place of PCl₃ and 1 equiv of an alkyl Grignard is added in the last step, then the alkylphenylphosphines (Me₃Si)₂NP(Ph)R, (**4**, R = Me,[6] and **5**, R = Et[10]) are obtained.

Results and Discussion

Treatment of a suspension of lithium bis(trimethylsilyl)-amide in ether at −78 °C with phosphorus trichloride followed by the addition of 2 equiv of an alkyl Grignard reagent at 0 °C affords the [bis(trimethylsilyl)amino]dialkylphosphines **1–3** (eq 1). Similarly, the use of dichlorophenylphosphine and

$$(Me_3Si)_2NLi \xrightarrow{Et_2O}$$

$$\xrightarrow[\text{(2) 2RMgX, 0 °C}]{\text{(1) PCl}_3,\ -78\ °C} (Me_3Si)_2NPR_2 \quad (1)$$

1, R = Me
2, R = Et
3, R = CH₂SiMe₃

$$\xrightarrow[\text{(2) RMgX, 0 °C}]{\text{(1) PhPCl}_2,\ -78\ °C} (Me_3Si)_2N\!\!-\!\!P\!\!\begin{array}{c}Ph\\R\end{array} \quad (2)$$

4, R = Me
5, R = Et
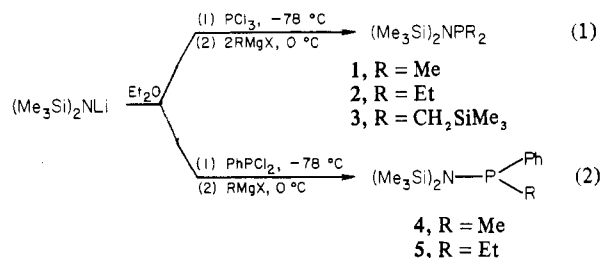
1 equiv of Grignard reagent permits the convenient preparation of the corresponding alkylphenylphosphines **4** and **5** (eq 2). With the exception of some ³¹P chemical shifts (Table I), the characterization of these compounds has generally been reported in other papers[4a,6] describing their reactivity.

These reactions are easily carried out on large scales (ca. 1–2 mol) with unpurified commercial reagents. The products are obtained in relatively high yields (Table I) and good purity after a single vacuum distillation. Generally, the (silyl-amino)phosphines are colorless, foul-smelling liquids, which are sensitive to oxidation and hydrolysis on exposure to the air. Nevertheless, their thermal stability is satisfactory, and they can be stored indefinitely in tightly sealed containers.

This simple, "one-pot" synthesis is actually more general than is indicated here. For example, several different silyl-amines have been used,[5,6] and in favorable cases it is possible to obtain monoalkylated products, e.g., (Me₃Si)₂NP(Cl)-CH₂SiMe₃.[4a] In more recent studies[11] involving very sterically congested systems, however, we find that reduced (P–H) or coupled (P–P) products are often obtained. Details of this work will be reported in subsequent papers.

Registry No. **1**, 63744-11-6; **2**, 73270-05-0; **3**, 76946-90-2; **4**, 68437-87-6; **5**, 82482-33-5; (Me₃Si)₂NLi, 4039-32-1; PCl₃, 7719-12-2; MeBr, 74-83-9; EtBr, 74-96-4; Me₃SiCH₂Cl, 2344-80-1; PhPCl₂, 644-97-3.

(10) ¹H NMR data: **2**, δ 0.34 (Me₃Si, J_{PH} = 0.6 Hz), 1.14 (CH₃, J_{PH} = 16.0 Hz, J_{HH} = 7.5 Hz), 1.4–2.0 (CH₂, multiplet); **5**, 0.25 (Me₃Si, J_{PH} = 0.6 Hz), 1.33 (CH₃, J_{PH} = 18.0 Hz, J_{HH} = 7.2 Hz), 1.9–2.2 (CH₂, multiplet), 7.1–7.4 (Ph, multiplet).
(11) Papers in preparation.

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Electrochemical Separation of Zirconium from Hafnium Using Chloroaluminate Melts

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The separation of zirconium and hafnium, elements whose chemical properties are very similar, has attracted considerable

attention. A large number of methods such as fractional precipitation, fractional distillation, ion exchange, and selective extraction has been proposed.[2] Only partial success has been achieved by electrolysis from chloride–fluoride melts at 650–850 °C.[2] In the molten LiCl–KCl eutectic at 450 °C the formal potentials for the Zr(IV)/Zr(0) and Hf(IV)/Hf(0) couples are too close to achieve efficient separation of these elements.[3]

In a previous paper from our laboratory[4] it was reported that the electrochemical reduction of Zr(IV) in molten Al-Cl₃–NaCl (51–52 mol % AlCl₃) at 175–220 °C results in the formation of insoluble ZrCl₃ at ∼120 mV before the reduction of Al₂Cl₇⁻ ions.[5] The chemical reduction of Zr(IV) to Zr(III) in molten aluminum halides using zirconium or aluminum metal was studied by Larsen and co-workers.[6] These workers noted that under the same experimental conditions the rate of Hf(IV) reduction is slow, allowing partial separation of the two elements. In this paper we report on the electroreduction of Hf(IV) in chloroaluminate melts of similar compositions and on the electrochemical separation of zirconium from hafnium using low-melting chloroaluminate melts.

Experimental Section

Melt preparation and other experimental procedures have been reported previously.[4,5,7,8] ZrCl₄ (from Alfa) and HfCl₄ (from Cerac) were purified by several sublimations under vacuum at 205 °C. X-ray fluorescence analyses were done with use of monochromatized Ag Kα radiation for excitation of the K peaks of Zr and the L peaks of Hf. Spectra were recorded with a Si(Li) energy-dispersive detector. Data were interpreted quantitatively by the method of fundamental constants.[9] The L peaks of hafnium are clearly resolved from the zirconium K peaks. Hf in a Zr matrix can be detected at concentrations less than 10 ppm.

Results and Discussion

1. Electrochemical Behavior of Hf(IV) in AlCl₃–NaCl Melts. Addition of HfCl₄ to AlCl₃–NaCl melts (ranging in composition from 50.3 to 52 mol % AlCl₃) resulted in a poorly defined voltammetric reduction wave that occurs at potentials somewhat *more negative* than the reduction of Al₂Cl₇⁻.[5] The cyclic voltammograms exhibit either one or two reoxidation peaks depending on the switching potential, concentration of Hf(IV), and melt acidity. The reoxidation peak at more negative potentials (∼+0.1 V with respect to an Al(III)/Al reference electrode in the melt of the same composition) is observed when the Hf(IV) concentration is small compared to that of Al₂Cl₇⁻. The reoxidation peak at more positive potentials (∼0.2 V with respect to the same reference electrode) increases with the Hf(IV) concentration.

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Table I

molality of solutes × 10²		initial atomic	atomic ratio of
Zr(IV)	Hf(IV)	ratio of Hf/Zr	Hf/Zr in product
6	6	1	0.005
0.98	0.94	0.96	0.003
1.18	0.48	0.41	Hf not detectable

For a determination of the nature of the reduction product, the black precipitate observed at the electrode after electrolysis at <0 V vs. the Al(III)/Al reference electrode was treated with molten Al_2Cl_6 (to remove remaining NaCl) and filtered. The residual Al_2Cl_6 was removed by sublimation under vacuum; the shiny black precipitate was examined by powder X-ray diffraction. The powder pattern showed that the precipitate was either Al_3Hf[10] or a mixture of Al_3Hf and aluminum. Thus a simultaneous reduction of Hf(IV) and Al(III) is observed; depending on the ratio of Hf(IV) to $Al_2Cl_7^-$ and the potential of the electrode, the product is either Al_3Hf or a mixture of that compound with aluminum.

2. Electrochemical Separation of Zirconium from Hafnium. Since the difference between the reduction of Zr(IV) and $Al_2Cl_7^-$ increases slightly when the chloroaluminate melts become less acidic, melts containing ~50.5 mol % $AlCl_3$ were used for the separation experiments. The solubility of $HfCl_4$ in these melts at 175 °C is ~8 × 10^{-2} m. In a typical controlled-potential electrolysis experiment 50 g of an $AlCl_3$–NaCl (50.5 mol % $AlCl_3$) melt containing ~10^{-2} m each of $ZrCl_4$ and $HfCl_4$ was used. The potential of a tungsten spiral cathode (area 3.5 cm²) was controlled at 0.09 V vs. the Al(III)/Al reference electrode in the melt of the same composition. A reticulated vitreous carbon cylinder (4 cm long, 0.5 cm in diameter) was used as an anode; it was separated from the main compartment by a Pyrex frit of medium porosity. After 14 h of electrolysis at 175 °C voltammograms obtained at a tungsten microelectrode indicated that most of the Zr(IV) was reduced. The product was scraped from the electrode; residual $ZrCl_4$, $HfCl_4$, and Al_2Cl_6 were removed by sublimation at 205 °C. The product after sublimation was examined by X-ray fluorescence. This analysis showed that the atomic ratio of Hf/Zr decreased from 0.96 before the electrolysis to 0.003 in the product of the electrolysis. The Raman spectrum of the product showed a sharp line at 212 cm⁻¹, characteristic of $ZrCl_3$.[4] Results of three experiments are given in Table I. An excess of charge was involved in the reduction step; for example, in the experiment described above 164 coulombs were consumed compared to the expected value of 47 coulombs. It is likely that some of the chlorine produced at the anode reached the cathode to oxidize the $ZrCl_3$ product.

In preliminary experiments using platinum as the anode, the black cathodic deposit contained significant amounts of platinum. Clearly the use of platinum as an anodic counterelectrode in molten chloroaluminates should be avoided. In summary, we have demonstrated that hafnium-free zirconium can be produced by controlled-potential electrolysis using slightly acidic chloroaluminate melts. The separation factors achieved electrochemically are better than those achieved previously by chemical reduction.[6]

Registry No. Zr, 7440-67-7; Hf, 7440-58-6.

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Synthesis of Substituted Octahedral Anions of Chromium(III), [R₄N][*cis*-Cr(L–L)X₄], and the Nature of Cr(L–L)₁.₅X₃ (L–L = Diphosphine or Diarsine; X = Cl, Br)

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Octahedral halo anions MX_6^{n-} are known for most transition metals, but substituted analogues containing neutral mono- (L) or bidentate (L–L) ligands are rare, especially in the 3d series.[2] The green [Ph₄P][*trans*-CrL₂Cl₄] (L = PEt₃, P-*n*-Bu₃) were obtained from [CrL₂Cl₃]₂ and Ph₄PCl in CH_2Cl_2.[3] During a study of chromium(III) complexes with soft donor ligands, as a prelude to examining small-molecule (O_2, NO, etc.) binding by chromium complexes, we isolated the *cis*-[Cr(L–L)X₄]⁻ (X = Cl, Br) ions as R₄N⁺ salts. Nyholm[4] obtained materials of empirical formula Cr(das)₁.₅X₃ (das = *o*-C₆H₄(AsMe₂)₂) from chromium(III) halides and the ligand in moist acetone or alcohol, for which the three most likely formulations are [Cr(das)₂X₂][Cr(das)X₄], [Cr(das)₃][CrX₆], and (das)X₃Cr(das)CrX₃(das). Since treatment with $HClO_4$ converted Cr(das)₁.₅X₃ into [Cr(das)₂X₂]ClO₄, and attempts to prepare [Cr(das)₃]³⁺ failed, Nyholm favored the first formulation. It should be noted however that a ligand-bridged dimeric structure was proposed for Cr(Ph₂PCH₂-CH₂PPh₂)₁.₅X₃·*n*H₂O.[5] Our synthesis of [Cr(L–L)X₄]⁻ led us to reinvestigate the Cr(das)₁.₅X₃ complexes.

Results and Discussion

The reaction of CrCl₃(THF)₃, *n*-Pr₄NCl, and the appropriate bidentate ligand (L–L) in dry CH_2Cl_2 produced the tetrapropylammonium *cis*-tetrachloro(ligand)chromate(III), [Pr₄N][*cis*-CrCl₄(L–L)] (L–L = *o*-C₆H₄(PMe₂)₂, *o*-C₆H₄-(AsMe₂)₂, Ph₂PCH₂CH₂PPh₂, *cis*-Ph₂PCH=CHPPh₂, *cis*-Ph₂AsCH=CHAsPh₂), as blue powders. The [Ph₃PCH₂Ph][Cr(*o*-C₆H₄(AsMe₂)₂)Br₄] was obtained similarly (Table I). Attempts to isolate these anions using smaller cations were unsuccessful. It should be noted that reaction of CrBr₃(THF)₃ with R₄NBr in a 1:1 ratio in CH_2Cl_2 produces deep green solutions that may contain [R₄N][Cr(THF)₂Br₄], although we have been unable to isolate these. The complexes are 1:1 electrolytes in 10^{-3} M nitromethane solutions and have magnetic moments ca. 3.88 μ_B as expected for d³ Cr(III). The [*n*-Pr₄N][Cr(*o*-C₆H₄(PMe₂)₂)Cl₄] complex is deliquescent, but the others are stable to moist air for short periods of time but are fairly readily decomposed by water or alcohols in solution. In spite of this, attempts to displace one halide from [Cr(*o*-C₆H₄(AsMe₂)₂)Cl₄]⁻ by stirring or heating CH_2Cl_2 or toluene solutions with monodentate ligands such as PhMe₂P, PPh₃, AsMe₂Ph, or MePhS (L), failed to give [Cr(*o*-C₆H₄-(AsMe₂)₂)LCl₃], most of the starting complex being recovered unchanged.

The far-IR spectra of a *cis*-[CrCl₄(L–L)]⁻ ion should show four chromium–chlorine stretching vibrations (2A₁ + B₁ + B₂), and despite the complications produced by absorptions of L-L in the same region, three or four bands were generally

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