average ca. 114°; the presence of a chlorine atom at tin does not permit the same degree of strain relief. The strain in BiR_3 is, however, not only restricted to the C atoms close to Bi but extends to the $SiMe_3$ moieties. The effect is similar in all three ligands and is revealed in the C-Si-Me angle (~112°) being larger than the Me-Si-Me angle (~107°). The average Si-C distance is 1.874 (±0.014) Å whereas the average Si···Si and Si···C interligand distances are 3.192 and 3.636 Å, respectively. For H···H the lowest value is 2.162 Å. It will be interesting to observe the change in geometry when the crowding at bismuth is relieved by forming Bi(V) compounds in which the angles at bismuth are 120° rather than 103°.

The large C-Bi-C angles (ca. 103°) seen in BiR_3 suggest that there may be a higher degree of hybridization of the 6s and 5p orbitals than is usually thought to exist in bismuth(III) compounds. This may serve to enhance its Lewis base characteristics. We are currently investigating the donor properties of this molecule, through examination of the IR spectra of $M(CO)_5(BiR_3)$ and $M(CO)_4(BiR_3)_2$, M = Cr, Mo, W, and various other metal complexes.

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Supplementary Material Available: A packing diagram, tables of hydrogen coordinates, anisotropic thermal parameters, and structure factors, and a full table of bond angles (41 pages). Ordering information is given on any current masthead page.

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Further Studies of Seven-Coordinate Complexes with Stoichiometry (Bidentate ligand)pentakis(unidentate ligand)metal. Crystal Structure of $[Mo(dppm)L_5](PF_6)_2$, with L = Cyclohexyl Isocyanide[1-3]

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The crystal and molecular structure of the cyclohexyl isocyanide complex $[Mo(dppm)(CNC_6H_{11})_5](PF_6)_2$ is reported (dppm = bis(diphenylphosphino)methane). The cations contain seven-coordinate molybdenum atoms in a distorted-pentagonal-bipyramidal configuration, with the equatorial plane consisting of the phosphorus atoms of the chelating diphosphine ligand and of three isocyanide ligands and the remaining two isocyanide ligands occupying axial positions. The distortion involves a puckering of the equatorial plane in such a way as to maintain an approximate molecular mirror plane, which passes through the molybdenum atom, the two axial ligand atoms, and the equatorial ligand atom farthest from the phosphorus atoms. This pseudo mirror plane bisects the four-membered chelate ring of the diphosphine ligand. The Mo-P distances are 2.527 (2) and 2.549 (2) Å, and the Mo-C distances range from 2.102 (9) to 2.132 (11) Å. Crystals of the compound $MoP_4F_{12}N_5C_{60}H_{77}$ are monoclinic, space group $P2_1$, with a = 12.179 (1) Å, b = 19.469 (2) Å, c = 13.807 (1) Å, β = 102.47 (2)°, and Z = 2. The final R value was 0.057 for 4782 observed X-ray diffractometer data. The published structures of several complexes containing the dppm ligand chelated to a single metal atom are analyzed.

Introduction

We have recently explored the influence of chelating diphosphine ligands on the stereochemistry of seven-coordinate complexes of the type $[M(BL)(UL)_5]$ (BL = bidentate ligand; UL = unidentate ligand).[5] In particular, we determined that the complexes $[Mo(dppm)(CNCH_3)_5](PF_6)_2$ and $[Mo(dppe)(CNCH_3)_5](PF_6)_2$ have pentagonal-bipyramidal stereochemistry and we compared the structures with theoretical models.[6,7] Here we examine the effect that modifying the alkyl isocyanide ligands has on the structure through a study of the cyclohexyl isocyanide-dppm complex $[Mo(dppm)L_5](PF_6)_2$, L = $C_6H_{11}NC$. The results extend our understanding of the factors that control the stereochemistry of these higher coordinate cations.

Experimental Section

The synthesis and characterization of (bis(diphenylphosphino)methane)pentakis(cyclohexyl isocyanide)molybdenum(II) hexfluorophosphate, $[Mo(dppm)(CNC_6H_{11})_5](PF_6)_2$, have been described previously.[8] The orange-red crystal used in the diffraction study was mounted in air on the end of a glass fiber. Crystal data and details of the collection of reflected intensities are given in Table I.

The X-ray measurements indicated a monoclinic system, with reflections $0k0$ having $k \neq 2n$ systematically absent. The space group is thus either the centrosymmetric group $P2_1/m$ (C_{2h}^2, No. 11)[9a] or the noncentrosymmetric group $P2_1$ (C_2^2, No. 4).[9b] Although a noncentric structure was suggested by the intensity statistics, the structure determination was initiated in space group $P2_1/m$. This choice was made partly because phases based on the P-Mo-P fragment of the cation, readily found by inspection of a Patterson map, inevitably impose a mirror plane on the calculated electron density. In addition, however, it was found that there was in fact an approximate mirror plane in the whole molecule. This approximate mirror symmetry can be seen clearly in the packing diagram of the final structure given in Figure 1.

The positions of 34 atoms in the cation were found by conventional Fourier methods assuming a centrosymmetric distribution. Further refinement in the centrosymmetric space group involved the need for disordered PF_6^- groups and led to unsatisfactory parameters for

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(1) Part 20 of a continuing series on higher coordinate cyanide and isocyanide complexes. For part 19 see ref 2.
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(3) Ligand abbreviations: dppm = bis(diphenylphosphino)methane; dppe = bis(diphenylphosphino)ethane.
(4) Permanent address: Chemistry Department, The King's College, Briarcliff Manor, NY 10510
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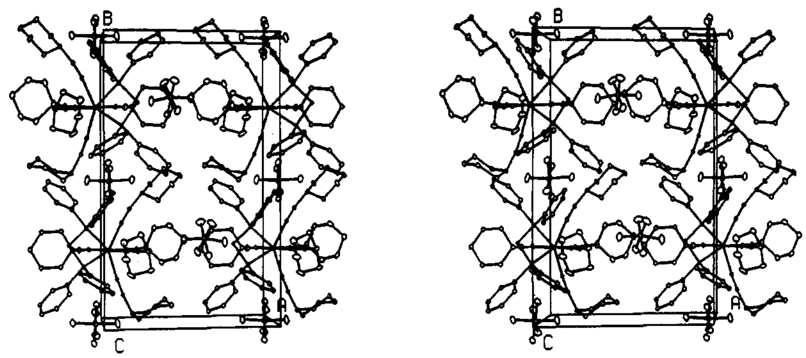

Figure 1. Stereochemistry and packing diagram for [Mo(dppm)(CNC$_6$H$_{11}$)$_5$](PF$_6$)$_2$.

Table I. Experimental Details of the X-ray Diffraction Study of (Bis(diphenylphosphino)methane)pentakis(cyclohexyl isocyanide)molybdenum(II) Hexafluorophosphate

(A) Crystal Parameters[a] at 23 °C

a = 12.179 (1) Å	space group: $P2_1$
b = 19.469 (2) Å	fw: 1316.1
c = 13.807 (1) Å	Z = 2
β = 102.47 (2)°	calcd density: 1.367 g/cm^3
V = 3196.6 (6) Å^3	formula: $MoP_4F_{12}N_5C_{60}H_{77}$

(B) Measurement and Treatment of Intensity Data[b]

instrument: Enraf-Nonius CAD-4F κ-geometry diffractometer
radiation: Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.710 73 Å), graphite monochromatized
scan range: 2° < 2θ < 55°
check reflcns: (4,0,−6), (1,8,0), and (2,2,2), monitored every 3 h, varied randomly with a net 2% decay
no. of data: 7524, 4782 of which had $I > 3\sigma(I)$
abs cor
cryst size: 0.5 × 0.4 × 0.3 mm
linear abs coeff: 3.7 cm^{-1}
transmission factors: 0.86–0.89 estimated; cor not made

(C) Final Model in the Least-Squares Refinement[c]

final R, R_w values: 0.0570, 0.0718
no. of observns: 4782
no. of parameters: 523
wts: $w = 1/\sigma^2$ with $\sigma = [\sigma^2(\text{counts}) + 0.005F^2]^{1/2}$
highest peak in final diff map: 1.0 e/Å^3 (60% of C peak)

[a] From a least-squares fit to the setting angles of 25 reflections with 2θ in the range 25–40°. [b] For procedures used in our laboratory, see: Silverman, L. D.; Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* 1980, *19*, 3379. [c] Refinements were carried out with the use of G. Sheldrick's SHELX program in the initial stages. Final refinements and calculations of molecular geometry were carried out with local versions of the Oak Ridge programs ORFLS and ORFFE. $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. Anisotropic thermal parameters for Mo, P, F, N, and C atoms were used, and H atom positions were fixed.

cyclohexyl group 4. The latter problem is now seen to have arisen from the different conformations of cyclohexyl ring 4 and of the pseudomirror-related cyclohexyl ring 5. At this point, the coordinate set was expanded to be consistent with space group $P2_1$, the coordinates of all of the atoms in the partial structure were fixed, and the coordinates of atoms in the hexafluorophosphate groups were added stepwise in such a manner as to break the pseudo mirror symmetry. It was now possible to locate and refine all of the remaining carbon atoms, after a large number of cycles of difference Fourier/least-squares calculations. The thermal parameters are large for the carbon atoms of cyclohexyl groups 1, 2, and 3, which straddle the pseudo mirror plane at $y = {}^1/_4$, and it proved impossible to refine successfully the carbon atoms of cyclohexyl group 1. The carbon and hydrogen atoms for this ring were fixed so that its geometry approximated the average geometry of the other four cyclohexyl rings. An overall temperature factor for the ring was refined, and the temperature factors of the H atoms were constrained to have B = 1 Å^2 greater than this group factor.

In the final least-squares refinement cycles, the temperature factors of the Mo, P, F, and N atoms were refined anisotropically, together with all of the cyclohexyl carbon atoms except those in ring 1. The phenyl rings, including H atoms, were refined as rigid groups, with C–C = 1.395 Å, C–H = 0.95 Å, and angles C–C–C = H–C–C = 120°. The carbon atoms of the phenyl rings were refined with individual isotropic temperature factors, and the temperature factors for the H atoms were fixed with B = 1 Å^2 greater than the temperature factors of the carbon atoms to which they were attached. Hydrogen atoms on the cyclohexyl rings were also fixed at calculated positions, and their isotropic temperature factors were constrained in a manner similar to that for the phenyl H atoms. These various constraints led to a model with 523 variables, which was refined by full-matrix least squares. Details of the final model are given in Table I. In the final cycle, several parameters associated with atoms C(25) and C(26) had shifts of 0.3–0.7 times the corresponding estimated standard deviations, and an orientation parameter for the rigid cyclohexyl group shifted 0.4 standard deviation. All other parameter shifts were less than 0.2 of the corresponding estimated standard deviation. Neutral-atom scattering factors for all atoms except H, and anomalous dispersion corrections for Mo and P, were obtained from ref 10 and scattering factors for bonded H from ref 11. Final positional parameters are listed in Table II, and details of the molecular geometry are given in Table III. Final observed and calculated structure factors, anisotropic temperature factors, parameters for the constrained carbon atoms, and hydrogen atom parameters are available as supplementary material in Tables S1–S4, respectively. The general packing is shown in Figure 1, and the stereochemistry and atom-numbering scheme for the cation are shown in Figure 2.

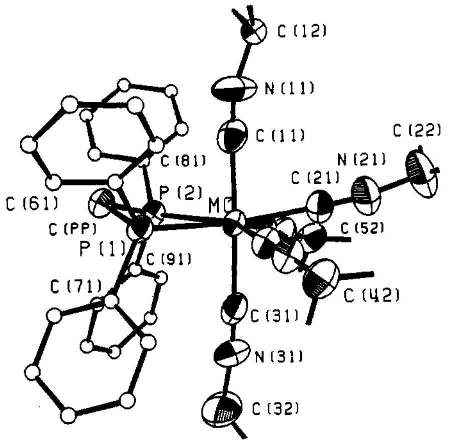

Figure 2. Inner coordination sphere, dppm ligand geometry, and atom-labeling scheme for the [Mo(dppm)(CNC$_6$H$_{11}$)$_5$]$^{2+}$ cation. Thermal ellipsoids are drawn at the 50% probability level. Cyclohexyl ring 1 (not shown for clarity) is bound at atom C(12), cyclohexyl ring 2 at C(22), etc. Phenyl rings A and C are on the same side of the P(1)–Mo–P(2) plane as is atom C(PP) while phenyl rings B and D are on the opposite side of this plane.

With the existence of the pseudo mirror plane, one would not expect the refinement to be very sensitive to a change in hand. Nevertheless, refinement was carried out with such a change, in view of the polar nature of the space group and the small differences found in the

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Table II. Final Positional Parameters for the Individually Varied Atoms Other Than Hydrogen for (Bis(diphenylphosphino)methane)pentakis(cyclohexyl isocyanide)molybdenum(II) Hexafluorophosphate[a, b]

Atom	x	y	z
Mo	0.04197(4)	0.2500	0.21209(4)
P(1)	-0.10390(20)	0.18756(13)	0.08162(19)
P(2)	-0.08746(19)	0.32858(12)	0.09369(19)
P(3)	0.0419(3)	0.4997(3)	0.5098(3)
P(4)	0.4195(4)	0.7985(3)	0.2436(4)
F(31)	0.0498(9)	0.4346(6)	0.4454(7)
F(32)	0.0367(14)	0.4549(8)	0.6016(8)
F(33)	0.1726(8)	0.5040(8)	0.5387(8)
F(34)	0.0348(10)	0.5642(7)	0.5751(7)
F(35)	0.0439(12)	0.5425(8)	0.4185(8)
F(36)	-0.0870(9)	0.5012(11)	0.4787(10)
F(41)	0.4541(12)	0.7492(15)	0.3305(12)
F(42)	0.3986(11)	0.7383(11)	0.1630(10)
F(43)	0.5385(10)	0.7955(11)	0.2284(10)
F(44)	0.2993(10)	0.7860(12)	0.2538(13)
F(45)	0.3790(18)	0.8490(10)	0.1639(11)
F(46)	0.4351(20)	0.8543(10)	0.3193(12)
C(11)	-0.0756(7)	0.2550(7)	0.3031(6)
N(11)	-0.1342(8)	0.2553(10)	0.3565(7)
C(12)*	-0.1776(15)	0.2600(23)	0.4456(18)
C(21)	0.1526(6)	0.2494(7)	0.3523(5)
N(21)	0.2097(6)	0.2492(7)	0.4307(5)
C(22)	0.2679(11)	0.2510(11)	0.5341(7)
C(23)	0.222(2)	0.3089(11)	0.5842(14)
C(24)	0.118(2)	0.2806(18)	0.606(2)
C(25)	0.141(4)	0.2274(15)	0.679(2)
C(26)	0.156(3)	0.1744(18)	0.607(3)
C(27)	0.2809(19)	0.1844(9)	0.5766(11)
C(31)	0.1566(6)	0.2488(8)	0.1165(6)
N(31)	0.2141(6)	0.2496(8)	0.0612(6)
C(32)	0.2769(10)	0.2556(16)	-0.0165(9)
C(33)	0.3270(17)	0.3250(13)	-0.016(2)
C(34)	0.418(2)	0.3340(13)	0.073(3)
C(35)	0.501(2)	0.2883(17)	0.080(2)
C(36)	0.459(2)	0.2191(16)	0.089(2)
C(37)	0.3714(20)	0.2005(11)	-0.0027(19)
C(41)	0.0921(8)	0.1469(5)	0.2436(8)
N(41)	0.1248(7)	0.0920(5)	0.2635(6)
C(42)	0.1793(8)	0.0259(5)	0.2865(8)
C(43)	0.2228(11)	0.0017(7)	0.2013(10)
C(44)	0.3232(11)	0.0445(8)	0.1851(10)
C(45)	0.4137(10)	0.0520(7)	0.2797(11)
C(46)	0.3678(10)	0.0768(7)	0.3613(10)
C(47)	0.2704(10)	0.0329(6)	0.3823(8)
C(51)	0.1179(8)	0.3486(6)	0.2422(8)
N(51)	0.1668(7)	0.3984(5)	0.2617(7)
C(52)	0.2405(8)	0.4556(5)	0.2991(8)
C(53)	0.3307(11)	0.4297(8)	0.3849(9)
C(54)	0.4104(12)	0.4864(9)	0.4259(10)
C(55)	0.4631(11)	0.5182(8)	0.3461(11)
C(56)	0.3749(12)	0.5426(7)	0.2617(11)
C(57)	0.2902(11)	0.4864(7)	0.2192(9)
C(PP)	-0.1901(6)	0.2638(4)	0.0410(6)
C(61)*	-0.2033(9)	0.1234(5)	0.1078(4)
C(71)*	-0.0610(5)	0.1526(3)	-0.0281(4)
C(81)*	-0.1724(8)	0.3965(5)	0.1306(4)
C(91)*	-0.0344(6)	0.3667(3)	-0.0067(4)

[a] Numbers in parentheses are errors in the last significant digit(s). [b] Atoms marked with an asterisk are those atoms of the rigid groups which are bonded to the rest of the molecule. They are included here for convenience. Full details of the rigid-group parameters are given in Table S4.

chemically equivalent Mo–P bonds. The ratio of weighted *R* factors showed a significant increase at the 99.5% confidence level,[12] confirming that the original choice of hand was most likely correct. The parameter shifts found on reversing the hand were such that the differences between chemically equivalent Mo–P distances were increased, rather than decreased.

Discussion

Description of the Structure. The crystal structure consists of discrete $[Mo(dppm)(CNC_6H_{11})_5]^{2+}$ cations and PF_6^- anions. The geometry about the seven-coordinate molybdenum atom is distorted pentagonal bipyramidal, with the equatorial plane

Table III. Interatomic Distances (Å) and Angles (deg) for (Bis(diphenylphosphino)methane)pentakis(cyclohexyl isocyanide)molybdenum(II) Hexafluorophosphate[a]

Coordination Sphere

Mo-P(1)	2.549(3)	Mo-C(31)	2.119(9)
Mo-P(2)	2.527(3)	Mo-C(41)	2.116(10)
Mo-C(11)	2.102(9)	Mo-C(51)	2.132(11)
Mo-C(21)	2.107(8)		

'equatorial' angles		'axial' angles	
P(1)-Mo-P(2)	65.7(1)	C(11)-Mo-P(1)	89.1(3)
P(1)-Mo-C(41)	79.6(3)	C(11)-Mo-P(2)	87.0(3)
P(2)-Mo-C(51)	76.4(3)	C(11)-Mo-C(21)	80.4(3)
C(41)-Mo-C(21)	73.0(5)	C(11)-Mo-C(41)	97.2(5)
C(51)-Mo-C(21)	70.2(5)	C(11)-Mo-C(51)	99.5(5)
P(1)-Mo-C(21)	149.0(4)	C(31)-Mo-P(1)	90.4(3)
P(2)-Mo-C(21)	141.6(4)	C(31)-Mo-P(2)	90.4(3)
P(1)-Mo-C(51)	140.7(3)	C(31)-Mo-C(21)	101.3(3)
P(2)-Mo-C(41)	145.0(3)	C(31)-Mo-C(41)	85.3(5)
C(41)-Mo-C(51)	136.1(3)	C(31)-Mo-C(51)	79.4(5)
		C(11)-Mo-C(31)	177.4(5)

Ligand Geometry

P(1)••••P(2)	2.755(3)		
P(1)-C(61)	1.828(11)	P(2)-C(81)	1.819(9)
P(1)-C(71)	1.836(6)	P(2)-C(91)	1.811(7)
P(1)-C(PP)	1.834(8)	P(2)-C(PP)	1.814(8)
Mo-P(1)-C(61)	125.2(2)	Mo-P(2)-C(81)	124.9(2)
Mo-P(1)-C(71)	118.7(2)	Mo-P(2)-C(91)	117.9(2)
Mo-P(1)-C(PP)	95.5(3)	Mo-P(2)-C(PP)	96.8(3)
C(61)-P(1)-C(71)	103.2(3)	C(81)-P(2)-C(91)	103.6(3)
C(61)-P(1)-C(PP)	104.7(4)	C(81)-P(2)-C(PP)	103.5(4)
C(71)-P(1)-C(PP)	107.1(3)	C(91)-P(2)-C(PP)	107.9(3)
P(1)-C(PP)-P(2)	98.1(3)		
C(11)-N(11)	1.131(10)	Mo-C(11)-N(11)	175.6(10)
C(21)-N(21)	1.153(9)	Mo-C(21)-N(21)	177.4(7)
C(31)-N(31)	1.142(10)	Mo-C(31)-N(31)	176.4(9)
C(41)-N(41)	1.152(12)	Mo-C(41)-N(41)	176.4(9)
C(51)-N(51)	1.140(13)	Mo-C(51)-N(51)	174.2(9)
mean *C-N*	1.144(5)	mean *Mo-C-N*	176.0(4)
N(11)-C(12)	1.444(27)	C(11)-N(11)-C(12)	162.6(12)
N(21)-C(22)	1.451(11)	C(21)-N(21)-C(22)	172.3(10)
N(31)-C(32)	1.450(13)	C(31)-N(31)-C(32)	173.2(13)
N(41)-C(42)	1.453(12)	C(41)-N(41)-C(42)	172.9(10)
N(51)-C(52)	1.453(12)	C(51)-N(51)-C(52)	170.8(11)
mean N-C	1.450(7)		

Cyclohexyl rings

	Ring 1	Ring 2	Ring 3	Ring 4	Ring 5
C(2)-C(3)	1.50	1.49(3)	1.48(4)	1.47(2)	1.52(2)
C(3)-C(4)	1.50	1.47(3)	1.48(4)	1.54(2)	1.50(2)
C(4)-C(5)	1.50	1.43(4)	1.34(3)	1.52(2)	1.52(2)
C(5)-C(6)	1.50	1.48(5)	1.46(3)	1.45(2)	1.48(2)
C(6)-C(7)	1.50	1.67(5)	1.51(3)	1.54(2)	1.53(2)
C(7)-C(2)	1.50	1.42(2)	1.55(3)	1.54(2)	1.49(2)
mean C-C		1.49			
max C-C		1.67			
min C-C		1.34			
C(7)-C(2)-C(3)	111.5	121(1)	111(1)	114(1)	112(1)
C(2)-C(3)-C(4)	111.5	104(2)	110(2)	112(1)	111(1)
C(3)-C(4)-C(5)	111.5	112(3)	113(3)	112(1)	112(1)
C(4)-C(5)-C(6)	111.5	94(2)	110(2)	112(1)	111(1)
C(5)-C(6)-C(7)	111.5	110(2)	110(2)	114(1)	113(1)
C(6)-C(7)-C(2)	111.5	100(2)	108(2)	109(1)	111(1)
mean C-C-C		110			
max C-C-C		121			
min C-C-C		94			
N-C(2)-C(3)	107	109(1)	111(2)	110(1)	108(1)
N-C(2)-C(7)	117	112(1)	110(2)	109(1)	111(1)

Anion Geometry:

min P-F	1.48(1)		
max P-F	1.60(2)		
mean P-F	1.534(4)		
min cis F-P-F	83.6(9)	min trans F-P-F	168.3(12)
max cis F-P-F	98.4(11)	max trans F-P-F	179.4(7)
mean cis F-P-F	90.0(2)	mean trans F-P-F	175.8(4)

[a] Standard deviations quoted for mean values are obtained by dividing the average of the individual standard deviations by the square root of the number of observations being averaged.

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Table IV. Comparison of the Coordination Geometries of Three $[MoL_5dppm]^{2+}$ Complexes[a]

Distances and Angles

	$[Mo(dppm)(CNC_6H_{11})_5]^{2+}$	$[Mo(dppm)(CNCH_3)_5]^{2+}$	$[Mo(dppe)(CNCH_3)_5]^{2+}$
Mo-P(1)	2.527	2.519	2.518
Mo-P(2)	2.549	2.538	2.557
Mo-C(axial)	2.111	2.099	2.120
Mo-C(equatorial)	2.118	2.127	2.118
sum of equatorial angles	364.9	362.0	368.9
sum of chelate ring angles	356.1	349.8	
Mo-C-N	176.0	177.0	174.9
C-N-C	172.3	175.5	174.3
av C≡N dist	1.144	1.144	1.144
av N-C dist	1.450	1.442	1.440
av dev of C(axial)-Mo-C(equatorial) from 90°	4.4	4.4	8.4

Angular Coordinates[b]

	$[Mo(dppm)(CNC_6H_{11})_5]^{2+}$		$[Mo(dppm)(CNCH_3)_5]^{2+}$		$[Mo(dppe)(CNCH_3)_5]^{2+}$	
	ϕ	θ	ϕ	θ	ϕ	θ
atom C, C(5)	108	11	108	−13	114	−11
atom E, C(4)	112	175	105	167	106	156
atom D, C(3)	90	90	94	82	96	79
atom F, C(1)	88	272	86	264	80	260
atom G, C(2)	168	288	172	242[c]	164	243
atom A, P(2)	33	0	32	0	39	0

[a] Distances and angles are expressed in angstroms and degrees, respectively. [b] The angle ϕ is defined as the angle X-M-A, where X is the point midway between P(1) and P(2) and A is the designated atom. The angle θ is defined as the signed dihedral angle P(2)-X-M-A. See ref 5 and 7 for further discussion. [c] This value corrects that reported previously in ref 5.

made up of the bidentate diphosphine ligand and the three monodentate isocyanide groups associated with cyclohexyl rings 2, 4, and 5 (Figure 2). With the space group chosen as $P2_1$, there is no crystallographically required symmetry for the cation or anions. There are approximate mirror planes of symmetry in the structure at $y = {}^1/_4$ and at $y = {}^3/_4$, however, as clearly seen in Figure 1. These approximate mirror planes are perpendicular to the equatorial plane of the cation inner coordination sphere, so that the point midway between the atoms P(1) and P(2), and the atoms C(11), C(21), C(31) and Mo, all have y coordinates at or very close to $y = 0.25$. The two remaining equatorial ligands, associated with cyclohexyl rings C(41) and C(51), are on opposite sides of the pseudo mirror plane. The two major features of the structure that show a deviation from $P2_1/m$ symmetry are the disposition of the PF_6^- ions and the conformations of the cyclohexyl rings 4 and 5. Atom P(3), with its associated F atoms, is situated 0.5 Å from what would be an inversion center in $P2_1/m$, and atom P(4), with its associated F atoms, lies 0.9 Å from the near mirror plane at $y = 0.75$. Cyclohexyl rings 4 and 5 are sterically different, in that the isocyanide nitrogen atom N(41) is an axial substituent for ring 4 while N(51) is an equatorial substituent for ring 5. The different conformations of these cyclohexyl groups, along with their well-defined geometry, and reasonable thermal parameters, confirm our conclusion that the space group is truly $P2_1$. The higher thermal parameters for atoms associated with cyclohexyl rings 1, 2, and 3 and with P(4) and its F atoms arise, we believe, from special problems in least-squares refinement of structures with pseudo mirror planes. Perhaps inclusion of the unobserved reflections would have led to improved refinements of these groups. In any case, the coordination sphere of the metal atom, the geometry of the diphosphine ligand, and the geometries of two of the cyclohexyl rings are well-defined.

The stereochemistry found here for the inner coordination sphere of the cation resembles that observed in our previous study[5] of the two very similar complexes $[Mo(dppm)(CNCH_3)_5]^{2+}$ and $[Mo(dppe)(CNCH_3)_5]^{2+}$. Salient features of the three structures are compared in Table IV. The average Mo–P distance in the present work is 2.535 Å, identical with the value of 2.533 Å found in the other structures. As in both of the other structures, there are small but significant differences in the two chemically identical Mo–P distances, 0.024 Å in the present case, compared with 0.021 and 0.039 Å in the other two structures. Small differences in equivalent M–P bond lengths are common in metal complexes containing dppm chelated to one metal atom (vide infra). In many cases, these differences can be related successfully to electronic effects associated with the ligands trans to the phosphorus atoms. Such a trans influence is not at all evident in the present case, however. The Mo–C bond opposite the longer Mo–P bond is actually 0.02 Å longer than the Mo–C bond opposite the shorter Mo–P bond. Perhaps the slight differences reflect the different repulsions exerted by the axially substituted cyclohexyl ring 5 and by the equatorially substituted ring 4.

The pentagonal-bipyramidal coordination sphere in the present complex is distorted in such a way as to maintain the approximate mirror plane throughout the entire complex. This mirror plane is perpendicular to the equatorial plane of the pentagonal bipyramid and contains axial ligands C(11) and C(31) as well as the Mo atom and equatorial ligand C(21) (Figure 2). The axial ligands C(11) and C(31) together with the Mo atom and the two P atoms form a regular fragment of the pentagonal bipyramid. The central equatorial ligand, C(21), is displaced symmetrically 10° up toward the axial ligand C(11), and the remaining equatorial ligands C(41) and C(51) are pushed symmetrically downward toward the opposite axial ligand C(31). These slight distortions are in the direction of a 4:3 piano-stool geometry,[13] with atoms A, B, and F (P(1), P(2), and C(11)) comprising the trigonal plane and D, E, G, and C (C(31), C(41), C(21), and C(51)) the tetragonal plane.[14] By contrast, the two methyl isocyanide complexes exhibit a twist distortion of C(11), C(31), C(41), and C(51), which moves the geometry toward that of a capped trigonal prism. The differences in the distortions are clearly seen in the θ values in Table IV. In the methyl isocyanide-dppm complex, the θ(D)–θ(F) values are all about 13° less than their ideal values, while in the cyclohexyl isocyanide complex of the present study, the θ value for atom D is 11° greater than ideal, and the θ value for atom E is 5° less than

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(14) This distorted stereochemistry has alternatively been referred to as a capped trigonal prism[7] or capped octahedron.[6]

Table V. Comparison of Structural Features (Å or deg) of Published dppm Complexes Having the Ligand Chelating a Single Metal Atom[a]

complex	coord no.	P–M–P angle	M–P dist	P···P dist	P–C–P angle	dist of C from P–M–P plane	torsion angles		geom	ref
							up	down		
$[Mo(dppm)_2(CO)_2Cl_2]$[b] (1)	7	63.5	2.49	2.67	90.0	0.81	139	86	CO–CTP	18
$[Mo(dppm)(CNCH_3)_5]^{2+}$ (2)	7	63.9	2.54	2.67	93.7	0.66	136	92	PB	5
$[Mo(dppm)(CNC_6H_{11})_5]^{2+}$ (3)	7	65.7	2.54	2.76	98.1	0.41	125	101	PB	this work
$[W(dppm)(CO)_3I_2]$ (4)	7	65.9	2.50	2.72	99.4	0.07	115	111	PB	19
$[Mo(dppm)(CO)_4]$ (5)	6	67.3	2.52	2.79	95.6	0.40	124	100	O	20
$[Ir(dppm)_2(O_2)]PF_6$ (6)	5	70.3	2.34	2.69	92.9	0.60	134	92	TB	21
$[Rh(dppm)_2(CO)]BF_4$ (7)	5	70.4	2.34	2.70	94.2	0.61	134	93	TB	22
$[Ir(dppm)_2(O_2)]ClO_4$ (8)	5	70.9	2.33	2.71	94.3	0.49	130	97	TB	21
$[Rh(dppm)_2ClH]^+$ (9)	6	72.5	2.33	2.75	96.7	0.34	125	103	O	23
$[Pd(dppm)Cl_2]$ (10)	4	72.7	2.24	2.66	93.0	0.50	131	96	SP	24
$[Pd(dppm)(SCN)_2]$ (11)	4	73.3	2.27	2.71	94.7	0.25	122	106	SP	25
$[Fe(dppm)(CO)_3]$ (12)	5	73.5	2.22	2.65	90.8	0.11	117	111	TB	26

[a] Abbreviations: CO, capped octahedron; CTP, capped trigonal prism; PB, pentagonal bipyramid; O, octahedron; TB, trigonal bipyramid; SP, square planar. [b] Only one of the dppm ligands is chelating in this compound.

ideal. θ and ϕ values for the axial atoms D and F are all very close to 90 or 270°.

The cyclohexyl rings are all in the chair form, and four of them have the isocyanide nitrogen atoms attached in an axial position, while cyclohexyl ring 5 has the nitrogen attached in an equatorial position. Several recent structural studies of complexes containing the cyclohexyl isocyanide ligand display both equatorial and axial attachment for the cyclohexyl ring in the same compound.[15-17] In the present complex, the mean values of the internal C–C–C–C dihedral angles for the cyclohexyl rings are 60, 58, 53, and 56° for rings 2, 3, 4, and 5, respectively. There is thus no special flattening associated with the ring being in an equatorially or axially substituted conformation. The N–C bond makes angles of 44, 39, 37, and 37° with the C(7)–C(1)–C(2) three-atom planes for these respective four cyclohexyl rings.

Analysis of dppm Stereochemistry. The bidentate diphosphine ligand dppm has found increasing application in inorganic chemistry in recent years, and it is of interest to analyze its geometry in metal complexes containing dppm coordinated to a single metal atom. Structural parameters for 12 such complexes are summarized in Table V. The complexes are listed in order of increasing bite angle, P–M–P. There is a tendency for the smaller bite angles to be associated with the longer metal–phosphorus bonds. Thus for the Mo and W complexes, with M–P distances of 2.49–2.54 Å, the P–M–P angles vary from 63.5 to 67.3° while for the complexes with shorter M–P distances, in the range 2.22–2.34 Å, the P–M–P angles are all larger, varying from 70.3 to 73.5°. This increase in bite angle with decreasing M–P bond length tends to keep the nonbonded P···P distances relatively constant, within a range of 2.65–2.79 Å, with a mean value of 2.71 Å. There is also a related tendency for the smaller bite angles to be associated with the higher coordination numbers. Indeed, with the exception of the iron carbonyl complex **12** and the hydridorhodium complex **9**, there is a close correlation between the coordination number and bite angle.

While the angle subtended at the metal atom by the diphosphine ligand can be related to the stereochemistry at the metal atom, no such relation holds for the puckering of the four-membered chelate ring. Thus, while compound **1**, with the smallest P–M–P bite angle, does in fact have the highest degree of puckering of the four-membered ring, as measured by the distance of the methylene carbon atom from the P–M–P plane, compound **4**, which also has a small bite angle, has a chelate ring which is nearly flat. Compound **10**, with one of the largest bite angles, is quite strongly puckered. The two iridium salts, compounds **6** and **8**, show different puckering, even though the cations are identical. Moreover, the rhodium salt, compound **7**, which differs from the iridium salt **6** by having a carbonyl group in place of the dioxygen ligand and a BF_4^- anion in place of the PF_6^- anion, has identical puckering. The puckering of the four-membered ring probably reflects packing requirements in the structure, the similar conformations in the rhodium and in the iridium complex arising because the two compounds are isostructural.[27] Increased pucker of the four-membered chelate ring pushes the phenyl groups A and C, which are on the same side of the P–M–P plane as the methylene carbon atom, outward away from the center of the molecule while pulling the phenyl groups B and D toward each other. Thus in compound **1**, which has the most puckered ring, phenyl rings A and C have their para (δ) carbon atoms 10.4 Å apart, while the δ carbon atoms of rings B and D are only 4.6 Å apart. Rings B and D in compound **1** are forced to lie almost parallel to one another, with an angle between their normals of only 20.7°. In the compound with the flattest chelate ring, however, the δ carbon atoms of the phenyl groups form an approximate square, with edges 7.8 and 7.3 Å. The puckering of the chelate ring is also neatly reflected in the P–M–P–C(α) torsion angles, which deviate symmetrically away from a mean of 113° with increased ring puckering. Angles of 139 and 86° are found for the most puckered system, the larger torsional angles occurring for the A and C phenyl rings. These angles are 115 and 111° for the tungsten complex, which has the least puckered ring. Within the chelate ring, the M–P–C angles are relatively constant, with a mean value of 95.2° and a range of

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(27) The unit cell for the iridium oxygen complex (**6** in Table V) is monoclinic, $P2_1/c$, with a = 11.40 Å, b = 19.26 Å, c = 22.06 Å, and β = 101.2°.[20] For the rhodium carbonyl (**7** in Table V), a = 11.28 Å, b = 19.04 Å, c = 22.08 Å, and β = 101.8° in a monoclinic cell, also space group $P2_1/c$.[21] The atomic coordinates in the two reports are related by $-x$, $^1/_2 - y$, $^1/_2 - z$.

93.8–97.8°. This result implies that the different ring puckerings are compensated for mainly by the P–C–P angle, which varies from 90.0° for compound **1** and 90.8° for compound **12** to 99.4° for compound **4**.

In all of these dppm complexes, the C(phenyl)–P–C(phenyl) angles and the C(phenyl)–P–C(sp^3) angles are less than tetrahedral, with ranges of 103–108 and of 104–109° and respective mean values of 105.1 and of 106.8°. The M–P–C(phenyl) angles are always larger than tetrahedral, however, and show a much greater range of values, from 111 to 127°. The mean value is 120.3°. These M–P–C(phenyl) angles are usually, but not always, larger for the phenyl rings A and C, the average value being 122.3° for these phenyl rings, with a smaller value of 118.4° found for the downward-pointing rings B and D. The P–C(phenyl) distances lie in the range 1.78–1.83 Å, with a mean value of 1.812 Å. The P–C(sp^3) distances are on average longer, with a mean value of 1.850 Å, and they show a wider range, from 1.824 to 1.89 Å. We were not able to find any correlation between the length of the P–C(sp^3) bond and the chelate ring geometry.

In nearly all of the dppm complexes listed, the two M–P distances within the chelate ring are not the same, with significant differences of 0.01–0.11 Å. For the iridium dioxygen complexes (**6** and **8**), the rhodium carbonyl complex (**7**), and the molybdenum carbonyl chloride (**1**), these differences are readily understood, as the diphosphine ligand bridges two nonequivalent sites in the metal coordination sphere. Various trans-influence effects have been invoked for several of the other complexes. It may be that the precise metal–phosphorus bond length is sensitive to nonsymmetrical environments for the bulky diphosphine ligand in the crystal, and variations of 0.01–0.02 Å could be due to nonbonded repulsions.

In conclusion, the widely differing shapes found for the chelating dppm ligand in these metal complexes arise mainly from variations in the amount of buckling of the four-membered chelate ring. This ring buckling is not correlated with the stereochemistry at the metal atom but may represent response to different packing requirements.

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Supplementary Material Available: Listings of final observed and calculated structure factors (Table S1), final anisotropic thermal parameters (Table S2), final hydrogen atom positional and thermal parameters (Table S3), and parameters for the constrained atoms (Table S4) (25 pages). Ordering information is given on any current masthead page.

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A Carbon-Bonded Tris(2,2′-bipyridine)iridium(III) Complex: (2,2′-Bipyridinyl-*C*³,*N*′)bis(2,2′-bipyridine-*N*,*N*′)iridium(III) Perchlorate–Water (3/1)

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The title compound has been prepared as large red diamagnetic crystals. X-ray analysis showed that there are three iridium(III) cations coordinated in distorted octahedra in an asymmetric unit containing six perchlorate ions and one water molecule. In each case the iridium is coordinated to five nitrogens and one carbon of the bipyridine ligands. The bond distances in the coordination sphere are 1.980 (6) Å for Ir–C, 2.131 (5) Å for the Ir–N trans to the Ir–C bond, and 2.053 (5) Å for the remaining four Ir–N bonds. New features in the ultraviolet and NMR spectra of solutions of the complex accord with the above structure. These spectra can be used as diagnostic for a C-bonded bipyridine complex. The possible mechanistic significance of C coordination for reactions of metal–bipyridine complexes is discussed.

Two yellow[2,3] and one orange[4] tris(2,2′-bipyridine)iridium(III) complexes have been reported. All contain a triply charged cation and are diamagnetic. The two former were separated from excess ligand and other Ir(III) products by elution from an exchange column and then isolated from aqueous acid. The latter, which was reported much earlier,[4] was a single product precipitated from aqueous sodium perchlorate. The main features of the different synthetic procedures are included in Scheme I. The spectra (UV, ^1H NMR, and ^{13}C NMR) of solutions of one of the yellow compounds[2,6] clearly show it to be the "normal" tris(2,2′-bipyridine-*N*,*N*′)iridium(III) complex written below as $Ir(bpy\text{-}N,N')_3^{3+}$. The analogous spectra of the second yellow complex show equally clearly that at least one of the ligands is modified; this complex is referred to below as Watts' complex.

Two recent papers are significant for discussion of the structure of Watts' complex. Serpone and co-workers[7] reported a preliminary crystal structure that showed, first, that Ir was bound to the six ligand rings and, second, that although a water molecule was in a position that could be hydrogen bonded to the H at what would be the 3-position in one ring, there were no OH groups bound to any of the ring atoms. Watts' compound therefore contains neither a monodentate ligand[3] nor the deprotonated form of a "covalent hydrate"[5] as previously suggested. In addition, Serpone et al. proposed that one of the bipyridine rings had rotated and that C3 of this ring was both deprotonated and ligated. The proton was suggested to be transferred to the N now occupying the

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