[Tempo] dependence predicted by eq 4 was also verified for **1a** at 78.0 °C and at [Co(II)]/[Tempo] ratios of 0, 0.026, 0.047, and 0.097 and k_1 and k_{-1}/k_2 values comparable to those available in the literature[14] were obtained from the slope and intercept, respectively, $k_1 = (1.7 \pm 0.9) \times 10^3\ \mathrm{s}^{-1}$ and $k_{-1}/k_2 = (2 \pm 1) \times 10$, although the range and precision of the data were limited by the growth of the overlapping peak at 460 nm from the reaction of $\mathrm{Co^{II}}\cdot$ + Tempo.

Under conditions with excess nitroxide where $k_{\mathrm{obsd}} = k_1$ (eq 3 and Figure 1) the temperature dependence of k_1 was obtained at 11 temperatures over a 60–90 °C range for $\mathrm{PhCH_2Co[C_2(DO)(DOH)_{pn}]I}$ and at 6 temperatures over a 65–90 °C range for $\mathrm{(CH_3)_3CCH_2Co[C_2(DO)(DOH)_{pn}]I}$, $\Delta H^{\ddagger} = 27.9 \pm 0.8$ kcal/mol, $\Delta S^{\ddagger} = 8 \pm 2$ eu and $\Delta H^{\ddagger} = 32.2 \pm 2.0$ kcal/mol, $\Delta S^{\ddagger} = 18 \pm 6$ eu, respectively,[15] to yield the first estimates of the $\mathrm{R{-}Co[C_2(DO)(DOH)_{pn}]I}$ bond energies ($\simeq \Delta H^{\ddagger} - 2$ kcal/mol)[2] of 26 (R = $\mathrm{PhCH_2{-}}$) and 30 (R = $\mathrm{(CH_3)_3CCH_2{-}}$) kcal/mol. The available $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values, including Schrauzer and Grates' estimates for cobalamins and cobinamides with O_2 as a trap, make an interesting comparison (Table I). Especially interesting are the observations that (a) the $\mathrm{RCo[C_2(DO)(DOH)_{pn}]I}$ complexes with their weak $\mathrm{I^-}$ axial ligands show the same $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values within experimental error as those for the base-off alkylcobinamide complexes and (b) the alkylcobinamide and $\mathrm{RCo[C_2(DO)(DOH)_{pn}]I}$ complexes exhibit a neopentyl vs. benzyl ΔBDE (ΔBDE ≡ BDE(neopentyl) − BDE(benzyl)) of only 4–5 kcal/mol. Clearly the B_{12} model chosen and the effect of the axial base are significant, and a collaborative program to determine the solid-state structures vs. the $\mathrm{RCo[C_2(DO)(DOH)_{pn}](base)^+X^-}$ R–Co BDEs for a series of alkyls and bases is under way.[16] In the case of cobalamins, preliminary experiments show, as expected on the basis of the similar $E_{1/2}$ values for $\mathrm{Co^{II}[C_2(DO)(DOH)_{pn}]^+}$ and $\mathrm{Co^{II}}$ $B_{12(r)}$, that $B_{12(r)}$ is relatively stable to nitroxides and that 1.0 equiv of $B_{12(r)}$ is produced by the thermolysis of benzylcobalamin in the presence of a nitroxide.[17] Studies of this and other alkyl cobalamins and cobinamides will be reported in due course.

Acknowledgment. Financial support was provided by NIH Grant AM-26214. R.G.F. is a Dreyfus Teacher-Scholar (1982–1987) and Alfred P. Sloan Foundation Fellow (1982–1984).

Registry No. **1a**, 87319-52-6; **1b**, 87319-53-7; **2**, 2564-83-2.

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(15) The k_1(obsd) values ($\mathrm{s^{-1}}$, ±15%) and temperatures (±0.5 °C) are as follows. (a) For **1a**: 5.9×10^{-3} at 90.5 °C; 5.0×10^{-3} at 88.0 °C; 3.4×10^{-3} at 86.0 °C; 2.3×10^{-3} at 83.0 °C; 1.3×10^{-3} at 78.5 °C; 1.7×10^{-3} at 78.0 °C; 6.8×10^{-4} at 72.0 °C; 4.4×10^{-4} at 69 °C; 3.0×10^{-4} at 64.5 °C; 2.4×10^{-4} at 64.0 °C; 1.8×10^{-4} at 60.5 °C. (b) For **1b**: 2.4×10^{-3} at 90.0 °C; 1.3×10^{-3} at 83.0 °C; 6.7×10^{-4} at 77.0 °C; 2.7×10^{-4} at 72.0 °C; 2.3×10^{-4} at 71.0 °C; 8.7×10^{-5} at 65.0 °C.

(16) Marzilli, L. G., and co-workers and Finke, R. G.; Mayer, B. J.; Molinero, A. A.; Myers, S. A., experiments in progress.

(17) Finke, R. G.; Hay, B., unpublished results.

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Alkali-Metal Insertion in the Pyrochlore Structure

Sir:

Intercalation or insertion reactions of alkali metals with transition-metal oxides or chalcogenides have been the subject of considerable research in recent years.[1-4] These reactions formally involve reduction of transition-metal ions with the change in charge being compensated by diffusion of alkali-metal cations into a host structure (eq 1). Ideally only small

$$\mathrm{A} + \mathrm{M}^n\mathrm{X}_y \rightarrow \mathrm{A}^+\mathrm{M}^{n-1}\mathrm{X}_y \qquad (1)$$

structural changes occur on insertion, which allows the reactions to be readily reversed by oxidation. The reaction rates, which are often fast at room temperature, are limited by the rate of alkali metal ion diffusion into the host structure. Many van der Waals bonded layer compounds such as graphite, $\mathrm{TiS_2}$, or $\mathrm{MoO_3}$ are able to accommodate a wide variety of ions because the weak interlayer bonding allows easy interlayer expansion and reorientation of the layers to create favorable sites for the inserted ions. More rigid, three dimensionally bonded hosts are also capable of insertion reactions with alkali metals, but the size and site requirements are more critical. Most of the oxide systems studied to date are lithium specific.[4-7] Insertion of the larger alkali metals in such oxides is not common. The recently synthesized hexagonal $\mathrm{WO_3}$[8] is the most versatile host for the larger alkalis, yielding compounds with the limiting formula $\mathrm{A_{1/3}WO_3}$ (A = Na, K, Rb, Cs).[9] In this paper we report the insertion of A = Na, K, Rb in the defect pyrochlore compounds $\mathrm{ANbWO_6}$ to give the corresponding $\mathrm{A_2NbWO_6}$. This is the largest stoichiometry change in an oxide for insertion reactions with these alkali metals.

The full pyrochlore stoichiometry is $\mathrm{A_2B_2X_6X'}$, and a wide variety of compositions are known with various permutations of large A cations (Na, K, Rb, Cs, Ca, Cd, Tl, Pb, Sc, Lu, Yb, etc.), smaller B cations (Ti, Nb, V, W, Ta, Re, Ru, etc.), X (O or F), and X′ (O or F).[10-15] The structure may be conveniently thought of as a $\mathrm{B_2X_6}$ framework composed exclusively or corner-shared $[\mathrm{BX_6}]$ octahedra interleaved with an $\mathrm{A_2X'}$ network as shown in Figure 1. The ideal structure is cubic with space group *Fd*3*m* and eight formula units per unit cell. The A, B, and X′ ions occupy the special positions 16d, 16c, and 8b, respectively. The X ions occupy the 48f positions. The A ion is linearly coordinated to two X′ and six approximately coplanar X ions. The X′ ion is coordinated tetrahedrally to four A ions. Defect pyrochlores have been synthesized with stoichiometries $\mathrm{A_2B_2X_6}$,[16] $\mathrm{AB_2X_6}$,[17-20] and

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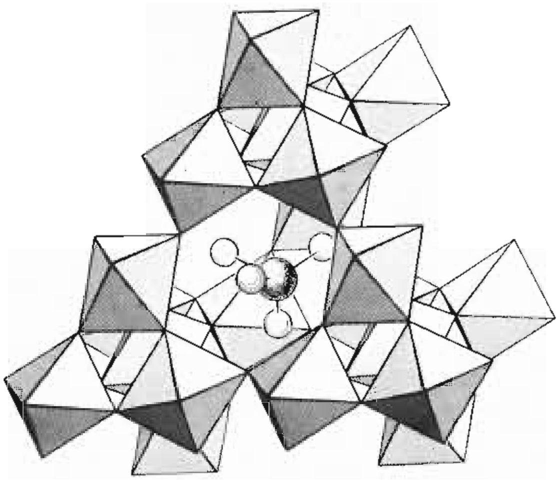

Figure 1. The pyrochlore structure. The octahedra are randomly occupied by Nb and W. The large sphere is the 8b site in the center of a truncated tetrahedral cavity, and the smaller spheres are the 16d sites.

$A_2B_2X_6X'_{1-y}$.[17,21,22] Structural studies have shown that the A ions may occupy the X′ (8b) site for some AB_2X_6[20] compounds or the more general 32e positions.[23] Ionic conductivity measurements of several AB_2O_6 compounds give low activation energies (~20 kcal/mol) for A ion mobility.[24,25] Ion-exchange studies also confirm ion mobility.[24,26] High ion mobility, vacant cation sites, and the presence of reducible W^{6+} suggested that insertion reactions of the type shown in eq 2 might

$$ANbWO_6 + A' \rightarrow AA'NbWO_6 \qquad (2)$$

occur. The series of reactions represented by eq 2 for A = Na, K, Rb, Cs and A′ = Na, K, Rb, Cs have been carried out with use of solutions of A′ in liquid ammonia. $KNbWO_6$ was synthesized directly from K_2WO_4, Nb_2O_5, and WO_3 in air at 600 °C. The Rb and Cs analogues were prepared by ion exchange in the molten alkali nitrates as previously reported,[24] but the Na compound could not be synthesized by this method without substantial inclusion of nitrate in the product, which could be removed only at 600 °C with irreversible structural change. However, exchange in aqueous NaCl solutions at 95 °C yielded $NaNbWO_6{\cdot}H_2O$, which could be dehydrated at 400 °C. The insertion reactions were run in H-cells loaded in a drybox with reactants separated by a frit. Ammonia was transferred on a vacuum line (10^{-5} torr). The metal ammonia solution was added to $ANbWO_6$ through the frit. After reaction the product was repeatedly washed with ammonia on the frit. Reactions with A and/or A′ = Na, K, Rb were generally complete in 4–5 h at −20 °C. All combinations with A or A′ = Cs failed to react.

Metal–ammonia intercalation reactions are often accompanied by decomposition to the alkali amide, cointercalation of NH_3, or ammonolysis. No ammonia was detected in these products by the Dumas method, and no significant quantity of hydrogen, a byproduct of decomposition of alkali-metal ammonia solutions, was produced during these reactions.

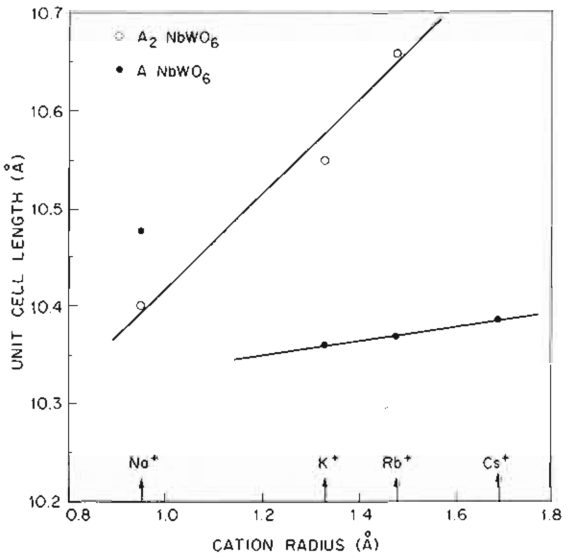

Figure 2. Cubic lattice parameters vs. ionic radii for $ANbWO_6$ and A_2NbWO_6. The $ANbWO_6$ points are anhydrous, and ion exchange was >98% by flame analysis. The alkali contents of A_2NbWO_6 are Na = 2.02, K = 1.95, and Rb = 1.93.

Reactions for A = A′ = Na, K, Rb each gave products with the limiting stoichiometry A_2NbWO_6. The unit cell lengths of $ANbWO_6$ and A_2NbWO_6 are plotted against the ionic radii of the alkali cations in Figure 2. There is a nearly linear relationship between the cubic unit cell length and the ionic radius of A for the A_2NbWO_6 compounds. This relationship suggests that the A ions in A_2NbWO_6 occupy the same set of sites for each A. The six-coordinate, hexagonal 16d sites occupied by A ions in the fully stoichiometric pyrochlores are the logical choice. The linear relationship observed for $ANbWO_6$ with A = K, Rb, Cs suggests that they also share a common site, but the large deviation for $NaNbWO_6$ suggests that Na occupies a different site in that compound. Previous studies have shown that Rb and Cs occupy the 8b site.[20] Thus it is likely that K also occupies 8b whereas Na prefers the smaller 16d site. Calculations of X-ray powder diffraction intensities and comparison to our observed patterns are consistent with the above assignments. The unit cells with K, Rb, and Cs are smaller than for Na because the 8b site is somewhat large for these ions and the structure contracts as much as possible. The dependence of cell size on ionic radii is much steeper for A_2NbWO_6 than for $ANbWO_6$. This is because the 16d site is smaller. It is interesting to note that the Na_2NbWO_6 cell is smaller than that of $NaNbWO_6$. This implies that Na^+ is slightly smaller than the ideal size for the 16d site, causing the structure to contract. The structure contracts further when fully occupied. The Cs reactions do not occur, presumably because Cs^+ is too large to occupy the 16d site.

We have demonstrated intercalation of Na, K, and Rb in the $ANbWO_6$ pyrochlore structure. Even though half of the potential alkali-metal sites are filled in the initial host, the observed stoichiometries of 0.5 alkali per transition metal are the highest observed for these alkalis in metal oxide hosts. A pyrochlore with all the potential A^+ sites vacant in the host could give stoichiometries of one alkali per transition metal. This is a major goal of our synthetic efforts.

Acknowledgment. The authors are indebted to A. L. Wayda for introducing them to a convenient new vacuum line, which was used for the metal–ammonia reactions.

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Registry No. $NaNbWO_6$, 37300-85-9; $KNbWO_6$, 18662-25-4; $RbNbWO_6$, 18662-27-6; $CsNbWO_6$, 18662-30-1; Na_2NbWO_6, 87566-88-9; K_2NbWO_6, 87566-87-8; Rb_2NbWO_6, 87566-89-0; Na, 7440-23-5; K, 7440-09-7; Rb, 7440-17-7; Cs, 7440-46-2.

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Surface Modification of Conducting Particles. A New Approach to Conducting Plastics

Sir:

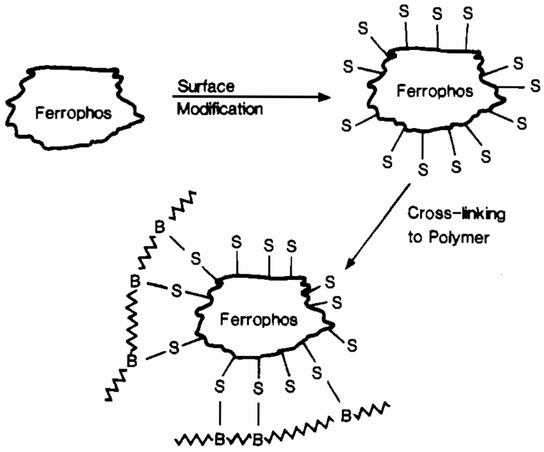
Conducting polymers have been the focus of avid study by chemists and physicists in recent years.[1] In addition to fundamental interest many potential commercial applications, e.g., batteries, radio-frequency interference, and electrophotography, are envisaged for conducting polymers. The most widely studied conducting polymers (e.g., polyacetylene) possess extended π systems that are partially oxidized or reduced with dopants. These polymeric conductors are frequently brittle and react with oxygen.

An alternate approach to developing conducting polymers is to use refractory conducting inorganic particles and covalently bond them to a polymeric matrix. The resulting conductive polymer would maintain some of the physical properties of the polymer.

Herein, using ferrophosphorus[2] (**1**) as an exemplary conducting pigment, we demonstrate that both surface-modified[3] and polymer-bound conducting particles can be achieved without deleteriously affecting the conductivity of the conducting particle (Scheme I).

Silanation of **1** with either alkoxy- or chlorosilanes does not directly occur. Pretreatment of **1** with 1 M NaOH (3 days, 25 °C) leads to hydroxylation of **1**[4]. Hydroxylated **1** may be silanated with chlorosilanes, but not ethoxysilanes, in toluene. With use of (3-chloropropyl)dimethylchlorosilane the $-OSiMe_2(CH_2CH_2CH_2Cl)$ pendant group is grafted onto **1**. The presence of this pendant group was confirmed with use of energy-dispersive X-ray (EDX) and ESCA analyses. The EDX spectra (Figure 1) show the presence of chlorine and enhanced abundance of silicon for the silanated **1**. With ESCA, chlorine is observed at a binding energy of 198.8 eV.

Scheme I. Generalized Procedure To Modify Ferrophosphorus[a]



[a] S is a surface group, and B is a point of attachment of S to a polymeric binder.

Scheme II. Reaction Sequences To Introduce EDX Tags to Styryl Groups on the Surface of 1

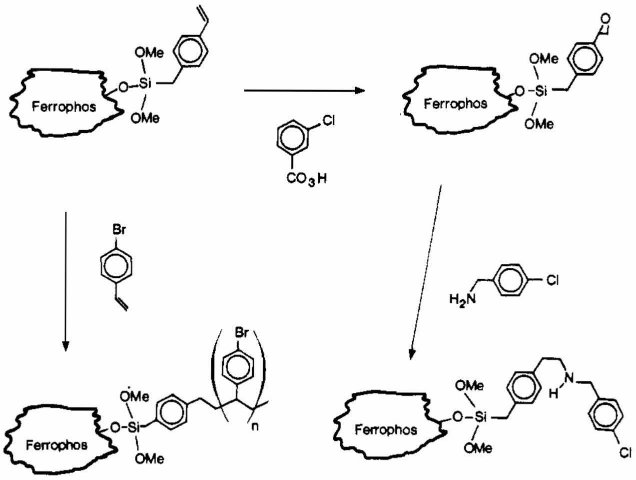
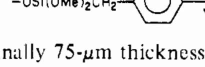


Table I. Surface Resistivity of Surface-Modified Ferrophosphorus

	surface resistivity,[a] Ω/in.	
	Ferrophos:PVC[b] ratio[c]	
attached surface group	9:1	8:2
none (unmodified)	4	9
$-OSiMe_2CH_2Cl$	3	7
$-OSiMe_2(CH_2)_3Cl$	3	7
$-OCH_2CH=CH_2$	3	3
$-OCH_2\underset{O}{CHCH_2}$	3	8
$-OSiCl_2C_{20}H_{42}$	3	6
	8	31

[a] Nominally 75-μm thickness. [b] PVC = poly(vinyl chloride). [c] Weight basis.

Attachment of the alkoxy pendant group was achieved by reacting allyl alcohol (containing 5% LiMe) with **1** (1 day, 25 °C). Confirmation of allylalkoxylation of **1** required introduction of an EDX tag. We epoxidized the allyl alkoxide with *m*-chloroperbenzoic acid and subsequently reacted the epoxide with a tagged epoxide-sensitive reagent, *p*-chlorobenzylamine. The ESCA spectrum of the epoxidized functional group shows a new peak at 288.3 eV assignable to the C_{1s} in the strained three-membered ring containing the electronegative oxygen. EDX spectra confirm the presence of chlorine resulting from the latter reactions.

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[4] Upon hydroxylation a new P Auger peak assignable to P^VOH appears at 398.7 eV.

[5] Control reactions, e.g., *p*-chlorobenzylamine and unmodified **1**, hydroxylated **1**, or allyl alcohol modified **1**, did not result in positive EDX tests for chlorine.

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