ond-order displacement reactions can occur in addition to formation of "minor species" involving axial coordination. These processes are also responsible for the loss of resolution found in the EPR spectra at copper:enkephalin ratios similar to those used in NMR.

Conclusion

[Leu^5]- and [Me^5]enkephalin binding to copper(II) has been demonstrated in water-simulating physiological serum conditions. As anticipated, complexation is pH dependent and different species are formed under varying conditions. However, at physiological pH, the natural enkephalins form a major species with copper by coordination through the tyrosine amino group, the glycine peptide linkages, and the C-terminal carboxylate functions. No evidence was found for participation of methionine sulfur in copper binding, as both enkephalins showed similar behavior. A well-defined species described by structure II is proposed for the enkephalin–copper complex, despite the difficulties in the determination of binding sites with the experimental conditions used causing interference by minor species. The peptides are strongly held by the metal ions, but the coordination sphere is somewhat flexible. A different kinetically inert complex, structure I, is formed under alkaline conditions; the metal ion is then coordinatively saturated, and the peptides cannot exchange with other potential ligands. These results show that metal ion complexation can eventually lead to conformational information on the mode of action of small biologically active peptides. Correlations between the peptide–metal complex structures and their biological activities could lead to better insight on the conformational requirements at the receptor sites.

Registry No. [Leu^5]enkephalin, 58822-25-6; [Met^5]enkephalin, 58569-55-4; Cu, 7440-50-8.

Contribution from the Departments of Chemistry, Columbia University, New York, New York 10027,
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Stereochemical Studies on Seven-Coordinate Complexes with Stoichiometry (Bidentate ligand)pentakis(unidentate ligand)metal. Crystal Structures of [Mo(dppm)$(CNCH_3)_5](PF_6)_2$ and [Mo(dppe)$(CNCH_3)_5](PF_6)_2$[1–3]

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The crystal and molecular structures of the two complexes [Mo(dppm)$(CNCH_3)_5](PF_6)_2$ (**1**) and [Mo(dppe)$(CNCH_3)_5](PF_6)_2$ (**2**) are reported [dppm = bis(diphenylphosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane]. Both compounds contain cations in which a seven-coordinate molybdenum atom is at the center of a distorted pentagonal bipyramid, the pentagonal plane being comprised of three unidentate methyl isocyanide ligands and the bidentate diphosphine ligand. Unidentate methyl isocyanide ligands occupy the remaining two axial sites in both cations. The Mo–C distances range from 2.090 (9) to 2.157 (6) Å in **1** and from 2.096 (7) to 2.150 (5) Å in **2**. The Mo–P distances are 2.519 (1) and 2.538 (1) Å in **1** and 2.518 (1) and 2.557 (2) Å in **2**. The geometries of the cations are compared with those predicted for complexes of stoichiometry (bidentate ligand)pentakis(unidentate ligand)metal by the ligand–ligand repulsion energy calculations of Kepert. Crystal data for **1** are as follows: a = 15.313 (2) Å, b = 17.328 (4) Å, c = 16.891 (3) Å, β = 115.04 (1)°, V = 4060.7 Å^3, Z = 4, monoclinic, Cc, final R = 0.033 for 3380 X-ray diffractometer data with $F_o > 4[\sigma(F_o)]$. Crystal data for **2** are as follows: a = 13.396 (3) Å, b = 14.254 (4) Å, c = 12.740 (2) Å, α = 96.21 (2)°, β = 112.92 (2)°, γ = 99.56 (2)°, V = 2169.1 Å^3, Z = 2, triclinic, $P\bar{1}$, final R = 0.054 for 6007 X-ray diffractometer data with $F_o > 4[\sigma(F_o)]$.

Introduction

Recently we have studied the structures of a variety of seven-coordinate molybdenum(II) and tungsten(II) isocyanide complexes containing unidentate ligands.[5] Criteria were developed for classifying the geometries and analyzing the factors that dictate the choice of stereochemistry for the ML_7^{2+}/ML_6X^+ families, where L = RNC and X = halide or pseudohalide. With the synthesis of the [Mo(diphosphine)(isocyanide)$_5]^{2+}$ cations,[6] exploration of related complexes having the stoichiometry [M(BL)(UL)$_5$] (BL = bidentate ligand; UL = unidentate ligand) became possible. In such molecules the constraints of the chelating ligand will influence the structure, and there are highly regarded[7] theoretical models[8,9] for analyzing the resulting stereochemistry.

Here we report the structures of the pentagonal-bipyramidal complexes [Mo(dppm)$(CNCH_3)_5](PF_6)_2$ (**1**)[3] and [Mo(dppe)$(CNCH_3)_5](PF_6)_2$ (**2**)[3] having four- and five-membered chelate rings, respectively. Prior to this study, the only structurally characterized [M(BL)(UL)$_5$] complexes were $[Nb(O_2)F_5]^{3-}$ and $[Ta(O_2)F_5]^{3-}$.[10,11]

Experimental Procedure and Results

Collection and Reduction of X-ray Data. (Bis(diphenylphosphino)methane)pentakis(methyl isocyanide)molybdenum(II) Hexafluorophosphate, [Mo(dppm)$(CNCH_3)_5](PF_6)_2$ (1). The synthesis and crystallization of **1** have been described previously.[6] The orange-red crystal used in the diffraction study had approximate dimensions 0.20 × 0.17 × 0.53 mm and was sealed in a capillary to minimize decomposition. Study on the diffractometer suggested that the crystal belonged to the monoclinic crystal system. Its quality was

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(1) Part 16 of a continuing series on higher coordinate cyanide and isocyanide complexes. For part 15 see ref 2.

(2) Giandomenico, C. M.; Lam, C. T.; Lippard, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 1263.

(3) Ligand abbreviations: dppm = bis(diphenylphosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane; dppp = 1,3-bis(diphenylphosphino)propane; diars = *o*-phenylenebis(dimethylarsine); *rac*-diars = *rac-o*-phenylenebis(methylphenylarsine); *meso*-diars = *meso-o*-phenylenebis(methylphenylarsine).

(4) (a) Columbia University. (b) Purdue University.

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Table I. Experimental Details of the X-ray Diffraction Studies of $[Mo(dppm)(CNCH_3)_5](PF_6)_2$ (1) and $[Mo(dppe)(CNCH_3)_5](PF_6)_2$ (2)

	1	2
(A) Crystal Parameters[a] at 26 °C		
a, Å	15.313 (2)	13.396 (3)
b, Å	17.328 (4)	14.254 (4)
c, Å	16.891 (3)	12.740 (2)
α, deg	90.00	96.21 (2)
β, deg	115.04 (1)	112.92 (2)
γ, deg	90.00	99.56 (2)
V, Å^3	4060.7	2169.1
mol wt	975.5	989.6
cryst syst	monoclinic	triclinic
space group	*Cc*	$P\bar{1}$
Z	4	2
ρ(calcd), g cm^{-3}	1.595	1.515
ρ(obsd),[b] g cm^{-3}	1.59 (1)	1.51 (1)
(B) Measurement of Intensity Data		
stds: 3 reflctns measd every 3600 s of X-ray exposure time, showed no decay	(002), (400), $(00\bar{2})$	(200), (111), $(\bar{2}00)$
no. of reflctns collected (non space group extinguished)	3709 [3° ≤ 2θ ≤ 50° (+*h*, +*k*, ±*l*)]	8217 [3° ≤ 2θ ≤ 50° (±*h*, ±*k*, +*l*), 3° ≤ 2θ ≤ 15° (±*h*, ±*k*, −*l*)]
reorientation control[c]	(1,1,12), $(3,3,\overline{12})$, (5,11,3)	$(\bar{4}\bar{3}\bar{6})$, $(1\bar{5}\bar{5})$, (436)
instrument: Enraf-Nonius CAD-4F κ-geometry diffractometer		
radiation: Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.710 73 Å) graphite monochromatized		
takeoff angle: 2.0°		
detector aperture: vertical, 4.0 mm; horizontal, variable (3.0 + tan θ) mm		
cryst-detector dist: 173 mm		
scan technique: coupled ω(cryst)-2θ(counter)		
scan width: variable, Δω = (0.7 + 0.35 tan θ)°		
scan rate: variable, 1.34–6.71° min^{-1} in ω		
scan range: 3° ≤ 2θ ≤ 50°		
prescan rejection limit: 1σ		
prescan acceptance limit: 100σ		
max counting time: 50 s		
bkgd measmts: moving cryst–moving detector, 25% added to scan width at both ends of each scan		
(C) Treatment of Intensity Data		
μ, cm^{-1}	5.54	4.45
transmission factor range[e]	0.88–0.93	0.92–0.94
averaging, R_{av}[d]		0.039
no. of reflctns after avging		7582
obsd unique data [$F_o > 4\sigma(F_o)$]	3380	6007
reduction to F_o and $\sigma(F_o)$: correction for background, attenuator, and Lorentz-polarization of monochromatized X radiation as described previously[d]		

[a] From a least-squares fit to the setting angles of 25 reflections with 2θ > 30°. [b] By suspension in a mixture of CCl_4 and $CHCl_3$. [c] Three reflections were recentered every 250 data, and if the position of any scattering vector deviated by more than 0.05° from its calculated position, a new orientation matrix was calculated on the basis of the recentering of 19 more reflections. [d] Reference 12. [e] Obtained with use of the Wehe-Busing-Levy ORABS program. Absorption corrections were not applied.

checked by taking open-counter ω scans of several strong low-angle reflections and was judged to be acceptable. The average width of the peaks at half-height was 0.09°. Further details of the data collection and reduction appear in Table I and ref 12.

(1,2-Bis(diphenylphosphino)ethane)pentakis(methyl isocyanide)molybdenum(II) Hexafluorophosphate, $[Mo(dppe)(CNCH_3)_5](PF_6)_2$ (2). The experimental procedures for **2** are similar to those for **1** and will only be elaborated where they differ. Synthetic details have appeared elsewhere.[6] The yellow crystal used for the diffraction study, which was grown from acetone/diethyl ether (4:1), had approximate dimensions 0.73 × 0.20 × 0.13 mm and was sealed in a capillary. Study on the diffractometer suggested that the crystal belonged to the triclinic crystal system, and a systematic search using TRACER-II[13] failed to reveal any higher symmetry. The average half-height width of the ω scan peaks was 0.10°. Table I and ref 12 further summarize the data collection and reduction procedures.

Determination and Refinement of the Structures. $[Mo(dppm)(CNCH_3)_5](PF_6)_2$ (1). The diffractometer output revealed the systematic absences to be *hkl* when $h + k \neq 2n$ and *h0l* when $l \neq 2n$, indicating either the noncentrosymmetric space group *Cc* (C_s^4, No. 9) or the centrosymmetric *C*2/*c* (C_{2h}^6, No. 15).[14a] With *Z* = 4, the molybdenum atoms would be required to lie on special positions in space group *C*2/*c*. Since it is unlikely that the conformation of the dppm[3] ligand would allow the cations to have crystallographically imposed 2-fold symmetry, and inversion symmetry could be ruled out on the basis of the stoichiometry of the cations, the space group *Cc* was chosen. This choice is supported by the successful solution and refinement of the structure. The position of the molybdenum atom was obtained from a Patterson map, and the remainder of the nonhydrogen atom positions were obtained from subsequent difference Fourier maps and cycles of least-squares refinement. Neutral-atom scattering factors and anomalous dispersion corrections for the nonhydrogen atoms were obtained from ref 15. Scattering factors for the hydrogen atoms were those of Stewart et al.[16] All nonhydrogen atoms were refined anisotropically, and no evidence for disorder was observed in any part of the structure.

Phenyl rings, including hydrogen atoms, were refined as rigid groups (C–C = 1.395 Å; C–H = 0.95 Å; C–C–C = H–C–C = 120°) pivoting on the carbon atom attached to phosphorus. Phenyl-ring hydrogen atoms were assigned a common isotropic temperature factor that converged at *U* = 0.075 (5) Å^2. In the final stages of refinement, methyl hydrogen atoms were set up and refined as rigid groups (C–H = 0.95 Å; H–C–H = 109.5°) pivoting on their respective carbon atoms. A common isotropic temperature factor for all these hydrogen atoms converged toward *U* = 0.148 Å^2. In the final cycles of refinement these methyl hydrogen atoms were included as invariants with all parameters fixed at the values obtained in the last cycle of rigid-group refinement. Methylene hydrogen atoms were placed in calculated positions (C–H = 0.95 Å), and a common isotropic temperature factor for these converged to *U* = 0.052 (12) Å^2.

Least-squares refinement, using SHELX-76,[17] was carried out in two alternating blocks. In the first block (341 parameters) the scale factor and parameters for the atoms of the cation were refined while the second block (130 parameters) contained the scale factor and parameters for the atoms of the anions. The final residual indices[18] were $R_1 = 0.033$ and $R_2 = 0.039$. That the correct hand had been chosen was verified by the R_2 value of 0.040 obtained from refinement of the alternate configuration and by a comparison of Friedel pairs. The function minimized in the least squares was $\sum w(|F_o| - |F_c|)^2$, where $w = 0.7450/[\sigma^2(F_o) + 0.000400F_o^2]$. In the final cycles of refinement no parameter shifted by more than 0.005 of its estimated standard deviation and the largest peak on the final difference Fourier map was 0.72 e Å^{-3} in the vicinity of the molybdenum atom. The average $w\Delta^2$ for groups of data sectioned according to parity group, $|F_o|$, (sin θ)/λ, |*h*|, |*k*|, or |*l*|, showed good consistency, and the weighting scheme was considered to be satisfactory.

Final nonhydrogen atom positional parameters, together with their estimated standard deviations, appear in Table II. Interatomic distances and angles, with estimated standard deviations, are given in Table IV. A listing of final observed and calculated structure

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(15) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99, 149.

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(17) Sheldrick, G. M. In "Computing in Crystallography", Schenk, H., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; p 34.

(18) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table II. Final Positional Parameters for the Nonhydrogen Atoms of $[Mo(dppm)(CNCH_3)_5](PF_6)_2$ (1)[a,b]

atom	x	y	z
Mo	0.00	0.46314(2)	0.50
P(1)	-0.06870(11)	0.34103(8)	0.41566(10)
P(2)	0.09454(10)	0.34037(8)	0.56249(10)
P(3)	0.52954(15)	0.49495(10)	0.46028(14)
P(4)	-0.28220(15)	0.25333(11)	0.76919(15)
F(31)	0.5444(7)	0.5103(5)	0.5561(5)
F(32)	0.4181(4)	0.5095(5)	0.4292(5)
F(33)	0.5114(4)	0.4798(4)	0.3619(4)
F(34)	0.5150(5)	0.4084(3)	0.4724(5)
F(35)	0.5467(4)	0.5833(3)	0.4503(4)
F(36)	0.6407(4)	0.4818(4)	0.4883(5)
F(41)	-0.3471(4)	0.1882(3)	0.7052(4)
F(42)	-0.3326(5)	0.3158(3)	0.6965(4)
F(43)	-0.2150(4)	0.3184(3)	0.8292(4)
F(44)	-0.2316(6)	0.1908(3)	0.8382(4)
F(45)	-0.2049(6)	0.2388(5)	0.7336(8)
F(46)	-0.3548(6)	0.2689(5)	0.8073(6)
N(11)	0.1043(5)	0.4809(3)	0.3705(4)
N(21)	-0.0140(4)	0.6521(2)	0.4923(4)
N(31)	-0.0960(5)	0.4484(3)	0.6391(4)
N(41)	-0.2211(4)	0.5052(3)	0.3629(4)
N(51)	0.2096(4)	0.5272(3)	0.6422(4)
C(11)	0.0649(5)	0.4732(3)	0.4137(4)
C(12)	0.1585(7)	0.4773(5)	0.3179(6)
C(21)	-0.0113(5)	0.5861(3)	0.4942(5)
C(22)	-0.0211(5)	0.7351(3)	0.4902(6)
C(31)	-0.0614(5)	0.4544(4)	0.5902(5)
C(32)	-0.1447(7)	0.4355(6)	0.6949(6)
C(41)	-0.1427(5)	0.4902(4)	0.4095(5)
C(42)	-0.3194(6)	0.5231(5)	0.3052(6)
C(51)	0.1363(5)	0.5049(4)	0.5964(4)
C(52)	0.3055(6)	0.5534(5)	0.6955(6)
C(61)	-0.1548(3)	0.28405(18)	0.4401(3)
C(62)	-0.2116(3)	0.32026(18)	0.4753(3)
C(63)	-0.2680(3)	0.27616(18)	0.5050(3)
C(64)	-0.2674(3)	0.19586(18)	0.4994(3)
C(65)	-0.2106(3)	0.15967(18)	0.4642(3)
C(66)	-0.1543(3)	0.20376(18)	0.4345(3)
C(71)	-0.1138(3)	0.3433(2)	0.29734(18)
C(72)	-0.0494(3)	0.3402(2)	0.25876(18)
C(73)	-0.0827(3)	0.3505(2)	0.16878(18)
C(74)	-0.1804(3)	0.3640(2)	0.11738(18)
C(75)	-0.2448(3)	0.3672(2)	0.15597(18)
C(76)	-0.2115(3)	0.3568(2)	0.24596(18)
C(81)	0.22508(19)	0.3443(2)	0.6014(2)
C(82)	0.26231(19)	0.3618(2)	0.5411(2)
C(83)	0.36093(19)	0.3744(2)	0.5696(2)
C(84)	0.42233(19)	0.3695(2)	0.6584(2)
C(85)	0.38509(19)	0.3519(2)	0.7187(2)
C(86)	0.28645(19)	0.3393(2)	0.6901(2)
C(91)	0.0691(3)	0.28476(19)	0.6427(2)
C(92)	0.0775(3)	0.32239(19)	0.7186(2)
C(93)	0.0576(3)	0.28283(19)	0.7810(2)
C(94)	0.0293(3)	0.20563(19)	0.7675(2)
C(95)	0.0210(3)	0.16799(19)	0.6916(2)
C(96)	0.0408(3)	0.20756(19)	0.6292(2)
C(P1)	0.0441(4)	0.2857(3)	0.4600(3)

[a] Atoms of the cation are labeled as shown in Figure 1. [b] For the anions, F(31)–F(36) are bound to P(3) and F(41)–F(46) are bound to P(4). Estimated standard deviations, in parentheses, occur in the last significant figure(s) for each parameter.

factors, anisotropic thermal parameters, and hydrogen atom positional parameters are available as supplementary material in Tables S1, S3, and S5. Figure 1 shows the geometry of the cation along with the atom-labeling scheme.

$[Mo(dppe)(CNCH_3)_5](PF_6)_2$ (2). Except as indicated below, the details of the structure analysis for **2** are the same as those for **1**. The diffractometer output showed no systematic absences indicating either space group $P1$ (C_1^1, No. 1) or $P\bar{1}$ (C_i^1, No. 2).[14b] With $Z = 2$, the latter centrosymmetric space group was chosen and has been used successfully for all subsequent work. The structure was solved with use of Patterson and Fourier maps. The common isotropic temperature factor for the phenyl-ring hydrogen atoms converged at $U = 0.096$ (5) Å^2. That for the methyl-group hydrogen atoms was fixed at $U = 0.169$ Å^2, and the common isotropic temperature factor for the methylene hydrogen atoms converged at $U = 0.053$ (8) Å^2.

Two alternating blocks were used in the least-squares refinement[17] and consisted of 352 and 130 parameters, respectively. Final residual indices[18] were $R_1 = 0.054$ and $R_2 = 0.069$. The weighting scheme was $w = 1.4709/[\sigma^2(F_o) + 0.000400F_o^2]$. The largest parameter shift in the final cycles of least-squares refinement was 0.004σ, and the two largest peaks on the final difference Fourier map were 0.98 and 0.93 e Å^{-3} in the vicinity of the molybdenum atom. All remaining peaks were <0.76 e Å^{-3}.

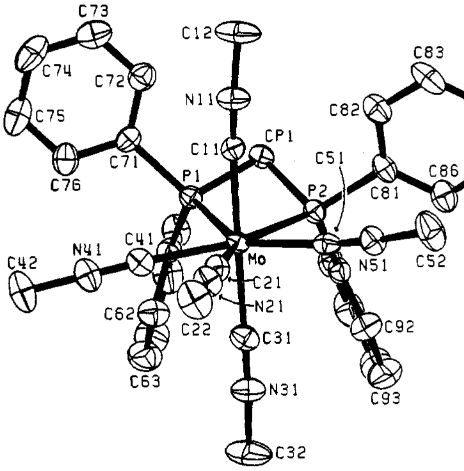

Figure 1. Geometry of the $[Mo(dppm)(CNCH_3)_5]^{2+}$ cation in **1** showing the atom-labeling scheme. Thermal ellipsoids are depicted at the 40% probability level. Hydrogen atoms are not shown. Ring 6 consists of atoms C(61)–C(66), ring 7 consists of atoms C(71)–C(76), etc. For clarity, not all atoms of rings 6 and 9 are labeled.

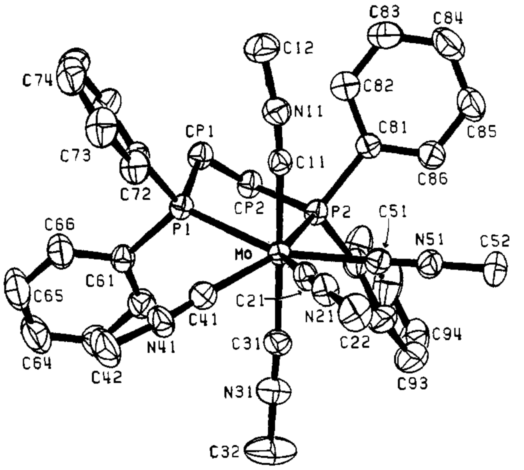

Figure 2. Geometry of the $[Mo(dppe)(CNCH_3)_5]^{2+}$ cation in **2** showing the atom-labeling scheme. Thermal ellipsoids are depicted at the 40% probability level. Hydrogen atoms are not shown. Ring 6 consists of atoms C(61)–C(66), ring 7 consists of atoms C(71)–C(76), etc. For clarity, not all atoms of rings 6, 7, or 9 are labeled.

Tables III and V list final nonhydrogen atom positional parameters and interatomic distances and angles. Final observed and calculated structure factors, anisotropic thermal parameters, and hydrogen atom positional parameters are available as supplementary material in Tables S2, S4, and S6. Figure 2 shows the geometry of the cation along with the atom-labeling scheme.

Discussion

Description of the Structures. Structures **1** and **2** both consist of discrete $[Mo(diphosphine)(CNCH_3)_5]^{2+}$ cations (where diphosphine = dppm for **1** and dppe for **2**)[3] and PF_6^- anions. The geometry about each seven-coordinate molybdenum atom in **1** and **2** is distorted pentagonal bipyramidal. This stereochemistry is rare for seven-coordinate molybdenum(II) and tungsten(II) isocyanide complexes and thus far has been limited to cations having bidentate ligands.[19] The equatorial plane of the pentagonal bipyramid is comprised of three unidentate methyl isocyanide ligands [C(21), C(41), C(51)] and the two phosphorus atoms [P(1), P(2)] from a chelating bidentate diphosphine (Figures 1 and 2). The two

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[19] Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1981**, *20*, 4069.

Table III. Final Positional Parameters for the Nonhydrogen Atoms of $[Mo(dppe)(CNCH_3)_5](PF_6)_2$ (**2**)[a,b]

atom	x	y	z
Mo	-0.22261(3)	0.18046(3)	-0.00579(3)
P(1)	-0.07427(10)	0.31763(8)	0.14309(10)
P(2)	-0.13969(10)	0.26328(8)	-0.13128(10)
P(3)	-0.33797(13)	-0.02284(13)	-0.65563(15)
P(4)	-0.62197(15)	0.36126(16)	-0.80881(17)
F(31)	-0.3449(4)	0.0633(3)	-0.5705(4)
F(32)	-0.2538(4)	-0.0550(3)	-0.5470(4)
F(33)	-0.4227(4)	0.0098(4)	-0.7622(4)
F(34)	-0.4375(4)	-0.0908(3)	-0.6446(5)
F(35)	-0.3283(4)	-0.1117(3)	-0.7366(4)
F(36)	-0.2394(4)	0.0447(4)	-0.6670(5)
F(41)	-0.5662(5)	0.2773(4)	-0.7664(5)
F(42)	-0.6311(7)	0.3839(7)	-0.6933(6)
F(43)	-0.7348(4)	0.2908(5)	-0.8576(7)
F(44)	-0.6140(8)	0.3371(6)	-0.9225(6)
F(45)	-0.6829(6)	0.4424(5)	-0.8515(6)
F(46)	-0.5107(5)	0.4329(5)	-0.7494(8)
N(11)	-0.0016(4)	0.0944(3)	0.0976(4)
N(21)	-0.3572(4)	-0.0242(3)	0.0103(4)
N(31)	-0.4275(4)	0.2894(3)	-0.1036(5)
N(41)	-0.2886(4)	0.2364(3)	0.2087(4)
N(51)	-0.3312(4)	0.0228(3)	-0.2514(4)
C(11)	-0.0828(4)	0.1201(3)	0.0588(4)
C(12)	0.1068(5)	0.0771(5)	0.1612(6)
C(21)	-0.3074(4)	0.0489(3)	0.0119(4)
C(22)	-0.4312(5)	-0.1161(4)	-0.0053(6)
C(31)	-0.3565(4)	0.2494(4)	-0.0732(5)
C(32)	-0.5149(6)	0.3393(6)	-0.1467(9)
C(41)	-0.2629(4)	0.2139(3)	0.1350(5)
C(42)	-0.3087(6)	0.2660(6)	0.3086(6)
C(51)	-0.2943(4)	0.0815(4)	-0.1696(4)
C(52)	-0.3817(5)	-0.0534(5)	-0.3537(5)
C(61)	-0.1154(3)	0.4251(2)	0.1928(3)
C(62)	-0.1870(3)	0.4669(2)	0.1089(3)
C(63)	-0.2149(3)	0.5518(2)	0.1421(3)
C(64)	-0.1712(3)	0.5949(2)	0.2592(3)
C(65)	-0.0997(3)	0.5531(2)	0.3430(3)
C(66)	-0.0717(3)	0.4682(2)	0.3098(3)
C(71)	0.0189(3)	0.2873(2)	0.2789(2)
C(72)	-0.0205(3)	0.2148(2)	0.3277(2)
C(73)	0.0515(3)	0.1920(2)	0.4298(2)
C(74)	0.1629(3)	0.2418(2)	0.4832(2)
C(75)	0.2023(3)	0.3143(2)	0.4344(2)
C(76)	0.1303(3)	0.3370(2)	0.3323(2)
C(81)	-0.0600(2)	0.1954(2)	-0.1877(3)
C(82)	0.0497(2)	0.1952(2)	-0.1166(3)
C(83)	0.1104(2)	0.1445(2)	-0.1601(3)
C(84)	0.0612(2)	0.0941(2)	-0.2746(3)
C(85)	-0.0485(2)	0.0943(2)	-0.3456(3)
C(86)	-0.1091(2)	0.1450(2)	-0.3021(3)
C(91)	-0.2288(3)	0.3014(2)	-0.2620(2)
C(92)	-0.3436(3)	0.2638(2)	-0.3147(2)
C(93)	-0.4095(3)	0.2952(2)	-0.4132(2)
C(94)	-0.3606(3)	0.3643(2)	-0.4591(2)
C(95)	-0.2458(3)	0.4019(2)	-0.4064(2)
C(96)	-0.1799(3)	0.3704(2)	-0.3079(2)
C(P1)	0.0228(4)	0.3682(3)	0.0829(4)
C(P2)	-0.0392(4)	0.3761(3)	-0.0437(4)

[a] Atoms of the cation are labeled as shown in Figure 2. [b] See footnote *b*, Table II.

Table IV. Interatomic Distances (Å) and Angles (Deg) for $[Mo(dppm)(CNCH_3)_5](PF_6)_2$ (**1**)[a,b]

Coordination Sphere			
Mo-P(1)	2.519(1)	Mo-C(31)	2.107(10)
Mo-P(2)	2.538(1)	Mo-C(41)	2.122(6)
Mo-C(11)	2.090(9)	Mo-C(51)	2.157(6)
Mo-C(21)	2.136(5)		
P(1)-Mo-P(2)	63.9(1)	C(11)-Mo-C(21)	86.4(3)
P(1)-Mo-C(11)	83.3(2)	C(11)-Mo-C(31)	178.2(2)
P(1)-Mo-C(21)	143.6(2)	C(11)-Mo-C(41)	97.3(3)
P(1)-Mo-C(31)	98.1(2)	C(11)-Mo-C(51)	84.5(3)
P(1)-Mo-C(41)	73.9(2)	C(21)-Mo-C(31)	93.0(3)
P(1)-Mo-C(51)	138.4(2)	C(21)-Mo-C(41)	73.0(2)
P(2)-Mo-C(11)	90.2(2)	C(21)-Mo-C(51)	74.6(2)
P(2)-Mo-C(21)	151.1(2)	C(31)-Mo-C(41)	84.2(3)
P(2)-Mo-C(31)	89.4(2)	C(31)-Mo-C(51)	93.6(3)
P(2)-Mo-C(41)	135.8(2)	C(41)-Mo-C(51)	147.3(2)
P(2)-Mo-C(51)	76.6(2)		
Ligand Geometry			
P(1)•••P(2)	2.674(2)	N(21)-C(21)	1.145(6)
P(1)-C(61)	1.829(5)	N(21)-C(22)	1.442(7)
P(1)-C(71)	1.818(3)	N(31)-C(31)	1.160(13)
P(1)-C(P1)	1.835(5)	N(31)-C(32)	1.445(15)
P(2)-C(81)	1.823(3)	N(41)-C(41)	1.153(8)
P(2)-C(91)	1.833(5)	N(41)-C(42)	1.438(9)
P(2)-C(P1)	1.832(5)	N(51)-C(51)	1.128(8)
N(11)-C(11)	1.135(12)	N(51)-C(52)	1.434(9)
N(11)-C(12)	1.450(15)		
Mo-P(1)-C(61)	119.6(1)	C(51)-N(51)-C(52)	175.4(9)
Mo-P(1)-C(71)	118.5(1)	Mo-C(11)-N(11)	176.1(5)
Mo-P(1)-C(P1)	96.4(2)	Mo-C(21)-N(21)	177.6(6)
C(61)-P(1)-C(71)	106.6(2)	Mo-C(31)-N(31)	178.8(5)
C(61)-P(1)-C(P1)	105.6(2)	Mo-C(41)-N(41)	177.5(8)
C(71)-P(1)-C(P1)	108.3(2)	Mo-C(51)-N(51)	175.2(8)
Mo-P(2)-C(81)	117.7(1)	P(1)-C(61)-C(62)	119.6(3)
Mo-P(2)-C(91)	119.1(2)	P(1)-C(61)-C(66)	119.9(3)
Mo-P(2)-C(P1)	95.8(2)	P(1)-C(71)-C(72)	119.9(2)
C(81)-P(2)-C(91)	107.3(2)	P(1)-C(71)-C(76)	119.8(3)
C(81)-P(2)-C(P1)	108.6(2)	P(2)-C(81)-C(82)	118.1(2)
C(91)-P(2)-C(P1)	106.8(2)	P(2)-C(81)-C(86)	121.5(3)
C(11)-N(11)-C(12)	170.5(6)	P(2)-C(91)-C(92)	117.9(3)
C(21)-N(21)-C(22)	177.7(8)	P(2)-C(91)-C(96)	122.1(3)
C(31)-N(31)-C(32)	174.8(7)	P(1)-C(P1)-P(2)	93.7(3)
C(41)-N(41)-C(42)	179.2(8)		
Anion Geometry			
min P-F	1.527(11)	mean cis F-P-F	90.0(4)
max P-F	1.587(5)	min trans F-P-F	176.9(4)
mean P-F	1.565(7)	max trans F-P-F	178.5(4)
min cis F-P-F	87.5(5)	mean trans F-P-F	177.9(4)
max cis F-P-F	93.1(4)		

[a] See footnote *a*, Table II. [b] Distances have not been corrected for thermal motion. Phenyl rings, including hydrogen atoms, were refined as rigid groups with bond distances and angles fixed as described in the text. Standard deviations, quoted for mean values, are the average of the standard deviations for the individual values.

apical positions are occupied by the remaining two methyl isocyanide ligands [C(11), C(31)] coordinated in a unidentate fashion. There is no crystallographically required symmetry imposed on the cations in either **1** or **2**.

The geometry within the $CNCH_3$ ligands of **1** and **2** is self-consistent and comparable to that observed in the recent structure determination of $[Mo(CNCH_3)_7](BF_4)_2$.[20] In **1** the $C\equiv N$, N—C distances and Mo–C–C, C–N–C angles average 1.144 Å, 1.442 Å, 177.0°, and 175.5°. In **2** these values average 1.144 Å, 1.440 Å, 174.9°, and 174.3°. The similar values for $[Mo(CNCH_3)_7](BF_4)_2$ are 1.14 Å, 1.47 Å, 176.6°, and 177.2°.

The values of the Mo–C bond lengths range from 2.090 (9) to 2.157 (6) Å in **1** and 2.096 (7) to 2.150 (5) Å in **2**. These are comparable to those observed in $[Mo(CNCH_3)_7](BF_4)_2$[20] where the shortest Mo–C length is 2.038 (9) Å and the remainder range from 2.075 (9) to 2.16 (1) Å. It is noteworthy that the shorter Mo–C distances in **1** and **2** are to the apical methyl isocyanide ligands [C(11), C(31)] in accord with the idea that the two apical sites of a pentagonal bipyramid are less sterically hindered than the five equatorial sites. The Mo–C distances in **1** and **2** also agree with similar distances observed in the recently determined structures of several *tert*-butyl isocyanide complexes. In $[Mo(CN\text{-}t\text{-}Bu)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)(CN)][B(C_6H_5)_4]$[19] the crystallographically independent Mo–CNR distances are 2.121 (5) and 2.143 (5) Å. In $[Mo(SnCl_3)(CN\text{-}t\text{-}Bu)_6][(Ph_3B)_2CN]$[21] the Mo–C distances range from 2.071 (18) to 2.138 (8) Å, and the Mo–C distances vary from 2.050 (10) to 2.114 (6) Å in $[Mo(CN\text{-}t\text{-}Bu)_6(CN)](PF_6)$.[5] In the cyclohexyl isocyanide complex $[Mo(CNC_6H_{11})_7](PF_6)_2$,[5] the Mo–C distances range from 2.049 (28) to 2.145 (8) Å.

In complex **1** the Mo–P distances differ significantly from one another, being 2.519 (1) and 2.538 (1) Å. The same phenomenon is observed in **2**, where these distances are 2.518 (1) and 2.557 (2) Å. This situation has also been observed[22] in other seven-coordinate molybdenum(II) complexes con-

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Table V. Interatomic Distances (Å) and Angles (Deg) for $[Mo(dppe)(CNCH_3)_5](PF_6)_2$ (2)[a]

	Coordination Sphere		
Mo-P(1)	2.518(1)	Mo-C(31)	2.119(5)
Mo-P(2)	2.557(2)	Mo-C(41)	2.096(7)
Mo-C(11)	2.101(5)	Mo-C(51)	2.150(5)
Mo-C(21)	2.107(5)		
P(1)-Mo-P(2)	78.8(1)	C(11)-Mo-C(21)	83.8(2)
P(1)-Mo-C(11)	76.2(1)	C(11)-Mo-C(31)	175.9(2)
P(1)-Mo-C(21)	131.4(1)	C(11)-Mo-C(41)	105.6(2)
P(1)-Mo-C(31)	101.3(1)	C(11)-Mo-C(51)	93.0(2)
P(1)-Mo-C(41)	69.9(1)	C(21)-Mo-C(31)	100.2(2)
P(1)-Mo-C(51)	152.3(2)	C(21)-Mo-C(41)	73.7(2)
P(2)-Mo-C(11)	88.9(2)	C(21)-Mo-C(51)	71.0(2)
P(2)-Mo-C(21)	145.2(2)	C(31)-Mo-C(41)	76.3(2)
P(2)-Mo-C(31)	87.4(2)	C(31)-Mo-C(51)	87.8(2)
P(2)-Mo-C(41)	140.7(1)	C(41)-Mo-C(51)	137.8(2)
P(2)-Mo-C(51)	75.5(2)		
	Ligand Geometry		
P(1)•••P(2)	3.223(2)	N(21)-C(21)	1.133(7)
P(1)-C(61)	1.842(4)	N(21)-C(22)	1.449(7)
P(1)-C(71)	1.843(3)	N(31)-C(31)	1.149(8)
P(1)-C(P1)	1.839(6)	N(31)-C(32)	1.427(10)
P(2)-C(81)	1.839(4)	N(41)-C(41)	1.152(9)
P(2)-C(91)	1.832(3)	N(41)-C(42)	1.434(11)
P(2)-C(P2)	1.835(4)	N(51)-C(51)	1.142(6)
N(11)-C(11)	1.146(7)	N(51)-C(52)	1.449(7)
N(11)-C(12)	1.439(8)	C(P1)-C(P2)	1.527(6)
Mo-P(1)-C(61)	118.9(1)	C(51)-N(51)-C(52)	177.5(6)
Mo-P(1)-C(71)	117.1(1)	Mo-C(11)-N(11)	174.7(4)
Mo-P(1)-C(P1)	109.2(1)	Mo-C(21)-N(21)	173.5(4)
C(61)-P(1)-C(71)	103.7(2)	Mo-C(31)-N(31)	176.2(5)
C(61)-P(1)-C(P1)	103.1(2)	Mo-C(41)-N(41)	175.6(5)
C(71)-P(1)-C(P1)	102.7(2)	Mo-C(51)-N(51)	174.3(5)
Mo-P(2)-C(81)	116.0(1)	P(1)-C(61)-C(62)	118.0(2)
Mo-P(2)-C(91)	120.8(1)	P(1)-C(61)-C(66)	121.9(2)
Mo-P(2)-C(P2)	109.2(2)	P(1)-C(71)-C(72)	120.8(2)
C(81)-P(2)-C(91)	101.4(2)	P(1)-C(71)-C(76)	119.2(3)
C(81)-P(2)-C(P2)	104.3(2)	P(2)-C(81)-C(82)	120.2(2)
C(91)-P(2)-C(P2)	103.4(2)	P(2)-C(81)-C(86)	119.8(2)
C(11)-N(11)-C(12)	170.2(5)	P(2)-C(91)-C(92)	121.3(3)
C(21)-N(21)-C(22)	172.8(5)	P(2)-C(91)-C(96)	118.7(2)
C(31)-N(31)-C(32)	177.0(8)	P(1)-C(P1)-C(P2)	111.2(3)
C(41)-N(41)-C(42)	174.0(5)	P(2)-C(P2)-C(P1)	112.3(3)
	Anion Geometry		
min P-F	1.501(9)	mean cis F-P-F	90.0(4)
max P-F	1.600(6)	min trans F-P-F	174.5(5)
mean P-F	1.553(6)	max trans F-P-F	179.8(1)
min cis F-P-F	85.2(5)	mean trans F-P-F	177.9(4)
max cis F-P-F	95.7(5)		

[a] See footnote *a*, Table III, and footnote *b*, Table IV.

taining dppe and dppp.[3] In $[MoI_2(CO)_3(dppe)]$[22] the Mo–P distances are 2.511 (3) and 2.638 (3) Å while in $[MoI_2(CO)_3(dppp)]$[22] they are 2.568 (4) and 2.631 (5) Å. In these latter two complexes this bond distance discrepancy can be rationalized in that the short Mo–P bond is trans to an iodine atom while the long Mo–P bond is trans to a carbonyl group. The iodine atom, being a π donor, would tend to build up electron density on the metal, which could then be removed by back-bonding to the phosphorus atom. The result would be a stronger, and hence shorter, Mo–P bond. The carbonyl ligand, being a good π acceptor, competes with a phosphorus atom trans to it for metal electron density, resulting in a weaker, and longer, Mo–P bond. The disparity between the Mo–P distances within **1** and **2** is not so obviously explained, however, since phosphorus is trans to isocyanide in all cases. It is noteworthy, nevertheless, that a long Mo–P bond lies approximately trans to a short Mo–CNR bond and a short Mo–P bond lies approximately trans to a long Mo–CNR bond. Long and short metal–P distances were not observed in the structure of $[WI_2(CO)_3(dppm)]$.[22] Disorder in the metal coordination sphere of this complex, however, among certain of the iodine and carbonyl ligands resulted in each phosphorus being opposite carbonyl ~50% of the time and opposite iodine the remainder. This disorder probably means that the structurally determined distances represent an average of two different W–P distances.

The P–C (ring) distances of the diphosphine ligands range from 1.818 (3) to 1.833 (5) Å in **1** and from 1.832 (3) to 1.843 (3) Å in **2**. These values are comparable to similar distances observed[22] in $[WI_2(CO)_3(dppm)]$, $[MoI_2(CO)_3(dppe)]$, and $[MoI_2(CO)_3(dppp)]$. The same may be said for the P–CH_2 distances, which are 1.835 (5) and 1.832 (5) Å for **1** and 1.839 (6) and 1.835 (4) Å for **2**. As observed before,[23] the Mo–P–CH_2 angles differ for dppm and dppe[3] complexes, being 96.4 (2) and 95.8 (2)° in **1** and 109.2 (1) and 109.2 (2)° in **2**. The same situation exists[22] in $[WI_2(CO)_3(dppm)]$ and $[MoI_2(CO)_3(dppe)]$. In the former the M–P–CH_2 angles are 99.3 and 99.2° while in the latter they are 111.0 and 109.6°. The C(ring)–P–C(ring) angles tend to be similar in the different complexes,[23] however, and are 106.6 (2) and 107.3 (2)° in **1** and 103.7 (2) and 101.4 (2)° in **2**. In $[WI_2(CO)_3(dppm)]$ these angles are 106.0 and 104.1°, and in $[MoI_2(CO)_3(dppe)]$ they are 104.8 and 102.8°.

The P–Mo–P angle and P···P distance in **1** are 63.9 (1)° and 2.674 (2) Å, respectively. These values are comparable to those in $[WI_2(CO)_3(dppm)]$, which are 65.9 (1)° and 2.722 (5) Å. In the dppe complexes, as a result of the replacement of the methylene bridge between the phosphorus atoms with an ethylene bridge, the P–Mo–P angle and P···P distance are larger, being 78.8 (1)° and 3.223 (2) Å in **2** and 76.3 (8)° and 3.182 (4) Å in $[MoI_2(CO)_3(dppe)]$. The conformations of the methylene and ethylene bridges in **1** and **2** are quite different from those observed in $[WI_2(CO)_3(dppm)]$ and $[MoI_2(CO)_3(dppe)]$. In **1**, atom C(P1) is −0.66 Å from the P(1)–Mo–P(2) plane while in $[WI_2(CO)_3(dppm)]$ this distance is only −0.07 Å. In **2**, atom C(P1) is −0.47 Å from this plane and C(P2) is 0.21 Å while in $[MoI_2(CO)_3(dppe)]$ these values are −0.66 and 0.02 Å.

The disposition of the phenyl rings of the dppm ligand in **1**, compared with that observed in the $[WI_2(CO)_3(dppm)]$ complex, is quite different. The cation in **1** has pseudomirror symmetry where the mirror plane passes through Mo and the midpoint of the line between P(1) and P(2) and also lies perpendicular to the P(1)–P(2) vector. The metal–diphosphine moiety, therefore, also has pseudomirror symmetry. In $[WI_2(CO)_3(dppm)]$, the metal–diphosphine moiety has pseudo-2-fold symmetry with the pseudo-2-fold axis passing through W and the midpoint of the P(1)–P(2) vector. In **1**, the dihedral angles between the plane through rings 6 and 9 is 39.0° while the dihedral angle between rings 7 and 8 is only 17.7°. In $[WI_2(CO)_3(dppm)]$ the dihedral angles between similar planes are 90.6 and 99.9°. The cation in **2** possesses pseudo-2-fold symmetry with the axis passing through Mo and the midpoint of the P(1)–P(2) vector. The metal–diphosphine moiety, then, also possesses pseudo-2-fold symmetry, and this is also the case in the complex $[MoI_2(CO)_3(dppe)]$, although the 2-fold symmetry in the latter case is less exact. In **2**, the dihedral angle between rings 6 and 9 is 96.4° while that between rings 7 and 8 is 81.2°. In $[MoI_2(CO)_3(dppe)]$ the comparable dihedral angles are 127.7 and 69.5°.

There is no evidence for disorder of any of the PF_6^- groups in either **1** or **2**, and their geometry is in agreement with that observed in recent structure determinations of a variety of similar compounds.[5]

Comparison of Stereochemistry with Repulsion Energy Calculations. Chelating ligands are known from theoretical considerations to help dictate the structures of seven-coordinate compounds.[7,8] For seven-coordinate complexes of stoichiometry $[M(BL)(UL)_5]$, ligand–ligand repulsion energy calculations[8,9] reveal that when the normalized bite of the bidentate ligand is less than 1.1, there are two minima of comparable energy of the potential energy surface. One of these is a capped trigonal prism (called stereochemistry A) and the other is a pentagonal bipyramid (called stereochemistry B). The "normalized bite" of a bidentate ligand is defined as b =

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(23) Palenik, G. J.; Mathew, M.; Steffen, W. L.; Beran, G. *J. Am. Chem. Soc.* **1975**, *97*, 1059.

Table VI. Comparison of Calculated and Experimental Angular Coordinates (Deg) for 1 and 2

	b^a	ϕ_A	ϕ_C	θ_C	ϕ_D	θ_D	ϕ_E	θ_E	ϕ_F	θ_F	ϕ_G	θ_G	ref
calcd for stereochemistry B^b	1.1	33.4	107	0	90	90	107	180	90	270	180	*c*	9
	1.3	40.5	110	0	89	90	110	180	89	270	180		9
$[Mo(dppm)(CNCH_3)_5](PF_6)_2$ (1)^d	1.06	31.9	108	−13	94	82	105	167	86	264	172	118	*e*
$[Mo(dppe)(CNCH_3)_5](PF_6)_2$ (2)^d	1.27	39.4	114	−11	96	79	106	156	80	260	164	117	*e*

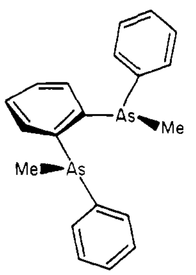
[a] The "normalized bite" of a bidentate ligand, *b*, is defined as AB/MA = AB/MB or as 2 sin ($\phi_A/2$) (Figure 3). [b] See Figure 3. [c] θ_G has no meaning when $\phi_G = 180°$. [d] P(2) occupies site A (Figure 3), C(21) occupies site G. [e] This work.

AB/MA = AB/MB (Figure 3). For normalized bites greater than 1.1 the situation becomes more complicated, but, in essence, there are now four minima of comparable energy. Stereochemistry A distorts somewhat while stereochemistry B splits into two separate minima, stereochemistry B as before and stereochemistry C. A fourth minimum also appears. This minimum is a capped trigonal prism (called stereochemistry D).

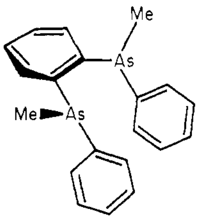
The cation in compound **1**, with a normalized bite of 1.06, and the cation in **2**, with a normalized bite of 1.27, are both closest to pentagonal bipyramidal (stereochemistry B). This identification can be seen from Table VI, which compares experimental and calculated angular parameters. For **1**, the most notable deviations from the calculated values are in θ_C and θ_E, which deviate by −13° in each case. This difference corresponds to a rotation of C(51) and C(41) by −13° relative to the bidentate ligand and results in a puckering of the pentagonal plane of the pentagonal bipyramid. This rotation causes C(51) to move toward C(11) and C(41) toward C(21). As a consequence, C(11) and C(21) also shift relative to the bidentate ligand, the result of which is a deviation of θ_D and θ_F by an average of −7° from the calculated values (−8° for θ_D and −6° for θ_F). All the observed ϕ values agree well with the calculated ones except perhaps for ϕ_G, which deviates by 8°. In **2**, a similar situation occurs. Specifically, θ_C deviates by −11° and θ_E by −26° from the calculated values. Again, θ_D and θ_F differ from the calculated values: θ_D by −11° and θ_F by −10°. The puckering of the pentagonal plane is thus much more pronounced in **2** than it is in **1**. The observed and calculated ϕ values also agree less well in **2**.

The puckering of the pentagonal plane in **1** and **2** probably results from the inability to fit three carbon atoms and two phosphorus atoms, the latter separated by 2.674 Å in **1** and 3.223 Å in **2**, in a plane around a central molybdenum atom. It is noteworthy that the puckering of the pentagonal plane is greater in **2**, where the P(1)···P(2) separation is larger. Since the repulsion energy calculations are performed by presuming points on a sphere, and do not take account of atom size, it is not unreasonable that theory and experiment deviate somewhat.

The puckering of the pentagonal plane in **1** and **2** does not appear to be a result of the disposition of the phenyl rings or the conformation of the bidentate diphosphine ligands. This result contrasts with that found for the complexes $[MoI_2(CO)_3(\textit{rac}\text{-diars})]$ and $[MoI_2(CO)_3(\textit{meso}\text{-diars})]$ in which substitution of the racemic ligand for the meso ligand had a marked effect on the stereochemistry of the remaining five unidentate ligands.[9] As noted above, the cation in **1** has pseudomirror symmetry while that in **2** has pseudo-2-fold symmetry. If the conformation of the diphosphine ligand were to dictate the stereochemistry of the five unidentate ligands in these complexes, it might be expected that the distortion of the pentagonal plane in **1** would be such as to maintain this pseudomirror symmetry while that in **2** would be so as to maintain the pseudo-2-fold symmetry. We have already seen, however, that the rotations of C(51) and C(41) in **1** and **2** both occur in the same (2-fold) sense about the line through Mo and the midpoint of the P(1)–P(2) vector; i.e., θ_C and θ_E both deviate in a negative sense in **1** as well as **2**. This result is also evident in the departures of C(51) and C(41) from the P(1)–Mo–P(2) plane. In **1**, these deviations are −0.48 and 0.47 Å for C(51) and C(41), respectively, while in **2** the deviations are in the same sense and are −0.38 and 0.81 Å. The different behavior for **1** and **2** compared with that for $[MoI_2(CO)_3(\textit{rac}\text{-diars})]$ and $[MoI_2(CO)_3(\textit{meso}\text{-diars})]$ is possibly due to the more crowded coordination spheres in the latter two complexes. In these complexes the molybdenum atom is bound to three carbon, two arsenic, and two iodine atoms while in **1** and **2** the molybdenum atom is bound to five carbon and two phosphorus atoms.



rac-diars



meso-diars

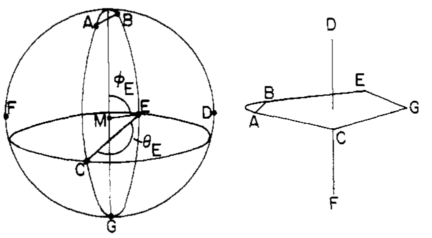


Figure 3. Axes used to define the stereochemistry of $[M(BL)(UL)_5]$ complexes in this work and ref 9. Note that the labeling scheme in ref 8 differs considerably. M represents the metal atom at the center of the sphere, and *b* is defined in footnote *a*, Table VI.

Even with the departures from ideality noted above, the present study emphasizes the utility of the repulsion energy model for rationalizing structural data in $[M(BL)(UL)_5]$ seven-coordinate complexes. The observed geometries correspond to one of the energy minima calculated by the model. Other minima on the potential energy surface, for example the capped trigonal prismatic stereochemistry A, may arise in different salts of these heptacoordinate cations since crystal-packing forces are known to influence the geometry of compounds in this class.[5]

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Registry No. **1**, 74081-65-5; **2**, 74096-47-2.

Supplementary Material Available: Listings of final observed and calculated structure factors (Tables S1 and S2), final anisotropic thermal parameters (Tables S3 and S4), and final hydrogen atom positional parameters for **1** and **2** (Tables S5 and S6, respectively) (46 pages). Ordering information is given on any current masthead page.