hydrolysis occurs, producing malondialdehyde, which condenses with the remaining A in two observable steps to form an intermediate (I) and subsequently C, a condensed dimer. k_0 for this process was estimated to be 3×10^{-8} s^{-1} at 25 °C. Direct reaction of malondialdehyde with A produces the same material (C), and 2-methylmalondialdehyde gives an analogue. The reaction of MDA with A in acid media follows the rate law $d[I]/dt = k_1[MDA][B]$ with $k_1 = 0.28$ M^{-1} s^{-1}, while the second reaction has the analogous rate law $d[C]/dt = k_2[I][B]$, $k_2 = 0.035$ M^{-1} s^{-1} at 25 °C. The UV–visible spectral properties and X-ray single-crystal structures are given for A–C, and some of the properties of I are also determined.

The heterocyclic aromatic ring has a high electron density at the C12 position and is quite reactive to aldehydes in general, including HCHO, CH_3CHO, CF_3CHO, and C_6H_5CHO, usually producing a C12-monosubstituted complex ion. The kinetic studies are to be presented in greater detail in a later paper.[20]

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Registry No. MDA, 542-78-9; MMDA, 16002-19-0; PnAO, 97466-94-9; $[Ni((PnAO)\text{-}6H)]^0$, 18195-22-7; $[Ni((PnAO)\text{-}5H)]^+ClO_4^-$, 69681-23-8; $[Ni((PnAO)\text{-}7H)_2(CH)_3]^+NO_3^-\cdot 2H_2O$, 97466-93-8; $[Ni((PnAO)\text{-}7H)_2(CHC(CH_3)CH)]^+$, 97466-95-0; $[Ni((PnAO)\text{-}6H)\text{-}CHCHCHO]$, 97466-96-1; $[Ni((PnAO)\text{-}6H)CHC(CH_3)CHO]$, 97466-97-2; 3,3′-[[(2-formylvinyl)-1,3-propanediylidene]dinitrilo]bis[3-methyl-2-butanone oxime], 97466-98-3; 3,3′-[[(2-formylpropenyl)-1,3-propanediylidene]dinitrilo]bis[3-methyl-2-butanone oxime], 97466-99-4.

Supplementary Material Available: Listings of hydrogen atom positions, complete listings of bond distances and angles, and tables of root-mean-square amplitudes of vibration, general temperature factor expressions, and observed and calculated structure factors for compounds A and B and listings of hydrogen atom positions, root-mean-square amplitudes of vibration, and observed and calculated structure factors for compound C (48 pages). Ordering information is given on any current masthead page.

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Reducing Properties of Potassium Silyl

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Potassium silyl has been found to act preferentially as a powerful reducing agent rather than as a nucleophilic substitution agent. Reactions with phosphorus trichloride and dimethylchlorophosphine gave polymers containing phosphorus–hydrogen bonds. Trimethylchlorosilane underwent transmetalation with its complicated consequences; carbon dioxide was reduced to carbon monoxide and potassium formate, and nitrous oxide gave nitrogen. Silane and polymeric silicon hydrides were produced in all reactions. Titration of potassium silyl with carbon dioxide showed that the reaction is stepwise and complex.

The earliest reactions of potassium silyl[1,2] ($KSiH_3$) were those of a nucleophile reacting with methyl chloride to give methylsilane quantitatively. A similar reaction with bromodeuteriosilane[2] was incomplete (43% of bromosilane recovered), exhibiting only slightly a nucleophilic displacement (3.4% deuterated disilanes formed) and being instead largely reductive (84% deuteriosilanes formed). These results led to the experiments reported here. The inquiry concerned whether the silyl anion had the properties of a nucleophile, as found for germyl and methyl anions, or behaved as a reducing agent in the manner of the complex hydrido anions of aluminum and boron. The substances considered as reactants were phosphorus trichloride, dimethylchlorophosphine, triethylamine–chloroborane, trimethylchlorosilane, carbon dioxide, nitrous oxide, and nitric oxide.

Experimental Section

Potassium silyl ($KSiH_3$) was prepared by the method of Ring and Ritter.[2] The method was modified slightly according to Ring et al.[3] The use of potassium sand greatly shortened the time needed for the preparation. Potassium sand was prepared according to Hershberg and Fieser.[4] The sand was poured directly into the reaction vessel, and after removal of the toluene, dry monoglyme and silane were added. Reaction was complete in 7–10 days.

After filtration, the potassium silyl solution was kept under dry nitrogen in a vessel equipped with a rubber septum. Transfers were made with a syringe. Solutions were standardized in a variety of ways. Base hydrolysis and measurement of the liberated hydrogen, reaction with gaseous hydrogen chloride to produce silane, silicon colorimetric analysis,[5] and gravimetric potassium analysis[6] gave reproducible and self-consistent results. The range of concentration of solutions prepared in this manner was typically from 0.3 to 0.7 M. The titer did not change over a period of several months. Reactions were carried out by introducing solutions

Table I. Reaction with Volatile Oxides[a]

	CO_2	N_2O	NO
	Reactants		
$KSiH_3$ in	1.4	0.90	1.14
gas in	4.96	5.4	4.6
gas out	2.04	3.8	0.135
gas consumed	2.92	1.6	4.5
	Gaseous Product		
SiH_4	0.67	0.21	0.163
other gases	1.46 (CO)	2.15 ($N_2 + H_2$)	1.18 (N_2O) 2.0 ($N_2 + H_2$)
	Solid Product		
K found	1.45		
H_2 from basic hydrolysis	0.41	0.78	1.03
Si in residue	0.9	0.8	

[a] All amounts in mmol.

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Table II. Titration of Potassium Silyl (2.22 mmol) with Carbon Dioxide[a]

CO_2 in	CO_2 in, subtotal	CO_2 out	SiH_4 out	SiH_4 out, subtotal	CO out	CO out, subtotal
0.174	0.174	0	0.13	0.13	0	0
0.174	0.348	0	0.109	0.239	0	0
0.185	0.533	0	0.163	0.402	0	0
0.174	0.707	0	0.119	0.521	0	0
0.141	0.848	0	0.109	0.630	0	0
0.163	1.011	0	0.076	0.706	0	0
0.206	1.217	0	0.087	0.793	trace	trace
0.206	1.423	0	0.054	0.847	0.051	0.051
0.266	1.689	0	0.01	0.857	0.086	0.137
0.196	1.885	0	0.03	0.887	0.137	0.274
0.250	2.135	0	0	0.887	0.034	0.308
4.58	6.715	3.55	0	0.887	0.308	0.616

[a] All amounts in mmol.

of potassium silyl via syringe and septum into vessels in which the various reagents had been condensed at −196 °C. Warming to room temperature initiated reaction.

Triethylamine–chloroborane was prepared according to the method of Nöth and Beyer.[7]

Dimethylchlorophosphine was synthesized by Parshall's method.[8,9]

$(PH)_n$ was synthesized by reaction of lithium hydride with phosphorus trichloride.[10]

Phosphorus trichloride, trimethylchlorosilane, nitrous oxide, nitric oxide, and carbon dioxide were used directly from commercially available sources.

Phosphorus trichloride (0.1 mL) and potassium silyl (3.4 mmol), combined initially at −196 °C and then warmed to room temperature, gave an immediate formation of a bright orange precipitate. After about 30 min, the vessel contained 0.17 mmol of a noncondensable gas (assumed to be hydrogen), 0.45 mmol of silane, and phosphine (a trace), as shown by its IR spectrum. The orange material was washed several times with water and with hydrofluoric acid to remove potassium chloride and silicon compounds, respectively. It was then washed with methanol and dried.

Bromate oxidation and colorimetric determination of phosphorus showed the oxidation number of phosphorus to be −1.[10-12] An X-ray powder pattern was identical with that of authentic $(PH)_n$. All other properties previously described for $(PH)_n$ were displayed by this preparation.

Dimethylchlorophosphine (8 mmol) and potassium silyl (8.9 mmol) gave a rapid reaction to produce a bright yellow solution and a white precipitate. After 1 h, the vessel was attached to the vacuum line and cooled to −80 °C. Hydrogen (0.72 mmol), silane (2.2 mmol), and dimethylphosphine (0.17 mmol) were found.

The bulk of the product material was viscous and nonvolatile, insoluble in benzene, hexane, or ether. Viscous solutions were formed in monoglyme and tetrahydrofuran. Qualitatively, the material appeared to be polymeric.

Triethylamine–chloroborane (58.5 mmol) and potassium silyl (23.4 mmol) were heated to 75–82 °C for 1 h. Small amounts of silane (0.1 mmol) and methylsilane (1.0 mmol) were found as minor products. The monoglyme solvent was removed from the reaction vessel cooled to −20 °C. Samples of the remaining colorless liquid were distilled at 55 °C into weighed vessels that could be sealed and reweighed after being filled. A sample tube containing 0.647 g of compound was placed in a flask containing 6 M hydrochloric acid. After the sample tube was broken, hydrogen (16.1 mmol) was found. H_2 calcd: for $Et_3N{\cdot}BH_2SiH_3$, 26.8 mmol; for $Et_3N{\cdot}BH_3$, 16.8 mmol. Boron analysis by the standard sodium hydroxide and mannitol technique found 5.40 mmol of boron. B calcd: for $Et_3N{\cdot}BH_3$, 5.6 mmol; for $Et_3N{\cdot}BH_2SiH_3$, 4.47 mmol. Colorimetric silicon analysis of the hydrolysate was negative. Infrared analyses of the product and a known sample of $Et_3N{\cdot}BH_3$ showed them to be identical.

Trimethylchlorosilane (1.12 mmol) and potassium silyl (1.17 mmol) were mixed in a vessel left open to the vacuum line, and the gases formed at room temperature were removed as rapidly as they formed. The formation of potassium chloride was slow, and the solution remained yellow. Silane (0.57 mmol) was found. After 1 h, part of the solvent was distilled through traps at −45, −80, and −196 °C. It was expected that $(CH_3)_3SiSiH_3$ would have been retained in the trap at −80 °C, but only monoglyme was found. The monoglyme was then returned to the original vessel, and hydrogen chloride (2.16 mmol) was added. The solution color changed from yellow to white. After distillation of the entire solution using traps cooled at −80 and −196 °C, trimethylsilane (0.14 mmol) was found condensed at −196 °C, as verified by its infrared spectrum.

Reaction with Carbon Dioxide. The following procedure is typical of many experiments: A solution of potassium silyl was placed in a 500-mL round-bottom flask, which was cooled to −196 °C and evacuated. Carbon dioxide was added, and the flask was then sealed and allowed to warm to room temperature. An immediate reaction took place with the formation of a white precipitate. After about $^1/_2$ h the flask was cooled to −196 °C, and the noncondensable gas was removed. After the flask was warmed to −80 °C, the volatile substances were removed and measured. A trap cooled to −183 °C allowed silane to pass but retained carbon dioxide.

The white precipitate was hydrolyzed in basic solution, and the evolved hydrogen was measured. Portions of the hydrolysate were analyzed for potassium and silicon (vide supra).

Another sample of the precipitate was extracted with neutral water without evidence of chemical reaction. The extract contained potassium formate, as verified by the formation of formo-*p*-toluidide (mp 51–53 °C). When the precipitate was extracted with anhydrous formic acid in an inert atmosphere, potassium formate was again found.

Noncondensable gas was identified by mass spectrometry. The results of an experiment are presented in Table I.

Titration with Carbon Dioxide. The results of one of many reactions of this type are shown in Table II. After each increment of carbon dioxide, a 10-min reaction time was allowed before removing the gases.

Reaction with Nitrous Oxide and Nitric Oxide. The procedures followed in these experiments were exactly those followed in the reaction with carbon dioxide. The nitrogen–hydrogen mixture resulting from the reaction with nitrous oxide was analyzed by mass spectrometry. Comparison of peak heights with known standards gave the mole fraction of nitrogen as 0.756. The mass spectrum of the noncondensable gas formed within the first 30–40 s of reaction showed almost pure nitrogen. Within a few minutes the amount of hydrogen reached the finally observed ratio of $H_2/N_2 = 3/1$. Titration with increments of nitrous oxide produced nitrogen and silane simultaneously. The solid product dissolved in water with evolution of hydrogen. Other runs with nitrous oxide varied with respect to the yield of silane. Results are given in Table I.

With nitric oxide the products were hydrogen, nitrogen, nitrous oxide, silane, water-soluble potassium hydridosilicate, and a trace of hyponitrite.

A qualitative test for hyponitrite[13] was performed on the solid product. A few milliliters of water and carbon dioxide were condensed onto the precipitate. After warming, nitrous oxide and excess carbon dioxide were found.

Results and Discussion

The reaction of potassium silyl with phosphorus trichloride was clearly a reduction, in contrast with the formation of trisilylphosphine ($(H_3Si)_3P$) from bromosilane and potassium dihydrogenphosphide.[14,15] With dimethylchlorophosphine a similar reduction appears to have occurred. Certainly no dimethylsilylphosphine was found.

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Unlike the result reported elsewhere,[16] no trimethyldisilane was found in the products from the reaction between potassium silyl and trimethylchlorosilane. Instead, the result can be ascribed to a transmetalation and the subsequent reactions of the products as shown by

$$KSiH_3 + (CH_3)_3SiCl \rightarrow (CH_3)_3SiK + H_3SiCl$$

$$H_3SiCl + KSiH_3 \rightarrow KCl + SiH_4 + (1/n)(SiH_2)_n$$

The trimethylsilane found after acidification must clearly have come from potassium trimethylsilyl in the condensed phase.

Potassium silyl reacting with trimethylamine–chloroborane ($Et_3N{\cdot}BH_2Cl$) gave none of the silicon–boron-bonded product reported elsewhere.[17] Instead there was a good yield of triethylamine–borane, clearly a reduction product.

Carbon dioxide and potassium silyl reacted to produce silane, carbon monoxide, potassium formate, and a solid residue containing silicon, oxygen, and hydrogen, which will be referred to as hydridosilica. The stoichiometry of the reaction was approximately

$$2KSiH_3 + 4CO_2 \rightarrow 2CO + 2KO_2CH + (1 - x)SiH_4 + Si_{1+x}H_{4x}O_2$$

This was completely different from the behavior of potassium germyl with carbon dioxide:[18]

$$KGeH_3 + CO_2 \rightarrow H_3GeCO_2K$$

Moreover, if carbon dioxide was added in small increments to the potassium silyl, no carbon monoxide was formed initially. Only silane was found. As more carbon dioxide was added, the amount of silane produced per increment diminished. Finally, carbon monoxide began to appear, and no silane was found.

Because the total stoichiometry of the "titration" reaction was inexact and because the reaction sequentially formed silane followed by carbon monoxide, it is believed that an unstable intermediate was formed. This intermediate, which also acted as a reducing agent toward carbon dioxide, was produced in a fast reaction between potassium silyl and carbon dioxide. Silane and potassium formate were also products of this initial reaction. The intermediate reacted more slowly with carbon dioxide than did the silyl anion, and in dilute solution it did nothing. After all the silyl anion was consumed, however, and the reducing power resided in the intermediate, it could react with carbon dioxide to produce carbon monoxide and hydridosilica. Up to the point at which the titration reaction seemed to have stopped, the overall consumption of carbon dioxide was less than in the single reaction. This may indicate an incomplete reaction by the more slowly reacting intermediate or a reaction of the intermediate not involving carbon dioxide.

The reaction of nitrous oxide with potassium silyl was similar in many respects to the reaction with carbon dioxide, but the stoichiometry was more variable from one experiment to the next. The equation for the reaction was approximately

$$2KSiH_3 + 3N_2O \rightarrow 3N_2 + H_2 + (1 - x)SiH_4 + K_2Si_{1+x}H_{4x}O_3$$

Nitrogen is isoelectronic with carbon monoxide, but in part the products differ from those from carbon dioxide because there is no nitrogen analogue of formic acid.

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Registry No. $KSiH_3$, 13812-63-0; PCl_3, 7719-12-2; SiH_4, 7803-62-5; $Et_3N{\cdot}BH_2Cl$, 13240-39-6; $(CH_3)_3SiCl$, 75-77-4; $Et_3N{\cdot}BH_3$, 1722-26-5; $(CH_3)_3SiH$, 993-07-7; CO_2, 124-38-9; KO_2CH, 590-29-4; N_2O, 10024-97-2; NO, 10102-43-9; CO, 630-08-0; N_2, 7727-37-9; H_2, 1333-74-0; dimethylchlorophosphine, 811-62-1; dimethylphosphine, 676-59-5.

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Phenylarsenic(III) and Phenylantimony(III) Bis(dialkyl dithiophosphates): Synthesis and Multinuclear (^1H, ^{13}C, ^{31}P) NMR and Mass Spectral Studies. Crystal and Molecular Structures of $C_6H_5M[S_2P(O\text{-}i\text{-}Pr)_2]_2$ [M = Sb(III) and As(III)]

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Bis(dialkyl dithiophosphate) derivatives of the type $PhM[S_2P(OR)_2]_2$ [M = As(III), Sb(III); R = Et, *n*-Pr, *i*-Pr, Ph] have been prepared and characterized by elemental analyses and molecular weight determinations. IR and NMR (^1H, ^{13}C, ^{31}P) spectral data have been used to investigate plausible structures of these complexes, and their fragmentation pathway has been suggested on the basis of mass spectral data. The crystal structures of $PhM[S_2P(O\text{-}i\text{-}Pr)_2]_2$, M = Sb(III) (**1**) and As(III) (**2**), have been determined at room temperature by using single-crystal counter data. The crystals are isomorphous with the space group $P2_1/c$, $Z = 4$, and unit cell dimensions $a = 12.451$ (2) Å, $b = 26.681$ (6) Å, $c = 9.026$ (4) Å, and $\beta = 109.70$ (2)° for **1** and $a = 12.454$ (6) Å, $b = 26.693$ (9) Å, $c = 8.901$ (5) Å, and $\beta = 109.44$ (4)° for **2**. The structures were refined by using full-matrix least-squares techniques using 2785 statistically significant reflections for **1** and 878 reflections for **2**. The dithiophosphate ligands chelate the central atom with asymmetric M–S bonds (**1**, 2.5 and 3.1 Å; **2**, 2.3 and 3.1 Å) so that the overall geometry is octahedral with a nonbonded pair of electrons occupying an axial position trans to the phenyl group.

Introduction

The preparation, characterization, and structural features of non-transition-metal complexes with the dialkyl dithiophosphate class of anions has recently been reviewed.[1] It has been noted that although the biological activity of the organometallic dithiophosphate derivatives of arsenic(III) has been reported, little is known of their chemistry and that of the corresponding antimony(III) derivatives. In each of the crystal structures reported for the series $Sb[S_2P(OR)_2]_3$, where R = Me,[2] Et,[3] and *i*-Pr,[2] the

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