periodate. Reaction of the aldehyde with [*methyl*-¹⁴C]isopropylidene-triphenylphosphorane and subsequent acetate hydrolysis gave [12,13-¹⁴C]farnesol which was converted, as above, to the pyrophosphate.[10]

(12) *trans*-Nerolidol was obtained by addition of vinylmagnesium bromide in methylene chloride to *trans*-geranylacetone.[13] Epoxidation and cleavage to the trisnoraldehyde ii as above was carried out on the free alcohol. Reaction of ii with [*methyl*-¹⁴C]isopropylidenetriphenylphosphorane gave
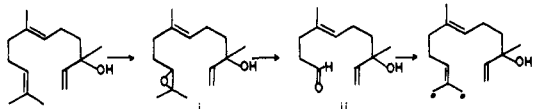
[12,13-¹⁴C]nerolidol. The pyrophosphate was prepared in the usual manner.[10]

(13) O. Isler, R. Rueegg, L. Chopard-dit-Jean, H. Wagner, and K. Bernhard, *Helv. Chim. Acta*, **39**, 987 (1956).
(14) See Beilstein's "Handbuch der Organischen Chemie", 1, 464, I 241, II 513, III 2041.
(15) Sofer and Rilling.[10]
(16) D. Arigoni, *Pure Appl. Chem.*, **41**, 219 (1975); cf. N. H. Anderson and D. D. Syrdal. *Tetrahedron Lett.*, 2455 (1972); D. V. Banthorpe, B. V. Charlwood, and M. J. O. Francis, *Chem. Rev.*, **72**, 115 (1972); S. Gotfredsen, J. P. Obrecht, and D. Arigoni, *Chimia*, **31** (2), 62 (1977); C. D. Gutsche, J. R. Maycock, and C. T. Chang, *Tetrahedron*, **24**, 859 (1968); K. Stephan, *J. Prakt. Chem.*, **58**, 109 (1898); W. Rittersdorf and F. Cramer, *Tetrahedron*, **24**, 43 (1968); S. Winstein, G. Valkanas. and C. F. Wilcox, *J. Am. Chem. Soc.*, **94**, 2286 (1972).
(17) The results obtained so far do not, of course, rigorously exclude the possibility that nerolidyl pyrophosphate might be isomerized back to farnesyl pyrophosphate which would then undergo conversion to **1** by an alternate pathway. This possibility is considered highly unlikely on grounds of mechanistic simplicity but can only be definitely ruled out by further experimentation.

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2-Methylpentadienyl- and 2,4-Dimethylpentadienylpotassium: First Examples of U-Shaped, though Open-Chain, Organometallics

Sir:

Whereas 2-alkenylpotassium compounds (e.g., butenyl-potassium, derived from anion **1**) show a strong preference for the endo configuration,[1] a clear predominance of the most out-stretched, so-called "W" form was reported for pentadienyllithium (**2-Li**) in tetrahydrofuran[2] as well as pentadienylpotassium **2-K**) in liquid ammonia.[3] At equilibrium, the alternative "S"- (sickle-) and "U"-shaped structures were represented only by minor populations, if at all.
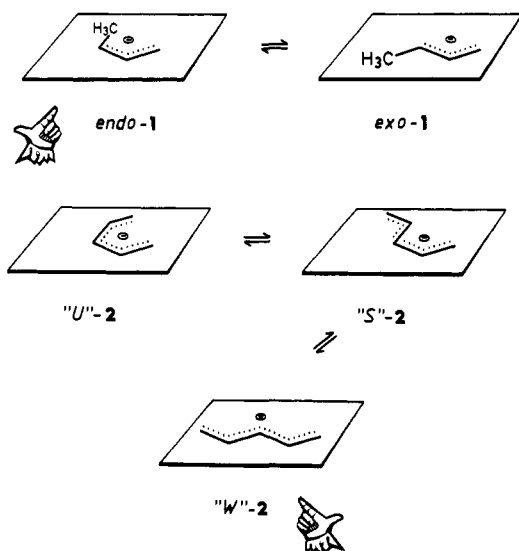

Scheme I
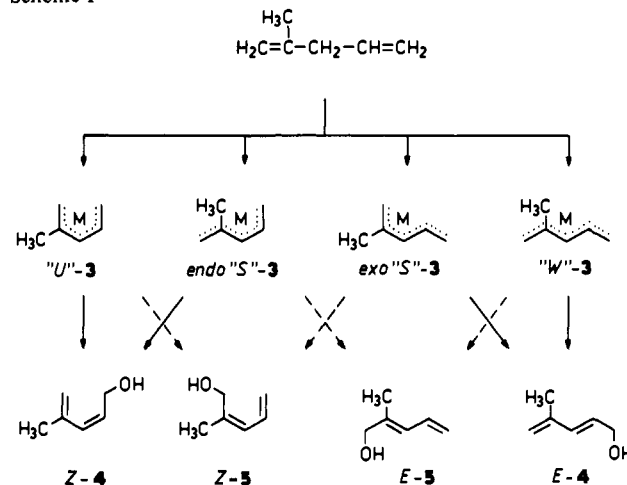
1-Methylpentadienyl metal (hexadienyl metal)[5,6] and 3-methylpentadienyl metal[6] compounds are also reported to exist preferentially as zigzag-like W anions.[7] In contrast, the ¹H NMR spectrum of 2-methylpentadienyllithium did not allow an unequivocal structure assignment, although it was tentatively attributed to a mixture of anions having the W form (W-**3**) and the sterically less hindered sickle form (that is, *exo*-S-**3**). Generally, the NMR approach will fail or lead to ambiguous conclusions, when applied to a multispin system of low symmetry or to a multicomponent mixture.[8] Under such circumstances, structure elucidation by chemical derivation is more reliable.

Of course, pentadienyl metal compounds or pentadienyl anions may react with an electrophile at any electron-rich site, that is, at any of three carbon atoms. Fortunately, the dimethoxyboration–oxidation sequence[9] was found to provide extreme regioselectivity. If there are terminal allylic positions available, they will be hydroxylated exclusively. Thus, no 2-methyl-1,4-pentadien-3-ol, the product derived from electrophilic attack to the central atom, is formed when 2-methyl-1,4-pentadiene was successively treated with the metalating agent (*sec*-butyllithium, butyllithium/potassium *tert*-butoxide,[10] or trimethylsilylmethylpotassium[11]), fluorodialkoxyborane, and alkaline hydrogen peroxide.[12] Still, a variety of hydroxylated derivatives has to be considered. Let us call the pentadienyl terminus adjacent to the methyl group the "head end" and the more distant terminal position the "tail end". Then every torsional isomer should give rise to one "head product" and one "tail product" (following the full-line arrow or, respectively, the broken-line arrow in Scheme I). Because of the steric bulk of the methyl group, the tail products should prevail slightly.

If the pentadienyl metal compound were present as a single torsional isomer, it would yeidl just one pair of such products, the configuration of which should disclose the shape of the organometallic precursor. Such a straightforward situation was met, when 2-methylpentadienyl*potassium* (**3**, M = K) was submitted to the dialkoxyboration–oxidation procedure at −78 °C. (*Z*)-4-Methyl-2,4-pentadien-1-ol ((*Z*)=**4**, 41%) and (*Z*)-2-methyl-2,4-pentadien-1-ol ((*Z*)-**5**, 22%) were identified as the almost exclusive products, the two corresponding *E* isomers being barely detectable (total yield 2%).[13] On the other hand, 2-methylpentadienyl*lithium* (**3**, M = Li) was converted into 10% (*Z*)-**4**, 12% (*Z*)-**5**, and 55% *E* isomers.[14] A similar product composition resulted from 2-methylpentadienylpotassium after keeping it for 24 h at −40 °C in the presence of 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane ("Kryptofix 222").

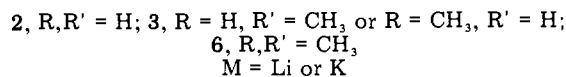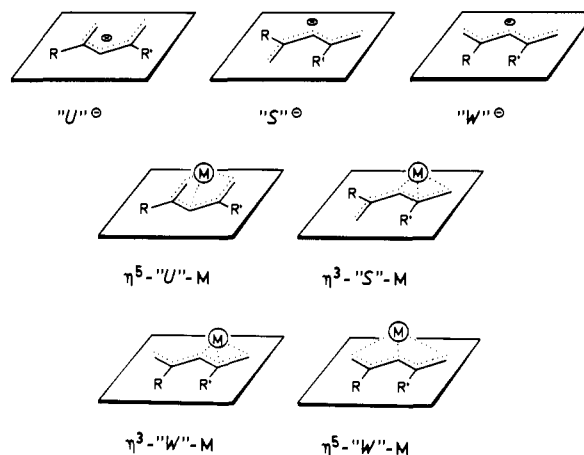Under the same conditions, both pentadienyllithium and

H_3C CH_3
$H_2C=C-CH=C-CH_3$

"*U*"-**6**   "*S*"-**6**   "*W*"-**6**

Z-**7**   *E*-**7**
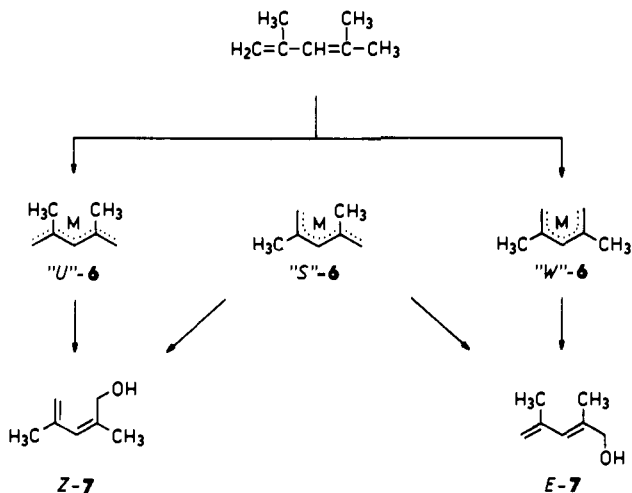
-potassium[15] (**2**, M = Li or K) were converted into (*E*)-2,4-pentadien-1-ol, whereas both 2,4-dimethylpentadienyllithium and -potassium (**6**, M = Li or K) afforded virtually pure (*Z*)-2,4-dimethyl2-4-pentadien-1-ol ((*Z*)-**7**, produced via U-**6**).[16]

In order to rationalize these findings, at least tentatively, we start out examining the various types of metal bonding[17,18] to a dienyl system. The presence of appreciable concentrations of free ions can be excluded in solvents like tetrahydrofuran. Solvent-separated ion pairs, almost indistinguishable from dissociated ions with respect to chemical reactivity and spectroscopic properties,[17,18] have to be expected whenever lithium derivatives of extensively delocalized anions (such as fluorenyllithium[19]) are concerned. With pentadienyl- and 2-methylpentadienyllithium, however, the formation of ion pairs is improbable[20] and, on the basis of our results, can even be ruled out for 2,4-dimethylpentadienyllithium and, of course, all potassium derivatives. If, thus, the structural problem is reduced to one involving contact-paired species only, several possibilities have still to be considered. The dienyl system may act as η^5 ligand (engaging the entire unsaturated system in a π-type interaction), as a η^3 ligand (involving only an allylic moiety in the π complexion), or finally as a σ ligand (i.e., generating a polarized, but partially covalent bond between the metal and a single carbon atom). The last possibility appears to be the least probable one and will be disregarded throughout the following discussion.[21]

For sake of clarity, let us next compare the relative stabilities of the cation-separated anions (U⁻, S⁻, and W⁻). Coplanarity of the carbon backbone is crucial, in order that the electron excess imposed on the organic moiety may spread out over the entire dienyl system. Therefore, only the strain-free W conformer offers an ideal geometry for the pentadienyl anion. The S conformer is disfavored to some extent (roughly 4 kcal/mol[22]); and the U conformer suffers from severe crowding and eclipsing effects (estimate for the steric repulsion ⩾10 kcal/mol[23]), which can certainly not be compensated by the postulated symmetry-allowed through-space stabilization,[24] if this is important at all. On the other hand, introduction of one or two methyl groups at positions 2 and 4 would hardly affect the free energy of the U conformer, whereas it leads to modest steric strain in the S conformers (the repulsions due to endos-ituated methyl being apparently counter balanced by attractions between the methyl group and the distant methylene terminus[1]) and to serious steric strain in the W conformer (W-**6** being destabilized by ~8 kcal/mol[25]). All in all, the following order of relative stabilities should be valid: **2**, W⁻ > S⁻ ≫ U⁻; **3**, W⁻ ⩾ exo-S⁻ ⩾ endo-S⁻ > U⁻; **6**, S⁻ ⩾ W⁻ > U⁻.

In general, W and S conformers will give rise to η^3-type in-

teractions between the metal and the dienyl system. Only the horseshoe-like U conformer satisfies all requirements for an advantageous η^5 coordination to the metal. Indeed, if, as in the case of the 2,4-dimethylpentadienyl anion, the U conformer is only slightly disfavored with respect to the corresponding S and W conformers, both the lithium and potassium derivatives adopt "open-sandwich" structures (η^5-U-**6**-Li and η^5-U-**6**-K). On the other hand, in the unsubstituted pentadienyl series the energy difference between the U and the W conformers is too large to be conpensated by better coordination, and consequently both metal compounds exist in the zigzag-like shape (η^3-W-**2**-Li and η^3-W-**2**-K or possibly η^5-W-**2**-K, since the large potassium atom may be capable to span from one terminus to the other, particularly if these are rotated out of the mean plane). Finally, metal-dependent differences in binding efficiences may explain the divergent behavior of 2-methylpentadienyllithium and -potassium, where the Li compound yields a supposed 3:7:5 mixture of endo-*S*, exo-S, and W forms

"*U*"⊖   "*S*"⊖   "*W*"⊖

η^5-"*U*"-M η^3-"*S*"-M

η^3-"*W*"-M η^5-"*W*"-M

2, R,R' = H; **3**, R = H, R' = CH_3 or R = CH_3, R' = H;
6, R,R' = CH_3
M = Li or K

(η^3-S-**3**-Li (R = H; R' = CH_3), η^3-S-**3**-Li (R = CH_3; R' = H), and η^3-W-**3**-Li), while the potassium compound affords the U-shaped open sandwich (η^5-U-**3**-K). Because of its small size, lithium exhibits much stronger η^3 interactions than potassium but, in contrast to the latter element, it cannot gain much by expanding its coordination to a η^5 type (bond strength sequence: η^5-Li > η^3-Li ⩾ η^5-K ≫ η^3-K).

A final comment on the reliability of the applied approach seems to be appropriate. The configurations of the isolated dienols may be correlated with the preferental structures of the organometallic precursors only if several requirements are fulfilled. (a) The yield of products carrying stereochemical information must be high, which they are indeed. Besides, no trace of a secondary dienol (or the corresponding boronic ester), resulting from electrophilic attack at the central carbon atom, has ever been detected. (b) The torsional equilibrium must be fully established. For pentadienyl- and 2-methylpentadienylpotassium the torsional interconversion was shown to be fast in tetrahydrofuran at −50 °C,[26] as it is for 1-methylpentadienylpotassium in liquid ammonia at −33 °C.[4,5] Addition of a macrocyclic or bicyclic polyether (such as Kryptofix 222), however, slows it down significantly, (c) The derivatives formed upon quenching must be configurationally stable. While there is no doubt about this for dienols, the boronic ester intermediates are structurally labile. For instance, dimethyl (*Z*)-2,4-dimethyl-2,4-pentadien-1-boronate isomerizes slowly at 25 °C to the more stable *E* conformer (yielding (*E*)-2,4-pentadien-1-ol as the main product after treatment with hydrogen peroxide). All evidence available, however, convinces us of the structural integrity of 2,4-dien-1-boronic

esters below −40 °C, the temperature at which the oxidation usually is carried out.[27]

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(3) G. J. Heiszwolf and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **86**, 807 (1967).
(4) G. J. Heiszwolf, J. A. A. van Drunen, and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **88**, 1377 (1969).
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(6) W. T. Ford and M. Newcomb, *J. Am. Chem. Soc.*, **96**, 309 (1974).
(7) Also 3-(2-tetrahydropyranyl)pentadienyllithium and -potassium adopt the W form, as demonstrated by the isolation of pure (*E*)-3-(2-tetrahydropyranyl)-2,4-pentadien-1-ol (90 %).
(8) Moreover, the most labile alkylpotassium compounds decompose at temperatures about −45 °C. Organometallics of the dienyl type are generally much more stable, but, at room temperature or higher, they may eliminate metal hydride or react with the solvent. Spectroscopic signals from secondary products can easily be confused with those from related organometallic intermediates.
(9) G. Rauchschwalbe and M. Schlosser, *Helv. Chim. Acta*, **58**, 1094 (1975); K. S. Y. Lau, G. Rauchschwalbe, and M. Schlosser, unpublished work.
(10) M. Schlosser, *J. Organomet. Chem.*, **8**, 9 (1967): M. Schlosser and J. Hartmann, *Angew. Chem.*, **85**, 544 (1973); *Angew. Chem. Int. Ed. Engl.*, **12**, 439 (1973).
(11) J. Hartmann and M. Schlosser, *Helv. Chim. Acta*, **59**, 453 (1976). and literature cited therein.
(12) In contrst, the branched product, which no longer delivers a stereochemical message, was found to predominate when electrophiles such as chloromethyl methyl ether were chosen as the reagent.
(13) Under somewhat modified reaction conditions typical product compositions were 50–52% (*Z*)-4, 20–22% (*Z*)-5, and 5–9% (*E*)-4 + (*E*)-5.
(14) The approximate ratio of (*E*)-4 and (*E*)-5 falls again in the range of 2:1, although the individual amounts cannot be precisely evaluated, because of insufficient chromatographic separation and spectroscopic distinction.
(15) J. Hartmann, R. Muthukrishnan, and M. Schlosser, *Helv. Chim. Acta*, **57**, 2261 (1974): G. Rauchschwalbe, unpublished results.
(16) Combustion analyses, mass, IR, and ^{1}H and ^{13}C NMR spectra confirm the identity and purity of all hydroxylated compounds.
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(18) M. Schlosser, "Struktur und Reaktivität polarer Organometalle", Springer Verlag, Berlin-Heidelberg-New York, 1973.
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(20) This assumption agrees well with the observation that pentadienyl metal compounds decompose fairly rapidly in the presence of macrocyclic or bicyclic polyethers as well as in 1,2-dimethoxyethane solution, that is under conditions where at least some ("loose") ion pairs should form.
(21) At present, no definitive decision can be made whether the true structure is a symmetrical π complex or an unsymmetrical, "fluctuating" σ compound undergoing rapid [1,3]-sigmatropic metal shifts through a π-bonded *transition state*. In the latter case, however, the barrier to 1,3-potassium shifts can hardly be higher than 5 kcal/mol. When 2-isopropylallyl potassium in tetrahydrofuran-d_8/dimethyl ether-d_8 was cooled to −155 °C, the ^{1}H and ^{13}C NMR peaks broadened only slightly, probably owing to a viscosity effect. The methyl signals, however, did not reveal any indication of diastereotopicity. (M. Stähle, J. M. F. Oth, and M. Schlosser, unpublished results, 1976.)
(22) For sake of comparison, the highest torsional barrier of 1,3-butadiene amounts to roughly 5 kcal/mol (J. G. Aston, G. Szasz, H. W. Wolley, and F. G. Brickwedde, *J. Chem. Phys.*, **14**, 67 (1946)). Probably it corresponds to the transition of the s-trans into the s-cis species, the latter again suffering from C(1)H/HC(4) repulsion.
(23) An estimate of the magnitude of C(1)H/HC(5) repulsions encountered in a horseshoe-like structural arrangement may be derived from the barrier (9.5 kcal/mol) to full rotation around the aryl/alkyl linkage in 5-(2,2-dimethyl-3-butyl)-1,2,3-trimethoxybenzene (S. Sternhell in "Dynamic Nuclear Magnetic Resonance Spectroscopy", L. M. Jackman and F. A. Cotton, Ed., Academic Press, New York, N.Y., 1975, p 177).
(24) R. Hoffmann and R. A. Olofson, *J. Am. Chem. Soc.*, **88**, 943 (1966).
(25) Calorimetrically evaluated as 6 kcal/mol (M. Mansson, *Act Chim. Scand.*, *Ser. B*, **28**, 677 (1974)). The peri strain in the structurally related 1,8-dimethylnaphthalene is still considerable, in spite of substantial distortion from the ideal geometry (D. Bright, I. E. Maxwell, and J. deBoer, *J. Chem. Soc., Perkin Trans. 2*, 2010 (1973)).
(26) 1,4-Pentadiene and 3-methyl-1,4-pentadiene produced *Z* and *E* derivatives, when the metalaction was performed with trimethylsilylmethylpotassium in tetrahydrofuran over a 15-min period at −80 °C and the mixture was immediately treated with fluorodimethoxyborane and peroxide. After the mixture was kept for 30 min at −60 °C, however, only (*E*)-2,4-pentadien-1-ol and (*Z*)-3-methyl-2,4-pentadien-1-ol, respectively, were obtained.
(27) We do not yet know whether allylic and dienylic boronic esters are π complexes or σ compounds. Currently we favor the less symmetric σ structure. In this case we assume the boron atom to be mainly linked to the unsubstituted allyl terminus, since boranes having primary alkyl ligands are thermodynamically more stable than those having secondary or tertiary alkyl ligands (H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **88**, 1433 (1966)). Small stationary concentrations of secondary boronic esters may still coexist owing to rapid [1,3]-sigmatropic shifts of the dialkoxyboron group. (For the fluxional behavior of allyl boranes, see B. M. Mikhailov, V. S. Bogdanov, G. V. Lagodzinskaya, and V. F. Pozdnev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 386; (1966); *Chem Abstr.*, **55**, 595c (1966); V. S. Bogdanov and B. M. Milhailov, *Dokl. Akad. Nauk SSSR*, **193**, 586 (1970); *Chem. Abstr.*, **74**, 12494e (1971).) However, we wish to emphasize that the conclusions drawn in the present communication do not depend on a particular structure postulate for dieneboronic esters. We have simply to worry about their torsional dynamics. The stereochemical information will be faithfully delivered only if cis/trans (endo/exo) isomerizations of the allylic (dienylic) system are slow at temperatures below −40 °C. This has been confirmed again in another way. The metalaction of cyclododecene (cis/trans mixture), followed by treatment with fluorodimethoxyborane and alkaline hydrogen peroxide, furnished only *cis*-cyclododecen-3-ol (mp 64–65 °C; configuration assignment based on ^{1}H NMR in the presence of varying amounts of tris(dipivalomethanato)europium)). If rotation around a carbon–carbon bond of the allylic system were feasible under the reaction conditions, the (*Z*)-cyclododeceneboronic ester would at least partially have been converted to the *E* isomer, trans-double bonds being generally favored in twelve-membered-ring systems.

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X-Ray Photoelectron Diffraction: A New Technique for Structural Studies of Complex Solids

Sir:

Whenever a guest species is substitutionally incorporated within a host solid the precise location of the dopant atoms is seldom capable of being determined directly. So far as isomorphous substitution in minerals is concerned, the classical studies of Mauguin[1] and others[2–4] have demonstrated the deductive principles which have enabled site assignments to be made for those ions which may, in principle, occupy more than one distinct structural location. There remains, however, a need for direct techniques which can identify specific occupied sites, be they regular or interstitial, especially when the degree of occupancy (dopant concentration) is low. X-ray photoelectron diffraction (XPD), as is described below, promises to fulfill that need.

It has for some years been recognized that photoelectrons generated below the surface of a single-crystal specimen may be elastically scattered (diffracted) before their escape into the vacuum, resulting in anisotropy of the ejected electron flux.[5–7] Interest in these phenomena has, however, been relatively slight, probably because on the one hand there existed no immediate prospect of any adequate quantitative interpretation of the diffraction patterns[8]—although this problem now seems closer to solution, at least for simple crystal structures[9]—while on the other their considerable potential value in chemistry has not been emphasized. We report here the first examples of the use of x-ray photoelectron diffraction (XPD) to derive (in an attractively direct noncomputational manner) valuable structural information relating to complex solids—information which would, indeed, be difficult, if not impossible, to obtain from established techniques. In this study, we are concerned with a class of solids, the micaceous sheet silicates, which possess a range of compositions within a fixed structural type. Much has been deduced, indirectly, concerning the structural chemistry of these solids and idealized formulae and structures of two such materials, muscovite and phlogopite, are shown in Figure 1. We seek here direct answers to questions such as these. Is the Al in muscovite indeed partly located at tetrahedral sites? Does phlogopite contain Al in octahedral sites? Do Na^+ and K^+ occupy *exactly* equivalent interlamellar sites?