ratios of the same order as IIIa, whereas the diol IIa, in which the primary hydroxyl group is at the terminus of a seven-carbon chain, gave the highly unfavorable 5:1 ratio (Table I).

The diol epoxide IIIa was selected for completion of the synthesis. It was prepared by borohydride reduction in isopropyl alcohol of the ozonide[1] of **3a**, followed by hydrogenolysis of the benzyl groups with 10% Pd/C in moist ethyl acetate, and epoxide closure with 1.1 equiv of KOH in methanol (overall yield from **3a** 82%). Reaction of IIIa with *rac*-3-*tert*-butyloxy-1-octynyldimethylalane[12] (10 equiv, 60°, 2 hr) produced a mixture of *rac*-IVb and its racemic 15-epimer (60%), which was debutylated with trifluoroacetic acid at −15° for 4 hr (87%) to form IVa; the latter was reduced with $LiAlH_4$ in boiling THF for 5 hr (80%) to a mixture of *rac*-VIIIa and its 15-epimer. Selective monotritylation at 25° afforded the racemate VIIIb and its 15-epimer,[13] which proved the most easily separable mixture of 15-epimers encountered by us. The more polar isomer VIIIb was acetylated to form VIIIc and the latter detritylated with 90% acetic acid at 25° for 15 hr and the triacetate alcohol VIIId oxidized with $CrO_3 \cdot 2py$ in CH_2Cl_2 at 25° for 15 min. The aldehyde triacetate IX (85% overall yield from VIIIb) was shown to be identical with that described in the preceding communication[1] by tlc, glc, and ir and mass spectra. When IX was subjected to a Wittig reaction followed by hydrolysis with 2% aqueous KOH at 25°, *rac*-$PGF_{2\alpha}$ (**11**) was obtained in 55% yield and identified as previously described.[1] In a parallel sequence the less polar isomer of VIIIb was converted to *rac*-15-epi-$PGF_{2\alpha}$.

Oxidation of VIIId with Jones reagent at 25° for 15 min followed by hydrolysis with 1% NaOH (1:1 H_2O–CH_3OH) furnished the Corey lactone (**12**)[14] in 85% yield, identified as previously described[1] and by glc and the mass spectrum of the tristrimethylsilyl ether–trimethylsilyl ester of the corresponding acid.

The above experimental conditions are equally compatible with the functionality present in the PGE_3 and $F_{3\alpha}$ side chains. This improved procedure should therefore be applicable to these prostaglandins as well.

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hydroboration and the latter by reaction with OsO_4 in pyridine, followed in both cases by debenzylation and epoxide ring closure (1 equiv of KOH in MeOH). The osmylation of **3a** furnished two glycols, epimeric at C-6 in a 4:1 ratio separable after debenzylation by tlc, of which only the more abundant one was convertible to the epoxide VII. Its 6-epimer furnished, instead, the isomeric tetrahydropyran derivative. This difference in the course of reaction was used to assign relative configuration at C-6. Molecular models of the tosylate precursor of VII clearly show that hydrogen bonding between the 6- and 9-hydroxyl groups prevents approach of the 5-hydroxyl group to C-12; thus, epoxide formation is preferred, whereas in its 6-epimer such hydrogen bonding forces the 5-hydroxyl group into position for bonding to C-12 leading to tetrahydropyran formation.

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The Structure of the Seven-Coordinate Cyano Complex of Vanadium(III)

Sir:

Seven-coordinate transition metal complexes containing simple monodentate ligands remain a rarity in chemistry.[1] While the classic example of seven coordination is IF_7,[2] metal complexes which have been found include the MF_7^{n-} species (M = Zr,[3] Nb,[4,5] U[6]) and UO_2F_5.[3–7] Among structures found are the pentagonal bipyramid (ZrF_7^{3-} [3,8]), the monocapped trigonal prism (NbF_7^{2-} [4]), and the tetragonal base–trigonal base structure ($Ph_4C_4Fe(CO)_3$[9]). The structure of the ZrF_7^{3-} ion described by Hurst and Taylor[3] is not unambiguous because of severe disordering. Brunton[8] has described the structure of $Rb_5Zr_4F_{21}$ in which both a pentagonal bipyramid and a distorted antiprism with one vacant position occur; however, these structures are not isolated units but instead are part of a ligand-bridged network. The structure of $Zr(acac)_3Cl$ has recently been reported to be derived from a pentagonal bipyramid.[10] Of late, there has been considerable interest in the cyano complex of vanadium(III),[11–13] the primary concern being a determination of the molecular formula and the coordination about the vanadium. The ir studies[11–13] on this compound have been restricted to the solid state; it has been shown, however, that structure determinations of cyano complexes on the basis of solid state ir evidence alone can be unreliable.[14] We now wish to report the results of a single crystal X-ray study of $K_4[V(CN)_7] \cdot 2H_2O$, potassium heptacyanovanadate(III) dihydrate, which contains a discrete seven-coordinate vanadium(III) ion.

Red crystals were prepared by a modification of the method of Locke and Edwards.[15] A nearly cubic-shaped crystal of dimensions of 0.20 × 0.22 × 0.24 mm was mounted into a thin-walled capillary tube under a nitrogen atmosphere. The compound crystallizes in the triclinic system, and the space group was

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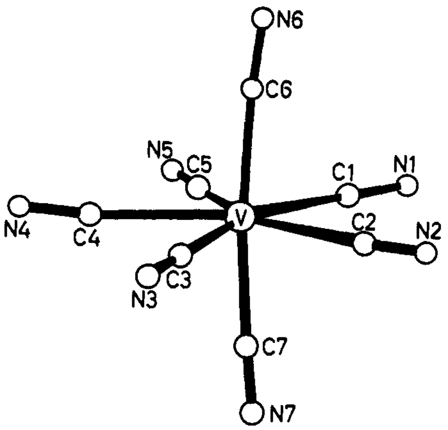

Figure 1. The structure of the $[V(CN)_7]^{4-}$ anion.

chosen as $I1$ with lattice constants $a = 9.229$ (1) Å, $b = 9.097$ (1) Å, $c = 9.341$ (1) Å, $\alpha = 90.02$ (1)°, $\beta = 92.49$ (1)°, and $\gamma = 90.00$ (1)°. The calculated density assuming $K_4[V(CN)_7]\cdot 2H_2O$ is 1.80 g/cc, which compares favorably with the observed density of 1.77 ± 0.02 g/cc. Diffractometer data were collected with Mo Kα radiation to a maximum 2θ of 45°. The structure was solved by Patterson methods, and the atomic coordinates and anisotropic thermal parameters were refined by block-diagonal least-squares techniques to a final R value of 0.025. Table I lists the individual distances and angles found.

Table I. Principal Bond Distances and Angles for the $[V(CN)_7]^{4-}$ Anion

	Distances,[a] Å		
V–C(1)	2.134 (8)	C(1)–N(1)	1.155 (12)
V–C(2)	2.155 (7)	C(2)–N(2)	1.139 (10)
V–C(3)	2.152 (7)	C(3)–N(3)	1.143 (10)
V–C(4)	2.152 (7)	C(4)–N(4)	1.146 (10)
V–C(5)	2.150 (7)	C(5)–N(5)	1.137 (10)
V–C(6)	2.131 (8)	C(6)–N(6)	1.148 (11)
V–C(7)	2.156 (8)	C(7)–N(7)	1.147 (11)
	Angles,[b] °		
C(1)–V–C(2)	72.5 (3)	V–C(2)–N(2)	179.0 (7)
C(1)–V–C(5)	72.5 (3)	V–C(3)–N(3)	178.5 (7)
C(2)–V–C(3)	72.3 (3)	V–C(4)–N(4)	177.9 (7)
C(3)–V–C(4)	70.5 (3)	V–C(5)–N(5)	179.3 (6)
C(4)–V–C(5)	72.3 (3)	V–C(6)–N(6)	172.2 (2)
C(6)–V–C(7)	171.0 (3)	V–C(7)–N(7)	172.8 (7)
V–C(1)–N(1)	179.5 (9)		

[a] Estimated standard deviations × 10^3 in parentheses. [b] Estimated standard deviations × 10 in parentheses.

The structure of the anion is a pentagonal bipyramid of approximate D_{5h} symmetry as illustrated in Figure 1. The average ∠C–V–C for adjacent carbons in the equatorial plane is 72.0 ± 0.6°. The two axial cyanides are not colinear but instead give rise to $\angle C_{ax}\text{–V–}C_{ax} = 171.0°$. The average V–$C_{eq}$ distance is 2.149 ± 0.006 Å and the average V–C_{ax} distance is 2.144 ± 0.012 Å, thus indicating no significant difference in the length of the equatorial and axial bonds. There are two distinct V–V distances of 7.87 and 8.10 Å. The potassium ions are arranged in an approximate tetrahedral arrangement about the vanadium; two of the distances are 4.44 Å and the other two are 4.15 Å All other interatomic distances are normal The standard deviation of the distances of the vanadium and the five equatorial carbons from a least-squares plane of these atoms is 0.031 Å with C(4) the greatest distance from the plane at 0.047 Å

It should also be noted that the V–C distances of 2.15 Å are the longest we know of for a first-row transition metal cyanide complex. However, the Cr(III)–C distance in the seven-coordinate $[Cr(O_2)_2(CN)_3]^{3-}$ anion is 2.09 Å,[16] and a V(III)–C bond is expected to be longer. This is the first definitive example of a seven-coordinate complex of a first-row transition metal containing seven identical ligands and the first ML_7 type complex in which L is a ligand other than fluoride. It is interesting to speculate that the compound $K_4Mo(CN)_7\cdot 2H_2O$, for which coordination number seven has been suggested,[17] may have the same structure as $K_4[V(CN)_7]\cdot 2H_2O$.

The structure of the anion persists in solution as evidenced by the fact that the electronic spectra are very similar in solution and in the solid state.[11,13] The difficulty encountered by Perumareddi, *et al.*,[18] in assigning the d–d electronic transitions based on O_h symmetry for the V(III) cyanide complex is therefore explained. More recently, Alexander and Gray[19] discussed the electronic structure, but they too assumed octahedral geometry. A reinterpretation of the electronic spectrum of $V(CN)_7^{4-}$ and a discussion of its electronic properties in light of this new structural evidence will be forthcoming.

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A Gas-Phase Photon-Induced Ion–Molecule Reaction Studied by Ion Cyclotron Resonance Spectroscopy

Sir:

The intermolecular reactions of photoexcited molecules have been studied photochemically for many decades for their mechanistic as well as synthetic interest.[1] More recently photoelectron spectroscopy[2] has shown that many cations have excited states accessible using visible and ultraviolet light. We wish to report the observation of a gas-phase photon-induced ion–molecule reaction and to interpret the wavelength dependence of the photochemical product as a probe of the absorption spectrum of the $C_3H_5^+$ cation.

The reaction observed was

$$C_3H_5^+ + C_2H_4 \xrightarrow{h\nu} C_3H_7^+ + C_2H_2 \qquad (1)$$

An ion cyclotron resonance spectrometer was used to produce cations from ethylene neutrals and to observe the light-induced cation products. The spec-

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