Circular dichroism spectroscopy showed that the M13 leader peptide (10^{-5} M) changed conformation from >70% random coil in aqueous solution to >55% helix in 33% hexafluoroisopropyl alcohol[18] (Figure 1). Interestingly, application of the Chou–Fasman rules showed that $\langle P_\alpha \rangle$ and $\langle P_\beta \rangle$ were nearly equal.[12,19] The peptide showed the same CD spectrum characteristic of a predominantly random structure in 1% acetic acid, acetate buffer (pH 4.7), and phosphate buffer (pH 2.8 and 6.8) and became helical upon addition of hexafluoroisopropyl alcohol or trifluoroethanol.

The M13 signal peptide formed stable monolayers at the air–water interface in a Langmuir trough (0.0125 M Tris·HCl, pH 7.4, 0.10 M NaCl). The monolayer was slowly compressed and expanded repeatedly over several hours without showing hysteresis in the surface pressure vs. area curve. A discontinuity in π vs. A was observed at 32 ± 1 dynes/cm, indicating collapse of the monolayer. A high collapse pressure appears to be characteristic of surface-active peptides, which have been studied in this laboratory.[20] The π vs. A curve obeyed the equation $\pi[A - A_\infty(1 - k\pi)] = c$, where the compressibility constant k was determined as 9.9×10^{-3} cm/dyne. We calculated A_∞, the limiting molecular area extrapolated to 0 pressure, as 425 Å^2/molecule or 18.6 ± 1.4 Å^2/residue. This value for the limiting area per residue is consistent with a compactly folded α-helical structure,[21] where the nonpolar side chains are oriented toward air and the polar moieties seek the water surface. The molecular weights calculated from these studies were consistent with the monomeric form of the M13 signal peptide.

To assess whether this synthetic leader peptide could bind spontaneously to lipid bilayer membranes, we prepared small unilamellar vesicles from egg lecithin by the ethanol injection method and chromatographed them on Cl-Sepharose 4B in either 0.16 M KCl or 0.01 M sodium phosphate buffer pH 6.8.[22,23] Upon addition of M13 peptide, the vesicle mixture became turbid. Vesicle aggregation was also indicated by an increase in light scattering. With phase-contrast microscopy, clumps of spherical particles resembling large vesicles with >0.5-μm diameter were observed. Because of the apparent fusogenic nature of this synthetic peptide, we are currently trying to determine K_D for the binding phenomenon by employing the recently developed lipid-coated polystyrene divinylbenzene bead technique.[24]

We have succeeded in synthesizing a complete, native leader peptide that is water soluble,[25,26] Our CD data show that this M13 peptide is capable of adopting different solvent-dependent conformational states. In fluorinated alcohol solutions, which promote intramolecular H bonding,[27] this leader peptide exhibits high helical content, suggesting that 13 out of 23 residues participate in an α-helix. At the air–water interface a stable monolayer is formed with a limiting molecular area which indicates that the peptide adopts a compact structure like that of a helix. These studies support the idea that this peptide most likely exists as some sort of helical structure in the membrane. We are now investigating the conformation and orientation of the M13 leader peptide when associated with polymeric lipid vesicles as well as synthesizing other leader peptides to further our knowledge of their secondary structure.

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Registry No. Met-Lys-Lys-Ser-Leu-Val-Leu-Lys-Ala-Ser-Val-Ala-Val-Ala-Thr-Leu-Val-Pro-Met-Leu-Ser-Phe-Ala-NH_2, 91178-69-7.

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A (Phosphavinylidene)molybdenum Complex. Two-Coordinate Phosphorus Involving Multiple Bonding to Both Carbon and Molybdenum

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Compounds with multiple bonds between main-group and transition elements are of interest because they feature markedly different centers of reactivity. We describe the synthesis of a new class of compound in which a two-coordinate phosphorus atom is engaged in multiple bonding to both carbon and a transition element.

In a typical preparation, 2.30 g (10.25 mmol) of $(Me_3Si)_2C{=}PCl$[1] was dissolved in 30 mL of THF and added slowly (25 °C) to a filtered solution of $K[Mo(CO)_3(\eta\text{-}C_5H_5)]$ prepared by treatment of 4.08 g (8.33 mmol) of $[Mo(CO)_3(\eta\text{-}C_5H_5)]_2$ with 0.70 g (17.45 mmol) of KH in 50 mL of THF.[2] After evacuation of the THF, 50 mL of *n*-hexane was added to the resulting brown residue. Concentration of the filtered *n*-hexane solution afforded bright orange crystals of $[Mo(CO)_2(\eta^1\text{-}P{=}C\text{-}(SiMe_3)_2)(\eta\text{-}C_5H_5)]$ (**1**) (mp 98–105 °C dec). Preliminary identification of **1** was based on elemental analytical and spectroscopic data. Thus, the 70-eV MS revealed a parent peak at *m/e* 408 and peaks at *m/e* 380, 352, and 343 corresponding to the loss of one CO, two CO's, and C_5H_5, respectively. The presence of only two CO's was also indicated by FT-IR ($\nu_{C\equiv O}$ = 1882, 1940 cm^{-1}), and the low coordination number at phosphorus was apparent from the deshielded $^{31}P\{^1H\}$ NMR chemical shift for **1** (36.43 MHz, CH_2Cl_2, δ + 497).

The structure of **1** was confirmed by X-ray crystallography[3] and is illustrated in Figure 1 along with the atom numbering scheme. The solid state of **1** comprises isolated molecules with no short intermolecular contacts.

The geometry around the molybdenum is of the familiar three-legged "piano-stool" type for which the three "legs" comprise two carbonyl groups and the η^1-$PC(SiMe_3)_2$ ligand. The Mo–P

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(3) A single crystal of **1** with dimensions 0.35 × 0.35 × 0.10 mm was sealed under dry nitrogen in a Lindemann capillary. Some crystal data for **1** are as follows: $C_{14}H_{23}MoPO_2Si_2$, monoclinic, space group $P2_1/c$ (No. 14), a = 18.90 (1) Å, b = 6.432 (1) Å, c = 17.009 (3) Å, β = 107.83 (3)°, V = 1968 (2) Å^3, Z = 4, D_c = 1.507 g cm^{-3}, and μ(Mo Kα) = 8.6 cm^{-1}. A total of 3670 symmetry-independent reflections was recorded (ω–2θ scans) to $2\theta_{max}$ = 50° using graphite-monochromated Mo Kα X-radiation with λ = 0.71069 Å. Of these, 2857 reflections ($I > 3.0\sigma(I)$) were used to solve (Patterson) and refine (difference Fourier, full matrix least squares) the structure of **1**. Final least-squares refinement gave $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.040$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.068$.

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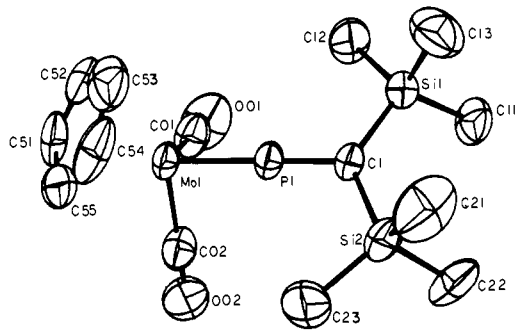
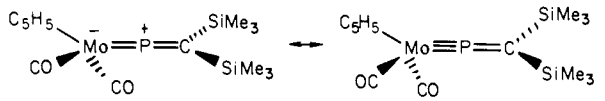


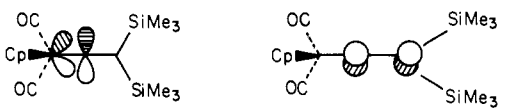
Figure 1. ORTEP view of $[Mo(CO)_2(\eta^1\text{-}P{=}C(SiMe_3)_2(\eta\text{-}C_5H_5)]$ (**1**). Pertinent metric parameters: Mo(1)–C(1) = 2.174 (1), P(1)–C(1) = 1.649 (4) Å; Mo(1)–P(1)–C(1) = 178.3 (2)°, P(1)–C(1)–Si(1) = 116.7 (3)°, P(1)–C(1)–Si(2) = 116.9 (3)°, Si(1)–C(1)–Si(2) = 126.3 (2)°.

bond length of 2.174 (1) Å is significantly shorter than those found in phosphine–Mo complexes (2.40–2.57 Å)[4] and also slightly shorter than the values (2.213 (1) and 2.207 (1) Å) that have been reported for $[Mo(CO)_2(\eta^1\text{-}PR_2)(\eta\text{-}C_5H_5)]$,[5] phosphenium ion complexes in which multiple Mo–P bonding has been implied. The P–C bond length (1.649 (4) Å) is shorter but similar to those in uncoordinated phosphaalkenes which span the range 1.665 (4)–1.72 Å[6] and should therefore be considered a double bond. In addition, the ligand configuration is such that the Mo(1)–P(1)–C(1) angle is almost linear (178.3 (2)°) and the methylene carbon, C(1), is trigonal planar. This plane is essentially orthogonal to the symmetry plane of the $Mo(CO)_2(\eta\text{-}C_5H_5)$ fragment. The electronic structure of **1** can thus be discussed in terms of canonical forms **2** and **3**. The phosphavinylidene structure



2 **3**

2 is isovalent with group 7B vinylidene complexes such as $(C_5H_5)(CO)_2M{=}C{=}CR_2$, M = Mn, Re (**4**). Such a structural assignment gains support from the fact that **1** and **4** are isostructural. As illustrated below, this conformation maximizes the interaction between the HOMO (a″) of the $C_5H_5M(CO)_2$ fragment[7] and a P(3p) orbital. In **3** the Mo–P bonding resembles that in group 6B terminal alkylidyne complexes, $(C_5H_5)(CO)_2M{\equiv}CR$, M = Cr, Mo, W.



a″

The reaction of $(Me_3Si)_2C{=}PCl$ with several organometallate anions is under active investigation as is a study of the reactivity of **1**.

Acknowledgment. We are grateful to the National Science Foundation and the Robert A. Welch Foundation for financial support.

Supplementary Material Available: Tables of bond lengths, bond angles, atomic coordinates, thermal parameters, and structure factors for **1** (35 pages). Ordering information is given on any current masthead page.

UV Resonance Raman Spectroscopy of the Aromatic Amino Acids and Myoglobin

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Resonance Raman spectroscopy in the near-UV and visible spectral region is an important technique for the study of biological molecules.[1] As part of a continuing investigation of the UV resonance Raman (UVRR) spectroscopy of aromatic molecules,[2] we have begun a detailed study of the excitation profiles of phenylalanine, tyrosine, and tryptophan in the region 200–280 nm.[3] The only previously reported UV Raman spectra of tyrosine and tryptophan were excited at 257.3 nm by using a frequency-doubled Ar^+ laser.[4] The shorter excitation wavelengths used in the present work clearly demonstrate the sensitivity and selectivity of UVRR for the study of aromatic amino acids in solution and in proteins. Spectra were easily obtained from solutions of the amino acids and proteins at millimolar concentrations with no interference from fluorescence. Particular excitation wavelengths provide a selective enhancement of the Raman spectrum of one amino acid over another. Photochemical decomposition of the sample was not significant during the individual 30-min Raman spectral measurements.

Typical UVRR spectra of solutions of each of the aromatic amino acids at pH 12 are shown in Figure 1. The spectra were obtained with an instrument based on a Nd/YAG pumped dye laser and associated doubling and mixing crystals, a triple monochromator, and a Reticon detector.[5] The aromatic amino acid samples were recirculated through a jet nozzle during laser irradiation to minimize sample decomposition.[5] The Raman intensities of the samples are referenced to the 932-cm^{-1} symmetric stretch of ClO_4^-, which is used as an internal standard.[6] Comparisons of the UVRR spectra of phenylalanine, tyrosine, and tryptophan to those of toluene, phenol, and indole (not shown) indicate that all of the features in the spectra may be assigned to normal modes of the aromatic rings of the amino acids. As indicated in Figure 1, these spectra were obtained in or near resonance with the $^1L_a \leftarrow {}^1A$ ($\pi^* \leftarrow \pi$) electronic transition. Tryptophan has a higher molar absorptivity than tyrosinate or phenylalanine at 225 nm and is thus a better Raman scatterer at this excitation wavelength.

Different amino acids may be selectively enhanced by changing the excitation wavelength. This is illustrated in Figures 2A and

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