlCl_3$–MeEtimCl melt is not surprising since rhenium(IV) species fall into the general classification of substitutionally "inert" complexes. Virtually identical results were obtained in the 49.0/51.0 mol % melt.

$[Bu_4N]_2[Re_2Cl_9]$. Basic melt solutions containing $[Bu_4N]_2[Re_2Cl_9]$ were violet in color. Electronic absorption spectra of solutions prepared with 49.0/51.0 mol % melt and with methylene chloride are shown in Figure 5, and data taken from these and similar spectra that were recorded in the 44.4/55.6 mol % melt are summarized in Table I. Also included in Table I are literature data for solutions known to contain the $[Re_2Cl_9]^{2-}$ complex ion. Inspection of this spectral data indicates that this complex ion is the only rhenium species present in the melt.

Cyclic voltammograms of a fresh solution of $[Re_2Cl_9]^{2-}$ in the 44.4/55.6 mol % melt are shown in Figure 6a,b. The voltammogram in Figure 6a exhibits an oxidation wave at ca. 0.58 V on the positive scan and reduction waves at approximately 0.52, –0.16, and –0.61 V on the reverse scan. A second scan reversal at –1.1 V shows an oxidation wave that is linked to the reduction wave at –0.61 V. The oxidation wave at 0.58 V and its associated reduction wave obviously arise from the reverse of the electrode reaction depicted in eq 3, since the $E_{1/2}$ value estimated for this process is virtually the same as that measured for the $[Re_2Cl_9]^{-/2-}$ electrode process (Table II). However, if the scan is first initiated in the negative direction, then the pair of waves attributed to the $[Re_2Cl_9]^{2-/-}$ electrode process that are seen on the reverse scan are much smaller than expected relative to the reduction waves at –0.16 and –0.61 V (Figure 6a), signifying irreversible con-

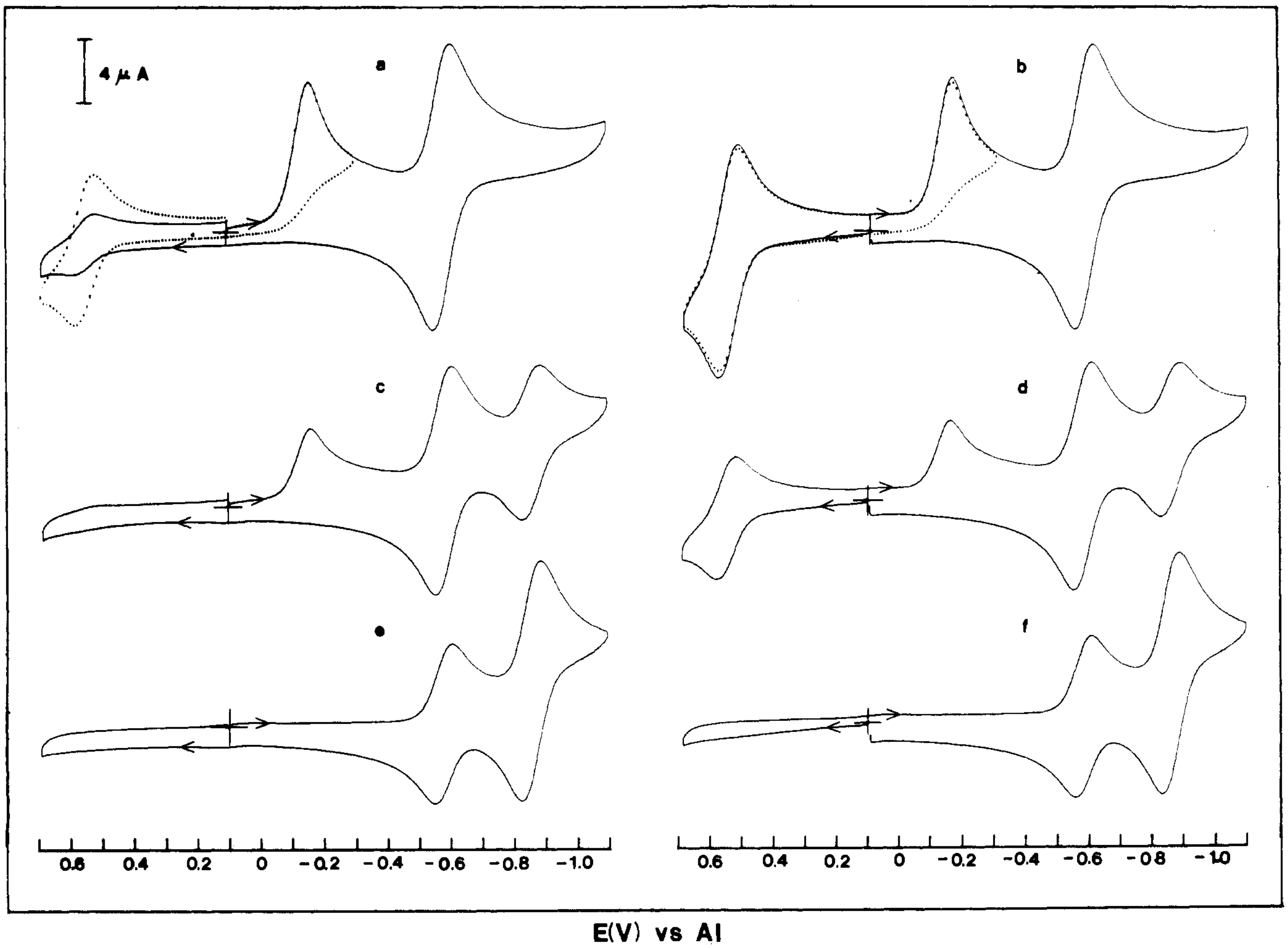

Figure 6. Cyclic voltammograms of 5.52 × 10^{-3} M $[Bu_4N]_2[Re_2Cl_9]$ in the 44.4/55.6 mol % $AlCl_3$–MeEtimCl melt at a glassy carbon electrode: (a and b) fresh solution; (c and d) solution in parts a and b after being heated to 80 °C for 5 min and allowed to cool; (e and f) solution in parts c and d after being heated to 100 °C for 1 h and allowed to cool. The sweep rates were 0.050 V s^{-1}, and the temperatures were 28 °C. The initial potential for each scan was 0.10 V. Cathodic currents are positive.

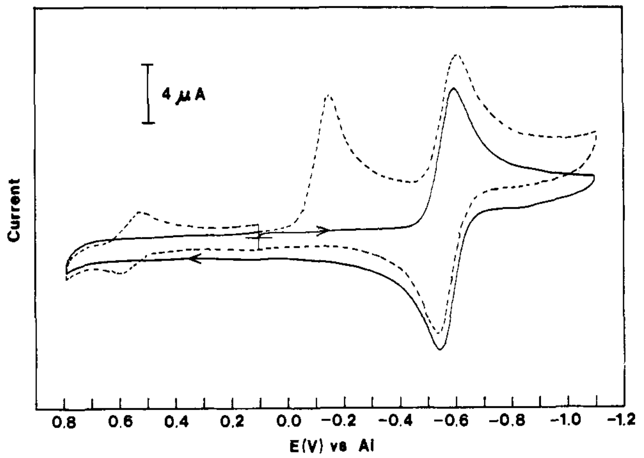

Figure 7. Cyclic voltammograms of 4.54×10^{-3} M $[Bu_4N]_2[Re_2Cl_9]$ in the 49.0/51.0 mol % $AlCl_3$–MeEtimCl melt at a glassy-carbon electrode: (–) after exhaustive reduction at an applied potential of −0.35 V and (– –) before electrolysis was commenced. The scan rates were 0.050 V s^{-1}, and the temperatures were 28 °C. Cathodic currents are positive.

sumption of $[Re_2Cl_9]^{2-}$ in the electrode diffusion layer during the initial negative scan.

In order to further probe the reduction process at −0.16 V, we conducted controlled-potential electrolysis experiments at an applied potential of −0.35 V with solutions of $[Re_2Cl_9]^{2-}$ in the 49.0/51.0 mol % melt. A cyclic voltammogram of one of these exhaustively reduced solutions is shown in Figure 7. Only the reduction wave at ca. −0.61 V and its associated oxidation wave are present in this voltammogram. The spectroscopic and electrochemical properties of this solution were identical with those of a solution containing the rhenium(III) dimer $[Re_2Cl_8]^{2-}$.[4] When corrected for the small differences in the $[Re_2Cl_9]^{2-}$ and $[Re_2Cl_8]^{2-}$ diffusion coefficients, the ratio of the current for the reduction wave at −0.61 V at the completion of electrolysis to the current for the reduction wave at −0.16 V before electrolysis was 1.0, signaling 100% conversion of the former complex into the latter. A similar conclusion can be reached by considering the concentration of $[Re_2Cl_9]^{2-}$ in the solution at the outset of the electrolysis experiment and the concentration of $[Re_2Cl_8]^{2-}$ in the solution after electrolysis as determined by voltammetry. Thus, the wave at −0.16 V must result from the following *overall* electrode reaction:

$$[Re_2Cl_9]^{2-} + e^- \rightarrow [Re_2Cl_8]^{2-} + Cl^- \qquad (5)$$

It is not possible to speculate about the mechanism of this reaction because no suggestion of an intermediate reduced species like $[Re_2Cl_9]^{3-}$ was detected, even at very fast scan rates. However, it is now clear that the reduction wave at ca. −0.61 V in Figures 4a and 6a,b originates from the reduction of $[Re_2Cl_8]^{2-}$ produced in the electrode diffusion layer by the reaction shown in eq 5, and that once reduced to $[Re_2Cl_8]^{2-}$, the $[Re_2Cl_9]^{2-}$ can not be reconstituted by electrochemical means.

Diffusion coefficients for $[Re_2Cl_9]^{2-}$ that were derived from CV, RDEV, and CA experiments involving the oxidation of this species to $[Re_2Cl_9]^-$ in freshly prepared solutions are collected in Table II along with the calculated Stokes–Einstein products. The average value of $\eta D/T$ for $[Re_2Cl_9]^{2-}$, 1.6×10^{-10} g cm s^{-2} K^{-1}, falls within the lower bound of the range of values found for some other chloride complexes with the same overall charge.[19]

Voltammetric studies conducted over a period of several days revealed that $[Re_2Cl_9]^{2-}$, like $[Re_2Cl_9]^-$, was not stable in the melt indefinitely and that it slowly converted to other complexes. However, the stability of the former complex was much greater than the stability of the latter species. In fact, the instability of $[Re_2Cl_9]^{2-}$ was not discernable at room temperature until 24 h after the solution was prepared or unless the solution had been heated. The cyclic voltammograms shown in Figure 6c,d were recorded after the solution in Figure 6a,b was heated to 80 °C for about 5 min and then cooled to 28 °C, and the voltammograms in Figure 6e,f were acquired after the same solution was heated to 100 °C for 1 h and then cooled to 28 °C. The first heating cycle causes a decrease in the height of both the $[Re_2Cl_9]^{2-}$ reduction wave at −0.16 V and the wave attributed to the reduction of $[Re_2Cl_8]^{2-}$, which is the product of the $[Re_2Cl_9]^{2-}$ reduction process (cf. eq 5). In addition, another reduction wave at ca. −0.90 V, which arises from the $[ReCl_6]^{2-/3-}$ electrode process, begins to appear in the solution. After the second heating cycle, the $[Re_2Cl_9]^{2-}$ oxidation and reduction waves are completely absent, and the resulting solution has the electrochemical and spectroscopic properties of a solution containing a mixture of $[Re_2Cl_8]^{2-}$ and $[ReCl_6]^{2-}$. The ratios of the peak currents at −0.61 and −0.90 V in Figure 6e to the peak current at −0.61 V in Figure 6a are 0.53 and 0.94, respectively, after appropriate corrections have been made for the differences in the diffusion coefficients of $[Re_2Cl_9]^{2-}$, $[Re_2Cl_8]^{2-}$, and $[ReCl_6]^{2-}$. This result indicates that the thermally induced conversion of $[Re_2Cl_9]^{2-}$ into $[Re_2Cl_8]^{2-}$ and $[ReCl_6]^{2-}$ takes place with the following stoichiometry:

$$[Re_2Cl_9]^{2-} + Cl^- \rightarrow \tfrac{1}{2}[Re_2Cl_8]^{2-} + [ReCl_6]^{2-} \qquad (6)$$

A similar conclusion about the stoichiometry of this reaction can be reached if the known concentration of $[Re_2Cl_9]^{2-}$ in the solution before heating is compared to the concentrations of $[Re_2Cl_8]^{2-}$ and $[ReCl_6]^{2-}$ in the solution after complete conversion of the $[Re_2Cl_9]^{2-}$ as estimated from the voltammetric reduction currents of these species.

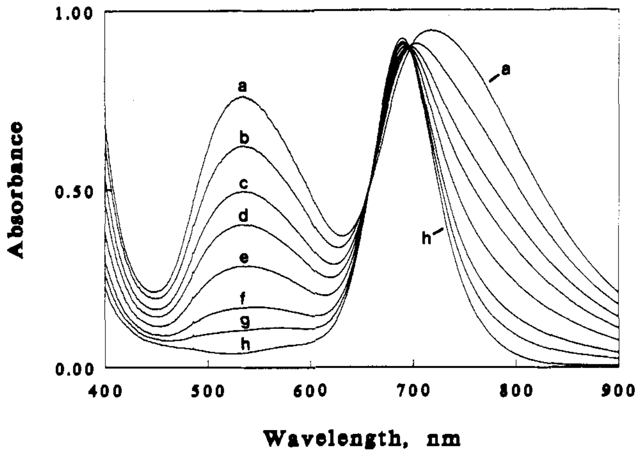

Figure 8. Electronic absorption spectra of a 7.96×10^{-4} M solution of $[Bu_4N]_2[Re_2Cl_9]$ in the 49.0/51.0 mol % $AlCl_3$–MeEtimCl melt at 100 °C at various times: (a) 2, (b) 4, (c) 6, (d) 8, (e) 12, (f) 20, (g) 30, and (h) 75 min.

The conversion process depicted in eq 6 can also be followed easily with electronic absorption spectroscopy. Figure 8 shows spectra that were recorded for a solution of $[Re_2Cl_9]^{2-}$ in the 49.0/51.0 mol % melt that was incubated at 100 °C for a period of 75 min in the cell compartment of the spectrophotometer. The spectrum recorded at the outset of the experiment (Figure 8a) is that for a solution containing only $[Re_2Cl_9]^{2-}$ while the spectrum recorded at the end of the experiment (Figure 8h) is that for a solution containing $[Re_2Cl_8]^{2-}$. Note that $[ReCl_6]^{2-}$ does not absorb significantly in the 400–900-nm wavelength region examined in this experiment (cf. Figure 1 and Table I). Similar experiments were conducted at 31 and 60 °C. Plots of the inverse of the absorbance of the 539-nm band for $[Re_2Cl_9]^{2-}$ increased linearly with time for the experimental data collected at each temperature, indicating that the reaction shown in eq 6 was second order in this complex over the range of temperatures and times that were studied. Experimental rate constants deduced from plots at 31, 60, and 100 °C were 7.34×10^{-3}, 9.02×10^{-2}, and 5.83 M^{-1} s^{-1}, respectively. An Arrhenius plot constructed from this data was reasonably linear and gave an activation energy of approximately 92 kJ mol^{-1}.

Conclusion

The metal–metal-bonded rhenium(IV) complex, $[Re_2Cl_9]^-$, slowly converts to the monomeric rhenium(IV) complex, $[ReCl_6]^{2-}$, at room temperature in basic melt through the incorporation of chloride ion. $[Re_2Cl_9]^-$ can be reduced to the dimeric rhenium(IV,III) complex, $[Re_2Cl_9]^{2-}$, at a glassy-carbon electrode in a reversible electrode reaction. Like $[Re_2Cl_9]^-$, $[Re_2Cl_9]^{2-}$ exhibits only limited stability in basic melt at room temperature and slowly converts to a mixture of $[ReCl_6]^{2-}$ and the dimeric rhenium(III) complex, $[Re_2Cl_8]^{2-}$. However, this metamorphosis is considerably slower than that involving $[Re_2Cl_9]^-$. $[Re_2Cl_9]^{2-}$ can be reduced electrochemically to $[Re_2Cl_8]^{2-}$ in a one-electron irreversible electrode reaction.

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Synthesis and Reactions of [Bis(trimethylsilyl)amido]aluminum Compounds

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The reaction of $LiN(SiMe_3)_2$ with $AlCl_3{\cdot}NEt_3$ and solid aluminum chloride produced $AlCl_2N(SiMe_3)_2{\cdot}NEt_3$, $AlCl[N(SiMe_3)_2]_2$, and $Al[N(SiMe_3)_2]_3$. $AlCl_2N(SiMe_3)_2{\cdot}NEt_3$ failed to react with hexamethyldisilazane; no trimethylchlorosilane was eliminated on pyrolysis. Pyrolysis of $AlCl[N(SiMe_3)_2]_2$ gave methane as the major volatile product, not the expected trimethylchlorosilane. Treatment of $[AlCl_2NHSiMe_3]_2$ with triethylamine did not lead to a simple complex. $[(Me_3Si)_2NAlNSiMe_3]_2$ was obtained from the reaction of $[AlCl_2NHSiMe_3]_2$ and $LiN(SiMe_3)_2$. Exposure of $[(Me_3Si)_2NAlNSiMe_3]_2$ to ammonia led to liberation of 1.5 mol of $HN(SiMe_3)_2$; thermolysis of the ammonolysis product was investigated. Reaction of boron trichloride with $Al[N(SiMe_3)_2]_3$ resulted in trimethylboron formation and some boron incorporation, accompanied by tetramethylsilane elimination and methyl group replacement by chlorine.

Introduction

(Trimethylsilyl)amino-substituted boron compounds were found to lead to processible boron nitride precursors[1-3] amenable, among other things, to fiber production. In view of the chemical similarities of boron and aluminum, it was of interest to extend those concepts to aluminum. The advantages of having (trimethylsilyl)amino substituents are the absence of metal-carbon bonds and the ease of formation and volatility of the potential leaving groups, namely Me_3SiCl, $(Me_3Si)_2NH$, and the intermediate Me_3SiNH_2. Furthermore, such an approach provides a possibility of synthesizing precursors of AlN·BN ceramics.

Initial investigations were directed at preparing aluminum analogues of $(Me_3Si)_2NBCl_2$ and $(Me_3Si)_2NB(Cl)NHSiMe_3$, utilizing the methods of Wells and Collins.[4] This approach was not successful; however, when $LiN(SiMe_3)_2$ was used, a series of bis(trimethylsilyl)amino-substituted aluminum compounds were prepared. We report here the syntheses and reactions of the products formed.

Experimental Section

General Procedures. Operations were carried out either in an inert-atmosphere enclosure (Vacuum/Atmospheres Model HE-93B), under nitrogen bypass, or in vacuo. Infrared spectra were recorded: solids as double mulls (Kel-F oil No. 10 and Nujol); liquids as capillary films; gases in 10-cm cells, on a Perkin-Elmer Model 1330 infrared spectrophotometer. The mass spectra (EI) were obtained from a Du Pont Model 21-491B spectrometer, using a heated solids probe. The spectrometer was attached to a Varian Aerograph Model 2700 gas chromatograph equipped with a flame ionization detector and a Du Pont 21-094 data acquisition and processing system. Gas chromatography was performed by employing a 10 ft × $^1/_8$ in. stainless steel column packed with 4% OV-101 on 80/100 mesh Chromosorb G and using a programming rate of 8 °C/min from 50 to 300 °C. NMR spectra were recorded on a JEOL FX90Q broad-band spectrometer, using either C_6D_6 or $CDCl_3$ as solvent and TMS as an external standard. Thermal gravimetric analyses (TGAs) were carried out in nitrogen from room temperature to 1000 °C at 10 °C/min with a Du Pont 990/951 system. Vacuum-line techniques were utilized where applicable; volatile products were separated by fractional condensation and measured and identified by a combination of volume measurement, quantitative infrared spectral analysis, and GC/MS. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Materials. Ammonia (Matheson Gas Products) was purified by trap-to-trap distillation and dried over potassium. The $AlCl_3{\cdot}HN(SiMe_3)_2$ complex,[5,6] $[AlCl_2NHSiMe_3]_2$,[5,6] and $LiN(SiMe_3)_2$[7] were prepared by known procedures. $AlCl_3{\cdot}NEt_3$ was prepared in hexane from triethylamine and aluminum chloride and recrystallized from benzene/heptane; mp 121-122 °C (lit.[8] 121.6-122.1 °C). Aluminum chloride, anhydrous, 99.99% (Gold Label; used without further purification), and $(Me_3Si)_2NH$ were obtained from Aldrich Chemical Co. All solvents were rigorously dried and degassed before use.

Treatment of $AlCl_3{\cdot}HN(SiMe_3)_2$ with Triethylamine. A mixture of $AlCl_3{\cdot}HN(SiMe_3)_2$ (1.0 g, 3.4 mmol) and triethylamine (1.72 g, 17.0 mmol) in benzene (5 mL) was refluxed for 20 h under nitrogen bypass. No precipitate was formed; the reaction mixture was evaporated in vacuo. The volatiles consisted of benzene, triethylamine, and $(Me_3Si)_2NH$. The solid residue (0.80 g) consisted of $AlCl_3{\cdot}NEt_3$ complex, as determined from comparison of its infrared spectrum with that of an authentic sample.

Reaction of the $AlCl_3{\cdot}NEt_3$ Complex with $LiN(SiMe_3)_2$. To a stirred solution of $AlCl_3{\cdot}NEt_3$ (1.40 g, 6.0 mmol) in benzene (5 mL) was added the lithium salt (1.00 g, 6.0 mmol) in benzene (10 mL) over a period of 10 min. After standing at room temperature for 3 days, the cloudy solution was evaporated in vacuo. The residue (2.26 g) was treated with benzene. The insoluble LiCl (240 mg, 96% yield) was filtered off. The solid (1.99 g, 92.6% yield) recovered after benzene removal was crystallized from hexane, giving 1.44 g (67.0% yield; mp 104-106 °C) of $AlCl_2N(SiMe_3)_2{\cdot}NEt_3$. Another recrystallization from hexane gave 0.66 g (mp 105-106 °C). Anal. Calcd for $C_{12}H_{33}AlCl_2N_2Si_2$: C, 40.10; H, 9.25; Al, 7.51; Cl, 19.73; N, 7.79. Found: C, 39.60; H, 9.02; Al, 7.21; Cl, 20.2; N, 7.91. Infrared spectrum (cm^{-1}, KBr plates): 2988 (m), 2950 (m), 2900 (m), 1452 (m), 1398 (w), 1388 (w), 1253 (s), 1178 (m), 1167 (w), 1156 (m), 1082 (m), 1031 (m), 1006 (w), 900 (s, br), 865 (s, br), 841 (s, br), 766 (m), 731 (m), 713 (m), 678 (m), 667 (m), 620 (w), 490

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