Inorg. Chem. **1987**, *26*, 4309–4311 **4309**

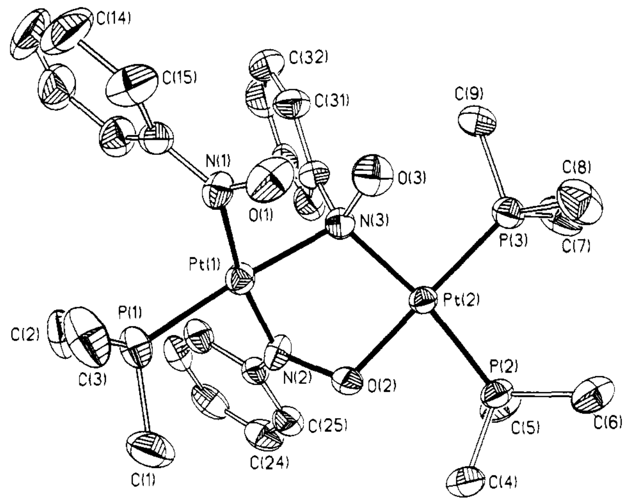
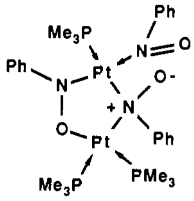


Figure 1. ORTEP diagram of complex **2** showing thermal ellipsoids at 50% probability. Key bond lengths (Å): Pt(1)⋯Pt(2), 3.502 (1); Pt(1)–N(1), 2.034 (10); Pt(1)–N(2), 1.976 (11); Pt(1)–N(3), 2.112 (11); Pt(1)–P(1), 2.231 (4); Pt(2)–N(3), 2.126 (11); Pt(2)–P(2), 2.243 (4); Pt(2)–P(3), 2.249 (4); Pt(2)–O(2), 2.043 (8); N(2)–O(2), 1.433 (15); N(1)–O(1), 1.296 (14); N(3)–O(3), 1.428 (27). Key bond angles (deg): P(1)–Pt(1)–N(1), 95.9 (3); P(1)–Pt(1)–N(2), 92.5 (3); N(1)–Pt(1)–N(3), 88.5 (4); N(2)–Pt(1)–N(3), 83.0 (4); P(2)–Pt(2)–P(3), 96.0 (1); P(2)–Pt(2)–O(2), 83.5 (3); P(3)–Pt(2)–N(3), 93.2 (3); N(3)–Pt(2)–O(2), 87.2 (4); Pt(1)–N(1)–O(1), 115.9 (8); Pt(1)–N(1)–C(16), 126.8 (7); Pt(1)–N(2)–O(2), 110.4 (7); O(2)–N(2)–C(26), 116.1 (9); Pt(1)–N(2)–C(26), 132.9 (9); O(3)–N(3)–C(36), 106.6 (15); Pt(1)–N(3)–Pt(2), 111.4 (5); Pt(2)–O(2)–N(2), 110.1 (7); O(1)–N(1)–C(16), 117.3 (9).

of 5 mL of Et_2O produced black crystals of a complex with the unusual stoichiometry[16] $Pt_2(PhNO)_3(PMe_3)_3$ (**2**) as the only isolable product (10% yield). This complex is not soluble in common organic solvents. Solid-state magnetic measurements of this compound using a vibrating-sample magnetometer[17] revealed that it is diamagnetic ($\mu_{eff} < 0.1\ \mu_B$). Complex **2** does not form by the direct reaction between PhNO and **1**.

The molecular structure[18] of complex **2**, shown in Figure 1, exhibits three distinct modes of platinum–nitroso bonding. The platinum atoms with two bridging nitroso groups form a puckered five-membered ring. The geometry about each platinum atom is square planar. The bridging η^1-nitroso group exhibits an N(3)–O(3) bond distance of 1.43 (3) Å. This is much longer than the N–O double bond of nitrosocyclohexane (1.27 Å)[5] and suggests a single bond, as does the O(3)–N(3)–C(36) angle of 106.6 (15)°. The bridging η^2-nitroso group also exhibits an N(2)–O(2) single-bond length of 1.43 (1) Å, similar to that of 1.410 (7) Å in $Pt(\eta^2\text{-}ONPh)(PPh_3)_2$.[11] These are among the longest distances recorded for nitrogen–oxygen bonds.[9,10] The third nitroso group replaces one phosphine ligand on Pt(1). The N(1)–O(1) distance of 1.30 (1) Å indicates retention of the N–O double bond and a dative bond of an electron pair on N(1) to Pt(1). The central, five-membered ring is severely puckered at N(2); the other four ring atoms deviate from planarity by 0.05–0.07 Å, whereas N(2) is displaced by 0.85 Å. A bonding scheme for **2** consistent with these results places each platinum atom in a square-planar, 16-electron environment, views each bridging nitrosobenzene as a dianionic ligand, and results in a diamagnetic complex:



Complex **2** is to our knowledge the first example of a compound containing three modes of nitroso–metal bonding. It is also the first structural determination of a μ-η^2-RNO group where the nitrogen and oxygen atoms bridge two metal atoms. In previous examples of bridging η^2-RNO groups, the nitrogen atom binds to both metal centers, while the oxygen atom coordinates to one metal.[8-10] Complex **2** shows no bonding contacts between Pt(2) and N(2). The structure of the η^2-PhNO group thus resembles that found in nitrone complexes IV.[12] These results also support the hypothesis that metal nitrosoarene complexes may be intermediates in the reduction of nitroarene compounds by transition-metal hydrides.

Acknowledgment. This research was supported by the U.S. Army Research Office (Grant DAAG29-85-K-0263). We thank Johnson Matthey for a sample of K_2PtCl_4 under their metal loan program.

Supplementary Material Available: Listings giving the details of the crystallographic data collection, positional and thermal parameters, and interatomic distances and angles (7 pages); a listing of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

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(15) Simulations of the EPR spectra of this solution suggest a complex of platinum containing two phosphorus atoms and one nitrogen atom. This species could not be isolated from the solution and may be an impurity present at a small concentration.

(16) Anal. Calcd for $Pt_2P_3N_3O_3C_{27}H_{42}$: C, 34.32; H, 4.86; N, 4.24. Found: C, 34.50; H, 4.51; N, 4.47. IR (Nujol): 1525 (s), 1345 (s), 950 (s), 850 (s), 700 cm^{-1} (s).

(17) (a) Foner, S. *Rev. Sci. Instrum.* **1959**, *30*, 548. (b) Determined by William Higgins, Department of Chemistry, University of California, San Diego.

(18) For $C_{27}H_{42}N_3O_3P_3Pt_2$ (293 K): monoclinic, $P2_1/n$, a = 10.329 (3) Å, b = 16.123 (5) Å, c = 20.120 (6) Å, β = 102.62 (2)°, V = 3269 (1) Å^3, Z = 4, D(calcd) = 1.909 g cm^{-3}, μ(Mo Kα) = 92.1 cm^{-1}, λ = 0.71073 Å, T(max)/T(min) = 0.067/0.040. From a black, well-formed crystal (0.28 × 0.28 × 0.30 mm) were collected 6170 reflections ($4° \leq 2\theta \leq 50°$) (Nicolet R3m), of which 5761 were independent (R(int) = 2.17%) and 3814 with $F_o > 4\sigma(F_o)$ were considered observed and corrected for absorption (XABS). The two Pt atoms were located by direct methods. Rigid-body constraints were applied to the phenyl rings. With all non-hydrogen atoms anisotropic and all hydrogen atoms as idealized isotropic contributions: $R(F)$ = 4.46%, $R_w(F)$ = 6.04%, GOF = 0.975, Δ/σ = 0.046, $\Delta(\rho)$ = 1.18 e/Å^3, N_o/N_v = 12.4. All computations, except XABS, used SHELXTL software (Nicolet Corp., Madison, WI); XABS calculates an empirical absorption tensor from an expression relating F_o and F_c (H. Hope, University of California at Davis).

(19) Presumably two molecules of water and one molecule of trimethylphosphine oxide are formed in this reaction, but they could not be detected in the paramagnetic reaction mixture.

Reactions of Phosgene with Oxide-Containing Species in a Room-Temperature Chloroaluminate Ionic Liquid

Sir:

We wish to report the facile in situ conversion of transition-metal oxide chloride complexes to chloride complexes in a basic room-temperature chloroaluminate ionic liquid and the apparent removal of all traces of oxide-containing species from this solvent with phosgene ($COCl_2$). Familiar examples of room-temperature chloroaluminate ionic liquids include aluminum chloride–1-(1-butyl)pyridinium chloride ($AlCl_3$–BupyCl) and aluminum chloride–1-methyl-3-ethylimidazolium chloride ($AlCl_3$–MeEtimCl).[1]

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The basic[2] compositions of these ionic liquids have been shown to be excellent solvents in which to conduct electrochemical and spectroscopic investigations[3] of anionic transition metal chloride complexes.[4] However, the inevitable presence of oxide in these solvents often complicates these studies. This adventitious oxide, which is represented here for convenience as "Al–O–Cl",[5] reacts with any transition-metal solute that exhibits an appreciable affinity for oxide and limits the species that can be studied. For example, both $[TiCl_6]^{2-}$[6] and $[MoCl_6]^{2-}$[7] exist in equilibrium with "Al–O–Cl" in these ionic liquids with the concomitant formation of their oxide chloride complexes $[MOCl_4]^{2-}$, where M = Ti or Mo. The equilibrium constant for the reaction involving $[TiCl_6]^{2-}$ was found to be approximately 9×10^2 at 40 °C in the basic $AlCl_3$–BupyCl ionic liquid.[6]

A sensitive method for estimating the oxide level in basic room-temperature chloroaluminates is based on electrochemical determination of the ratio of $[TiCl_6]^{2-}$ to $[TiOCl_4]^{2-}$ in the melt.[8] Using this method, we find that most room-temperature chloroaluminate melts are typically 3–5 mM in oxide in spite of meticulous purification of the melt components and conscientious handling of both the components and prepared melts in either a glovebox in a high-quality moisture- and oxygen-free nitrogen atmosphere or a vacuum-sealed cell. Other workers report similar difficulties with oxide impurities in chloroaluminate melts.[8]

$COCl_2$ has long been used to convert certain metal oxides and sulfides to their pure metal chlorides at high temperatures.[9] Recently, Seddon and co-workers[10] added $COCl_2$ to a room-temperature ionic liquid containing "Al–^{17}O–Cl", which was produced by the dissolution of $H_2{}^{17}O$, and obtained ^{13}C and ^{17}O NMR and mass spectrometric evidence for the formation of ^{17}O-labeled CO_2. They suggested that $COCl_2$ may be used to remove oxide impurities from these melts. This report prompted us to investigate in situ reactions of $COCl_2$ with selected transition-metal oxide chloride complexes in these ionic liquids in order to determine the overall efficacy of $COCl_2$ for removing oxide from these solvents, the relative ability of this reagent to convert oxide chloride complexes to their pure chloride complexes, the electrochemical characteristics of dissolved $COCl_2$, and the ease with which excess $COCl_2$ can be removed from the melt.

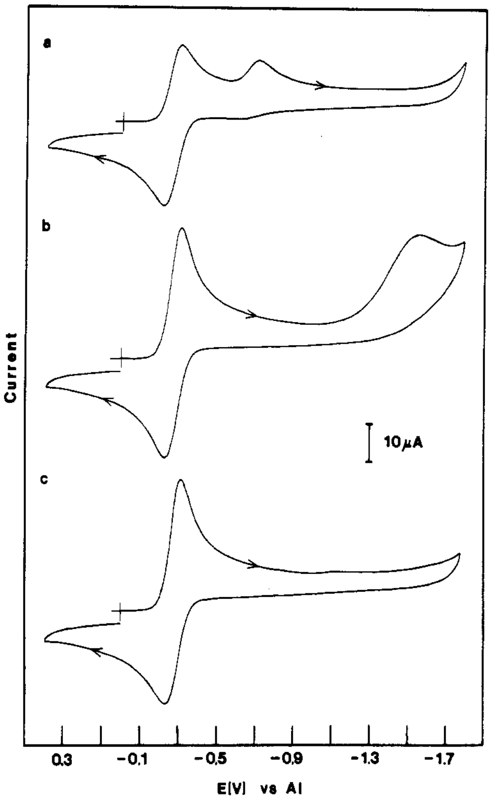

Figure 1. Cyclic voltammograms of a 14.2 mM solution of titanium(IV) chloride in the 49.0:51.0 $AlCl_3$–MeEtimCl ionic liquid at 28 °C: (a) melt 5.1 mM in oxide; (b) melt after the addition of excess $COCl_2$ to the solution in part a; (c) melt after removal of the excess $COCl_2$ from the solution in part b. The sweep rate was 50 mV s^{-1}.

Safety caution! Phosgene is an insidiously poisonous gas and should be handled only in a well-ventilated fume hood.

A cyclic voltammogram[11] for a solution of titanium(IV) chloride in the 49.0:51.0 mol % $AlCl_3$–MeEtimCl melt, which contains 5.1 mM oxide,[12] is shown in Figure 1a. The voltammetric reduction waves in this figure are typical of those observed for a melt containing both the $[TiCl_6]^{2-}$ and $[TiOCl_4]^{2-}$ complex ions.[6] $COCl_2$ is very soluble in the melt, and when a quantity of $COCl_2$ in excess of the total number of moles of titanium(IV) is added to this solution, the reduction wave for the oxide chloride species, which appears at a voltammetric peak potential $E_p{}^c$ of about −0.72 V, *disappears* in a matter of minutes while the reduction wave for the $[TiCl_6]^{2-}$ ($E_p{}^c = -0.31$ V) *increases* substantially (Figure 1b). In addition, a broad wave at $E_p{}^c = -1.55$ V, which must arise from the irreversible reduction of dissolved $COCl_2$ since CO_2 appears to be electroinactive in these melts, is now evident. If the melt is warmed gently and then evacuated continuously at 0.025 Torr for 1 h, a cyclic voltammogram (Figure 1c) indicates that both the oxide chloride complex and the excess $COCl_2$ are absent.

As a further test, we prepared a solution of niobium(V) chloride in 49.0:51.0 mol % $AlCl_3$–MeEtimCl melt that contained a large

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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.

(2) Basic melts contain a molar excess of the organic salt relative to $AlCl_3$ while acidic melts contain a molar excess of $AlCl_3$ relative to the organic salt; the excess chloride ion in basic melt can act as a Lewis base (cf. ref 1).

(3) Appleby, D.; Hussey, C. L.; Seddon, K. R.; Turp, J. E. *Nature* (*London*) **1986**, *323*, 614.

(4) For a representative list of the transition-metal ions that have been studied see: Sun, I.; Ward, E. H.; Hussey, C. L.; Seddon, K. R.; Turp, J. E. *Inorg. Chem.* **1987**, *26*, 2140 and references therein.

(5) The exact nature of the oxide-containing species in room-temperature haloaluminate ionic liquids is not known at the present time. $[AlOCl_2]^-$ has been inferred from potentiometric measurements in basic $AlCl_3$–NaCl melt that contained $BaCO_3$ as the oxide source (Gilbert, B.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1978**, *100*, 2725). However, in subsequent studies of this system in which the weak acidity of the Ba^{2+} ion was taken into account, $[Al_2OCl_5]^-$ was suggested to be the major oxide-containing component (Taulelle, F.; Piolet, C.; Tremillon, B. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *134*, 131. Taulelle, F.; Tremillon, B.; Gilbert, B. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *134*, 141). Species of the type $(AlOCl)_2([AlCl_4]^-)_m$ were proposed in basic, neutral, and acidic $AlCl_3$–NaCl melts on the basis of potentiometric and cryoscopic results (Zachariassen, K.; Berg, R. W.; Bjerrum, N. J.; von Barner, J. H. *J. Electrochem. Soc.* **1987**, *134*, 1153). Data from a SIMS study of the $AlCl_3$–MeEtimCl system, which was conducted in the presence of atmospheric moisture, suggested the presence of the $[Al_2OCl_5]^-$, $[Al_2Cl_6OH]^-$, and $[Al_3Cl_6O_2]^-$ ions (Franzen, G.; Gilbert, B. P.; Pelzer, G.; DePauw, E. *Org. Mass Spectrom.* **1986**, *21*, 443).

(6) Linga, H.; Stojek, Z.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 3754.

(7) Scheffler, T. B.; Hussey, C. L.; Seddon, K. R.; Kear, C. M.; Armitage, P. D. *Inorg. Chem.* **1983**, *22*, 2099.

(8) Stojek, Z.; Linga, H.; Osteryoung, R. A. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *119*, 365. A similar analytical method based on tantalum(IV) has been demonstrated in the $AlCl_3$–NaCl melt (Laher, T. M.; McCurry, L. E.; Mamantov, G. *Anal. Chem.* **1985**, *57*, 500).

(9) *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed.; Mark, H. F., Othmer, D. F., Overberger, C. G., Seaborg, G. T., Eds.; Wiley: New York, 1982; Vol. 17, pp 417–418.

(10) Abdul-Sada, A. K.; Avent, A. G.; Parkington, M. J.; Seddon, K. R.; Welton, T.; Ryan, T. A. *J. Chem. Soc., Chem. Commun.*, in press.

(11) Cyclic voltammograms were recorded at a glassy-carbon disk electrode (area = 0.071 cm^2) in an vacuum-tight cell with the equipment described in ref 4. All potentials are reported versus a reference electrode consisting of an aluminum wire immersed in the 66.7–33.3 mol % $AlCl_3$–MeEtimCl melt, separated from the bulk melt by means of a fine-porosity fritted Pyrex membrane.

(12) Oxide can be introduced into the melt by the dissolution of Li_2CO_3 (cf. ref 6).

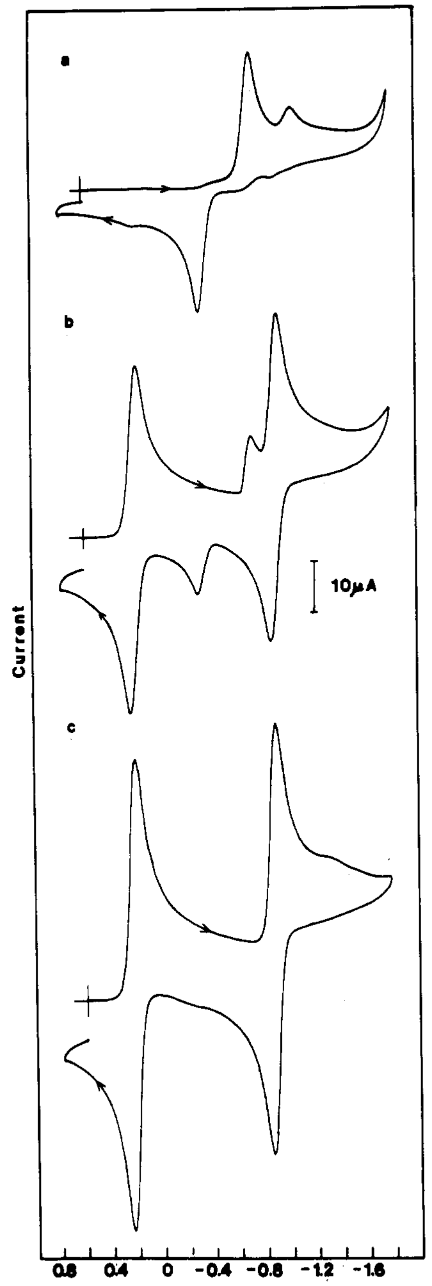

Figure 2. Cyclic voltammograms of a 13.6 mM solution of niobium(V) chloride in the 49.0:51.0 mol % $AlCl_3$–MeEtimCl ionic liquid at 28 °C: (a) melt containing a stoichiometric excess of oxide relative to the niobium(V); (b) melt after the addition of a small amount of $COCl_2$ to the solution in part a; (c) melt after treatment of the solution in part b with a large excess of $COCl_2$ relative to the niobium(V) chloride followed by removal of the excess $COCl_2$. The sweep rate was 50 mV s^{-1}.

excess of oxide relative to the niobium(V). We find that niobium(V) exhibits a much greater affinity for oxide in these melts than either molybdenum(IV)[7] or titanium(IV)[6] i.e., the reaction between niobium(V) and "Al–O–Cl" appears to go to completion.[13] A cyclic voltammogram of this solution is shown in Figure 2a, and it is typical of that found when niobium(V) is completely converted to a dimeric oxide chloride species.[13] Figure 2b shows a cyclic voltammogram of this solution after a small amount of $COCl_2$ has been added. Several new reduction and oxidation waves are apparent while the reduction and oxidation waves for the oxide chloride complex located at ca. $E_p^c = -0.72$ and $E_p^a = -0.32$ V, respectively, are decreased in size relative to those for the original solution (Figure 2a). A large excess of $COCl_2$ relative to the niobium(V) was then added to this solution, the solution was stirred for approximately 1 h under gentle heating, and then the excess $COCl_2$ was removed by evacuation (vide supra). A voltammogram of this solution (Figure 2c) shows only two reversible voltammetric waves with half-wave potentials of ca. +0.23 and −0.87 V. These waves are identical with those observed for the $[NbCl_6]^{-/2-}$ and $[NbCl_6]^{2-/3-}$ redox reactions,[13] respectively. Figure 2c suggests that $[NbCl_6]^-$ is the only significant niobium(V) species now present in the solution. The reduction and oxidation waves at $E_p^c = -0.72$ and $E_p^a = -0.32$ V that are found in the original oxide-loaded solution (Figure 2a) are no longer present.

Taken together, these results suggest that $COCl_2$ is capable of effecting complete removal of oxide from basic room-temperature chloroaluminate ionic liquids at or near room temperature. Also, it appears that $COCl_2$ can serve as a facile reagent for the in situ conversion of oxide chloride complexes to chloride complexes, even in the case of those transition-metal species with a very large affinity for oxide.

Experiments similar to those reported above were conducted with thionyl chloride ($SOCl_2$) and the titanium(IV) system. However, the results obtained were less satisfactory than those for $COCl_2$. $SOCl_2$ appears to react with and remove the $[TiOCl_4]^{2-}$ complex, but a new species different from $[TiCl_6]^{2-}$ is produced during the process. In addition, $SOCl_2$, which is less volatile than $COCl_2$, is much more difficult to remove from the melt than $COCl_2$.

The ability to eliminate oxide from room-temperature ionic liquids should be of great value both to researchers who wish to use these melts as solvents for the investigation of transition metal chloride and oxide chloride chemistry and to those who are studying the speciation of oxide-containing anions in these melts. These results may also be applicable to the alkali-metal chloroaluminates. Additional studies concerning the stoichiometry and kinetics of the reactions of $COCl_2$ with oxide-containing species in room-temperature chloroaluminate ionic liquids are in progress.

Acknowledgment. We wish to acknowledge Dr. Kenneth R. Seddon, University of Sussex, U.K., for generously providing a preprint of his results and for helpful discussions and suggestions about our work. This research was supported by the National Science Foundation, Grant Nos. CHE-8412730 and CHE-8715464.

Registry No. $COCl_2$, 75-44-5; $AlCl_3$, 7446-70-0; MeEtimCl, 65039-09-0; $TiCl_4$, 7750-45-0; $[TiCl_6]^{2-}$, 16871-46-8; $[TiOCl_4]^{2-}$, 18177-78-1; $NbCl_5$, 10026-12-7; $[NbCl_6]^-$, 21640-06-2; $SOCl_2$, 7719-09-7; oxide, 16833-27-5.

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[13] A manuscript describing the chemistry and electrochemistry of various niobium chloride and oxide chloride complexes in basic $AlCl_3$–MeEtimCl is in preparation.