that 1:1 and 1:2 $SnCl_4$ adducts of the Pt complexes readily form in solution.

As in the case of the Ni and Pd complexes, in situ reaction of the $SnCl_4$ adducts in the ESR in situ cell at room temperature produced strong ESR signals consisting of a strong central line flanked by two satellites. When the solutions were frozen, the spectra became anisotropic, and evidence of the satellite lines remained in the frozen-solution spectrum. The solution spectrum for the 1:1 complex is shown in Figure 3a. In this case the satellite lines show a distinct inequality in intensity (particularly for the 1:1 complex), and the intensities are too high to be due to ^{117,119}Sn hyperfine coupling. The closest simulations of the observed spectra were obtained by assuming that the satellites are due to coupling with ^{195}Pt (33.7%, $I = {}^1/_2$), although the inequality in the intensities cannot be explained in this way. The frozen-solution spectrum of the 1:1 complex (Figure 3) appears to be axially symmetric, with the satellite structure resolved in the perpendicular region only. The coupling constant in this region is about 23×10^{-4} cm^{-1}, compared to 11.0×10^{-4} cm^{-1} in the isotropic solution spectrum, this value being obtained by a simulation of the spectrum with both the isotopes of platinum being included. Thus it appears that relative signs of the perpendicular and parallel components of the hyperfine interaction are of opposite sign (for example if a_{isotopic} was positive and $A_\perp$ positive, $A_\parallel$ would have to be negative to give $a_{\text{iso}} = 11 \times 10^{-4} = (2A_\perp + A_\parallel)/3 = (2 \times 23 \times 10^{-4} + (-13 \times 10^{-4}))/3$. This feature has been observed in other Pt radical anonic species.[15]

Registry No. I, 60240-65-5; $[Ni(S_2C_2O_2)_2]^{2-}$, 49871-88-7; $[Ni(S_2C_2O_2)_2(SnCl_4)]^{2-}$, 82374-22-9; $[Pd(S_2C_2O_2)_2]^{2-}$, 37578-58-8; $[Pd(S_2C_2O_2)_2(SnCl_4)]^{2-}$, 82374-23-0; $[Pd(S_2C_2O_2)_2(SnCl_4)_2]^{2-}$, 82374-24-1; $[Pt(S_2C_2O_2)_2]^{2-}$, 46165-21-5; $[Pt(S_2C_2O_2)_2(SnCl_4)]^{2-}$, 82374-25-2; $[Pt(S_2C_2O_2)_2(SnCl_4)_2]^{2-}$, 82374-26-3; $[Ni(S_2C_2O_2)_2(SnCl_4)]^{3-}$, 82374-27-4; $[Ni(S_2C_2O_2)_2(SnCl_4)_2]^{3-}$, 82444-31-3; $[Pd(S_2C_2O_2)_2(SnCl_4)]^{3-}$, 82374-28-5; $[Pd(S_2C_2O_2)_2(SnCl_4)_2]^{3-}$, 82444-32-4; $[Pt(S_2C_2O_2)_2(SnCl_4)]^{3-}$, 82374-29-6; $[Pt(S_2C_2O_2)_2(SnCl_4)_2]^{3-}$, 82444-33-5.

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Contribution from the Department of Chemistry,
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Synthesis of (Silylamino)phosphines by the Wilburn Method†

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The importance of (silylamino)phosphines, e.g. $(Me_3Si)_2NPMe_2$, as reagents for the synthesis of organosubstituted phosphazene polymers[1] and other novel organophosphorus compounds[2,3] is now well established. Interest in these and related Si–N–P compounds as ligands in organometallic complexes[4] is also developing, and many other synthetic applications are likely to follow.

Most (silylamino)phosphines are prepared from commercially available reagents by a simple "one-pot" synthesis first utilized by Wilburn.[5,6] In earlier papers[4a,6] we have described the preparation of a few specific compounds on relatively small scales (50–100 mmol). Because of the synthetic value of these reagents, however, we report here the complete details for the convenient, large-scale (ca. 1–2 mol) synthesis of (silylamino)phosphines via the Wilburn procedure.

Table I. Physical and ^{31}P NMR Data for Some (Silylamino)phosphines, $(Me_3Si)_2NPRR'$

compd	R	R′	bp, °C (*P*, mm)	yield, %	$\delta(^{31}P)^a$
1	Me	Me	55–60 (4)	75	31.7
2	Et	Et	68–69 (1.6)	71	57.2
3	CH_2SiMe_3	CH_2SiMe_3	80–85 (0.3)	67	42.9
4	Me	Ph	90–95 (0.8)	81	37.6
5	Et	Ph	85–90 (0.1)	59	50.9

[a] Chemical shifts downfield from external H_3PO_4, measured in $CDCl_3$ solution.

Experimental Section

Materials and General Procedures. All reactions and other manipulations were carried out under an atmosphere of dry nitrogen. Ethyl ether was distilled from calcium hydride prior to use. The following reagents were obtained from commercial sources: PCl_3, $PhPCl_2$, $(Me_3Si)_2NH$, *n*-BuLi, MeMgBr, and EtMgBr. The silylmethyl Grignard Me_3SiCH_2MgCl was prepared as needed according to the published procedure.[7]

Preparation of [Bis(trimethylsilyl)amino]dimethylphosphine (1). A 5-L, three-necked flask equipped with a paddle stirrer, a N_2 flow, and a 500-mL addition funnel was charged with $(Me_3Si)_2NH$ (1.0 mol, 209 mL) and Et_2O (ca. 1.0 L). One bottle of *n*-BuLi (ca. 1.0 mol, 2.0 M in hexane) was transfered to the addition funnel under nitrogen pressure by means of a flexible, double-ended syringe needle[8] and was added dropwise to the stirred silylamine solution at 0 °C. The addition funnel was then washed with ca. 30 mL of ether and charged with PCl_3 (1.0 mol, 87.2 mL). After the $LiN(SiMe_3)_2$ mixture was stirred at room temperature for ca. 90 min, it was cooled to −78 °C, and the PCl_3 was added dropwise. Upon completion of the addition, the −78 °C bath was removed. During the warm-up period the orange solution gradually turned white as LiCl precipitated. After ca. 1 h the mixture was cooled to 0 °C, and the addition funnel was again rinsed with Et_2O. Two bottles of MeMgBr (ca. 2.0 mol, 3.0 M in Et_2O) were transfered via the double-ended needle to the addition funnel and added dropwise to the stirred reaction mixture at 0 °C over ca. 2 h. The mixture was stirred for 3 h and then allowed to stand overnight at room temperature. Under a stream of N_2, the supernatant solution was decanted into a large one-necked flask. The solids were washed with two 500-mL portions of Et_2O, and the washings were added to the first decantate. Most of the solvent was removed under reduced pressure, and ca. 500 mL of hexane was added to facilitate precipitation of the remaining Grignard salts. Filtration under N_2 followed by solvent removal left a viscous orange residue. Distillation through a short- or semishort-path distilling head gave $(Me_3Si)_2NPMe_2$[5,6] as a colorless liquid (166 g, 75% yield,[9] bp 55–60 °C (4 mm)) of high purity based on ^{1}H and ^{31}P NMR spectra.

Preparation of Other (Silylamino)phosphines. The same procedure using either commercial EtMgBr or freshly prepared Me_3SiCH_2MgCl[7] affords the corresponding dialkylphosphines $(Me_3Si)_2NPR_2$ (**2**, R = Et,[10] and **3**, R = CH_2SiMe_3[4a]). Alternatively, if $PhPCl_2$ is used in

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† Dedicated to the memory of Dr. James C. Wilburn, 1953–1981.

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(9) Yields up to 86% have been obtained by more careful and repeated washing of the solids.

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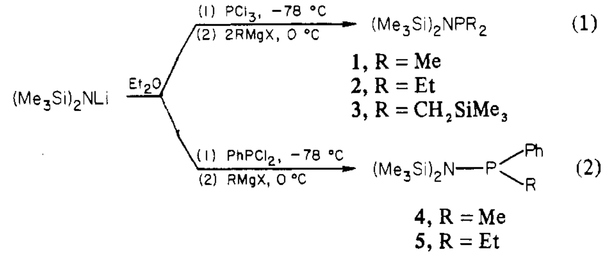
place of PCl_3 and 1 equiv of an alkyl Grignard is added in the last step, then the alkylphenylphosphines $(Me_3Si)_2NP(Ph)R$, (**4**, R = Me,[6] and **5**, R = Et[10]) are obtained.

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 1 equiv of Grignard reagent permits the convenient preparation of the corresponding alkylphenylphosphines **4** and **5** (eq 2). With the exception of some ^{31}P 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 (silylamino)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 silylamines have been used,[5,6] and in favorable cases it is possible to obtain monoalkylated products, e.g., $(Me_3Si)_2NP(Cl)CH_2SiMe_3$.[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.

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Registry No. **1**, 63744-11-6; **2**, 73270-05-0; **3**, 76946-90-2; **4**, 68437-87-6; **5**, 82482-33-5; $(Me_3Si)_2NLi$, 4039-32-1; PCl_3, 7719-12-2; MeBr, 74-83-9; EtBr, 74-96-4; Me_3SiCH_2Cl, 2344-80-1; $PhPCl_2$, 644-97-3.

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(10) ^1H NMR data: **2**, δ 0.34 (Me_3Si, $J_{PH} = 0.6$ Hz), 1.14 (CH_3, $J_{PH} = 16.0$ Hz, $J_{HH} = 7.5$ Hz), 1.4–2.0 (CH_2, multiplet); **5**, 0.25 (Me_3Si, $J_{PH} = 0.6$ Hz), 1.33 (CH_3, $J_{PH} = 18.0$ Hz, $J_{HH} = 7.2$ Hz), 1.9–2.2 (CH_2, 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 $AlCl_3$–NaCl (51–52 mol % $AlCl_3$) at 175–220 °C results in the formation of insoluble $ZrCl_3$ at ~120 mV before the reduction of $Al_2Cl_7^-$ 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] $ZrCl_4$ (from Alfa) and $HfCl_4$ (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 $AlCl_3$–NaCl Melts. Addition of $HfCl_4$ to $AlCl_3$–NaCl melts (ranging in composition from 50.3 to 52 mol % $AlCl_3$) resulted in a poorly defined voltammetric reduction wave that occurs at potentials somewhat *more negative* than the reduction of $Al_2Cl_7^-$.[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 $Al_2Cl_7^-$. 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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