one may conclude that the GH ligand is less electron donating that the DH ligand in agreement with the findings of Schrauzer's group (vide supra).

This conclusion gains further support from the ligand exchange rate data in Table IV. The DH compounds undergo ligand exchange of the neutral axial ligand at rates ~14–115 times faster than those for the GH compounds. Steric factors are probably not as important as electronic factors in influencing these decreased relative rates. If steric factors were important, we would have expected that, for the bulky triphenylphosphine leaving ligand, the relative rate would have been greater than for the nonbulky trimethyl phosphite leaving ligand. All the results, therefore, suggest that the differences in spectral properties and reaction rates are a consequence of electronic effects rather than steric effects. Slight differences are observed in comparisons of structures of the DH and GH compounds, but these have no appreciable effects on the relative chemistry of the two ligand systems.

One of the striking features of our studies with the DH model compounds is the relatively similar bond length and bond angles about the Co–C–C moieties in models[7–11,33] and in coenzyme B_{12}.[34,35] Considering the vast difference in steric and electronic properties between the natural corrin equatorial ligand and dioxime ligands, one would not have a priori expected such similarities in the Co–C bond length and Co–C–C bond angle. However, if the primary determinant of these parameters involves nonbonded interactions between the close-in atoms, particularly between the β-C moiety and the inner coordination sphere, then the similarities are more easily understood. Clearly, further work is needed to more precisely define the steric factors which control Co–C bond length and Co–C–C bond angles, particularly as these might pertain to the promotion of Co–C bond homolysis by B_{12}-dependent enzymes.

Acknowledgment. This work was supported in part by a NATO grant (L.G.M. and L.R.), in part by a grant to L.R. from the CNR, Rome, Italy, and in part by NIH Grant GM 29225 (L.G.M.). We are grateful to these organizations.

Note Added in Proof. While this paper was in press, a preparation of $Co(GH_2)Cl_2$ appeared (Egharevba, G. O.; Megnamisi-Belombe, M. *Transition Met. Chem.* **1982**, *7*, 357) that was analogous to the method reported here. The crystal structures of $H_2OCo(GH)_2Br$ (Megnamisi-Belombe, M.; Endres, H.; Rossato, E. *Acta Crystallogr., Sect. C* **1983**, *C39*, 705) and the complex salt $[Co(H_2O)_6][Co(GH)_2Br_2]_2$ (Egharevba, G. O.; Megnamisi-Belombe, M.; Endres, H.; Rossato, E. *Acta Crystallogr., Sect. B* **1982**, *B38*, 2901) have been determined.

Registry No. **1**, 87155-69-9; **2**, 87155-70-2; $Co(GH_2)Cl_2$, 84724-51-6; $pyCo(GH)_2Cl$, 87155-61-1; 4-*t*-$BupyCo(GH)_2Cl$, 87155-62-2; $(CH_3O)_3PCo(GH)_2Cl$, 87155-63-3; $Bu_3PCo(GH)_2Cl$, 87155-64-4; $pyCo(GH)_2CH_3$, 27073-09-2; $pyCo(GH)_2C_2H_5$, 87155-65-5; $pyCo(GH)_2$-*i*-C_3H_7, 87155-66-6; 4-*t*-$BupyCo(GH)_2CH_3$, 87155-67-7; $H_2OCo(GH)_2CH_3$, 87155-68-8; $(c\text{-}C_6H_{11})_3PCo(GH)_2CH_3$, 87155-71-3; $H_2OCo(GH)_2C_2H_5$, 87155-72-4; $(CH_3O)_3PCo(GH_2)C_2H_5$, 87155-73-5; $H_2OCo(GH)_2P(O)(OCH_3)_2$, 87174-15-0; $(CH_3O)_3PCo(GH)_2P(O)(OCH_3)_2$, 87174-16-1; 1-methylimidazole, 616-47-7.

Supplementary Material Available: Tables of anisotropic thermal parameters, bond lengths and relevant bond angles, equations of least-squares planes for the non-hydrogen atoms, parameters for the hydrogen atoms, and calculated and observed structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

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A Compound with Severely Distorted Geometry at Ligated Carbon: Synthesis and X-ray Crystal Structure of $Bi[CH(SiMe_3)_2]_3$, a Trialkylbismuth Complex with High Thermal Stability[†]

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Received December 14, 1982

The high-yield synthesis and the X-ray crystal structure of $Bi[CH(SiMe_3)_2]_3$ are described. At 140 K the crystals are monoclinic, space group $P2_1/c$, $Z = 4$, with $a = 8.351$ (3) Å, $b = 21.615$ (12) Å, $c = 19.060$ (7) Å, and $\beta = 94.47$ (3)°. This is the first reported example of a crystal structure determination of a bismuth trialkyl. The geometry at bismuth is trigonal pyramidal with an average Bi–C distance of 2.328 (±0.013) Å and an average C–Bi–C angle of 102.9 (±0.5)°. Both the Bi–C distance and the angle at bismuth are large compared with those of the few previously reported structures containing Bi–C bonds. An outstanding feature of the structure is the severe distortion found in the geometry of the ligand, particularly at the carbon atom attched to bismuth. An average difference of about 14° in the two Bi–C–Si angles in each alkyl substituent is observed, whereas the distortion at the Si atoms amounts to 5°. The average C–Si distance is 1.874 (±0.014) Å. The compound has high thermal stability, not decomposing until 148 °C.

Introduction

Antimony and bismuth are among the least studied heavier main-group elements. The chemical and physical properties of their compounds are less well-known than those involving tin, lead, indium, thallium, or tellurium. The lack of interest is particularly striking compared with the large volume of publications on the lighter group 5A elements.[1] Recent publications on the use of organobismuth compounds to provide mobile functional groups in organic synthesis,[2] as well as the revival of interest in main-group metal clusters,[3] may indicate increasing interest in the area. Nevertheless, basic information

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0020-1669/83/1322-3421$01.50/0

Table I. Crystal Data for $Bi[CH(SiMe_3)_2]_3$

fw	687.17
mp, °C	148 dec
cryst dimens, mm	0.35 × 0.35 × 0.50
color	yellow-pale green
unit cell dimens (140 K)	
a, Å	8.351 (3)
b, Å	21.615 (12)
c, Å	19.060 (7)
β, deg	94.47 (3)
V, $Å^3$	3429.99
space group	$P2_1/c$, monoclinic
calcd density (140 K), Mg m^{-3}	1.33
F(000)	1400
Z	4
radiatn, λ, Å	Mo Kα, 0.71069
monochromator	graphite
$\mu_{\text{Mo K}\alpha}$, cm^{-1}	53.48
scan type ($2\theta_{max}$, deg)	ω (50)
scan range, deg	1.6
bkgd offset, deg	1.0
bkgd/scan time	1
scan speed, deg min^{-1}	60
check reflcns [interval, reflcns]	(2,1,2), (2,3,−2) [198]
no. of unique data	6094
no. of data with $F > 6\sigma(F)$	3985
R for 3985 reflcns, 6094 reflcns	0.0597, 0.0910
R_w for 3985 reflcns, 6094 reflcns	0.0605, 0.0762

on organobismuth compounds is scant; only two crystal structures of arylbismuth(III) compounds[4,5] and one crystal structure of an organobismuth(V) complex[6] have been reported. One electron diffraction study of $BiMe_3$ has also appeared.[7]

We are currently interested in the stabilization and structural determination of compounds with the less well-known oxidation states I and IV of antimony and bismuth and in the oxidation state III of lead, as either charged or neutral species. We are employing large substituents such as $CH(SiMe_3)_2$, $C(SiMe_3)_3$, BHT, and $N(SiMe_3)_2$ in this endeavor. The present paper deals with the X-ray crystal structure of a bismuth(III) alkyl that serves as one of the precursors in our current work.

Experimental Section

All manipulations were carried out under a purified nitrogen atmosphere in Schlenk apparatus. Ether and *n*-hexane were purified by distillation under nitrogen from Na/K/benzophenone ketyl and degassed three times. Bis(trimethylsilyl)methyllithium was synthesized as previously described[8] from lithium powder and bis(trimethylsilyl)methyl chloride[9] in ether. Anhydrous bismuth(III) chloride (Aldrich) was used as purchased. ^1H NMR spectra were recorded on a Nicolet NT-200 instrument.

Tris[bis(trimethylsilyl)methyl]bismuth(III). A suspension of bismuth(III) chloride, 1.0 g (3.17 mmol) in ether (35 mL) at 0 °C, was treated dropwise with 19.5 mL of a 0.52 M solution of bis(trimethylsilyl)methyllithium in ether. The solution gradually became yellow. Stirring was continued overnight at room temperature. The volatiles were removed in vacuo, and the residue was dissolved in hexane (20 mL). After filtration through a Celite pad and reduction of the volume to ca. 10 mL, the product crystallized as large yellow plates in 90% yield (mp 148 °C dec). The ^1H NMR spectrum in C_6H_6 displayed singlets at δ 0.27 and 1.34, which were integrated in the ratio 18:1 and were assigned to $Si(CH_3)_3$ and C*H* protons, respectively.

Table II. Atomic Positional Parameters (×10^4) for $Bi[CH(SiMe_3)_2]_3$

atom	*x*	*y*	*z*
Bi	3712 (1)	633 (1)	2478 (1)
C(1)	2659 (16)	1172 (7)	3396 (7)
Si(1)	1447 (5)	771 (2)	4040 (2)
C(11)	−546 (17)	484 (7)	3618 (7)
C(12)	2500 (18)	91 (7)	4473 (7)
C(13)	938 (19)	1306 (9)	4773 (8)
Si(2)	4331 (4)	1696 (2)	3786 (2)
C(21)	5529 (17)	1315 (8)	4539 (8)
C(22)	3456 (18)	2433 (8)	4090 (8)
C(23)	5814 (17)	1914 (7)	3138 (7)
C(2)	2333 (16)	1065 (7)	1475 (6)
Si(3)	1036 (4)	1764 (2)	1549 (2)
C(31)	−750 (16)	1609 (7)	2043 (7)
C(32)	2110 (17)	2444 (7)	1951 (8)
C(33)	204 (18)	2021 (7)	660 (8)
Si(4)	3888 (4)	1123 (2)	796 (2)
C(41)	4963 (16)	1877 (7)	847 (7)
C(42)	2884 (17)	1020 (7)	−106 (7)
C(43)	5475 (15)	505 (6)	893 (7)
C(3)	2542 (15)	−330 (6)	2542 (7)
Si(5)	1100 (4)	−615 (2)	1792 (2)
C(51)	−795 (18)	−157 (8)	1741 (8)
C(52)	1941 (17)	−604 (7)	911 (7)
C(53)	441 (19)	−1435 (7)	1925 (8)
Si(6)	4162 (5)	−904 (2)	2845 (2)
C(61)	5124 (19)	−1231 (7)	2067 (8)
C(62)	3369 (19)	−1542 (7)	3372 (8)
C(63)	5789 (19)	−543 (7)	3417 (8)

Table III. Bond Lengths (Å) for $Bi[CH(SiMe_3)_2]_3$[a]

Bi–C(1)	2.331 (14)	Bi–C(2)	2.347 (13)
Bi–C(3)	2.306 (13)	C(1)–Si(1)	1.864 (14)
C(1)–Si(2)	1.904 (14)	Si(1)–C(11)	1.895 (14)
Si(1)–C(12)	1.871 (16)	Si(1)–C(13)	1.888 (17)
Si(2)–C(21)	1.875 (15)	Si(2)–C(22)	1.864 (17)
Si(2)–C(23)	1.876 (15)	C(2)–Si(3)	1.871 (15)
C(2)–Si(4)	1.909 (14)	Si(3)–C(31)	1.855 (15)
Si(3)–C(32)	1.856 (15)	Si(3)–C(33)	1.865 (15)
Si(4)–C(41)	1.859 (15)	Si(4)–C(42)	1.866 (14)
Si(4)–C(43)	1.881 (13)	C(3)–Si(5)	1.900 (13)
C(3)–Si(6)	1.891 (13)	Si(5)–C(51)	1.863 (16)
Si(5)–C(52)	1.870 (15)	Si(5)–C(53)	1.877 (16)
Si(6)–C(61)	1.879 (16)	Si(6)–C(62)	1.858 (16)
Si(6)–C(63)	1.848 (15)		

[a] In Me the C–H bond lengths are fixed at 0.96 Å.

Table IV. Bond Angles (deg) for $Bi[CH(SiMe_3)_2]_3$[a]

C(1)–Bi–C(2)	102.9 (5)	C(1)–Bi–C(3)	103.0 (5)
C(2)–Bi–C(3)	102.7 (5)	Bi–C(1)–Si(1)	121.2 (7)
Bi–C(1)–Si(2)	106.4 (6)	Si(1)–C(1)–Si(2)	116.1 (7)
C(1)–Si(1)–C(11)	112.1 (6)	C(1)–Si(1)–C(12)	113.2 (7)
C(11)–Si(1)–C(12)	107.3 (7)	C(1)–Si(1)–C(13)	111.6 (7)
C(11)–Si(1)–C(13)	105.9 (7)	C(12)–Si(1)–C(13)	106.3 (7)
C(1)–Si(2)–C(21)	111.6 (7)	C(1)–Si(2)–C(22)	109.7 (7)
C(21)–Si(2)–C(22)	109.6 (7)	C(1)–Si(2)–C(23)	113.2 (6).
C(21)–Si(2)–C(23)	105.9 (7)	C(22)–Si(2)–C(23)	106.6 (7)

[a] Data given for one ligand only. The values for corresponding angles in the other ligands are similar.

X-ray Data and Structure Determination. After the crystals were removed from the Schlenk tube, they were protected from air contamination by a layer of hydrocarbon oil. A large crystal was cut to a suitable size, attached to a mounting glass fiber, and immediately placed in the cold stream (140 K) of a locally modified Syntex LT-1 low-temperature device on a Syntex $P2_1$ diffractometer. All X-ray data were collected with this apparatus, by using a procedure described earlier.[10] Further details are in Table I.

All calculations were carried out on a Data General ECLIPSE computer using the SHELXTL program system. The atomic form factors

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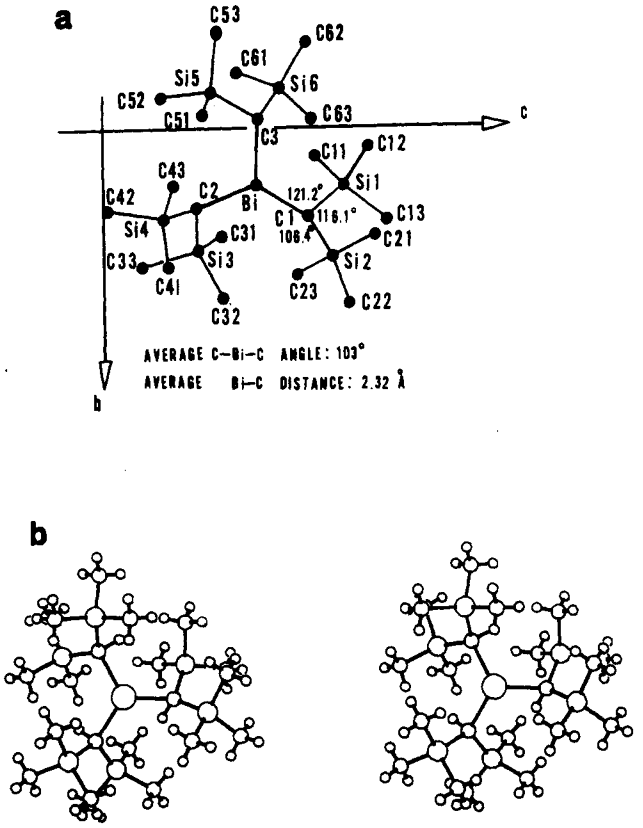

Figure 1. (a) Atomic positions in the reference molecule of $Bi[CH(SiMe_3)_2]_3$ relative to the *b* and *c* axes, with *a* above the paper plane. Only angles at C(1) are shown; other data are in Tables III and IV. (b) Stereoview, including H atoms. The atoms are identified from (a), which shows a corresponding orientation of the reference molecule.

including anomalous scattering were from ref 11. The structure was solved by Patterson methods, with the resulting Bi coordinates used to phase difference electron density maps in consecutive steps. Although the precise stoichiometry was unknown initially, the correct structure was found and subsequently refined to $R = 0.063$ by least-squares methods, with anisotropic thermal parameters for the non-hydrogen atoms. Of the 57 H atoms, 36 were detected in a difference electron density map; their sites compared well with coordinates calculated according to carbon hybridization and internal geometry. The hydrogen atoms in the methyl groups were included in the refinements with fixed methyl geometry, starting with calculated coordinates. The H atoms at C bonded to Bi were constrained to a C–H distance of 1.00 (3) Å, with no angular constraint. The refinement converged with R = 0.0597 for the 3985 reflections used. *R* is 0.0909 for the 6094 reflections comprising the full data set.

Final positional coordinates are in Table II, bond lengths in Table III, and representative bond angles in Table IV. Anisotropic thermal parameters, hydrogen coordinates and their *U* values, and structure factor tables are available as supplementary material.

Results and Discussion

This is the first example of an X-ray crystal structure determination of a bismuth(III) alkyl. The molecule is represented by the diagram and stereoview in Figure 1. A packing diagram for the structure is available as supplementary material.

The synthesis and structure of the compound have several features worthy of comment. For example, the synthesis represents the first instance of a simple one-step preparation in which three of these large alkyl groups have been attached to a main-group metal atom. For the elements phosphorus, arsenic, and antimony it is possible to substitute only two of the chlorides, affording $MClR_2$ ($R = CH(SiMe_3)_2$, M = P, As, or Sb) under similar conditions.[12] Indeed, removal of the chlorine radical from these products affords stable two-coordinate divalent derivatives in the case of phosphorus and arsenic, which shows how well these large groups shield the central atom.[12,13] Similarly, in the case of reaction of LiR with $GeCl_4$ or $SnCl_4$ only two of the halides are substituted.[13] The crystal structure of $SnClR_3$ has been reported, but the compound was obtained by the oxidative-addition reaction of SnR_2 and RCl.[14] It is likely that the large size of bismuth and the ionic character of the Bi–Cl bond allow the ready substitution of all three groups. The exchange reaction of $BiCl_3$ with the trialkyl to afford mixed haloalkylbismuth compounds and their subsequent reduction to subvalent species will be discussed in a forthcoming publication.[15] $Bi[CH(SiMe_3)_2]_3$ is also remarkably stable (mp 148 °C dec). For example, $Bi(CH_2SiMe_3)_3$ decomposes at room temperature.[16] We attribute this stability to shielding of the Bi center by the bulky $CH(SiMe_3)_2$ groups.

The structure of the title compound may be discussed in the context of the reported structures of $BiPh_3$,[4,6] $Bi(mesityl)_3$,[4] $BiPh_2[SC(S)(O\text{-}i\text{-}Pr)]$,[5] and an electron diffraction study of $BiMe_3$.[7] The most important structural features are the bismuth–carbon bond distances and the angles at bismuth. In the case of $Bi[CH(SiMe_3)_2]_3$ the average Bi–C distance is 2.328 (±0.013) Å and the average angle is 102.9 (±0.5)°. These values are significantly larger than the corresponding values in the compounds previously reported; for $BiPh_3$[4,6] the Bi–C distances are 2.21 (2), 2.25 (2), and 2.25 (3) Å and the C–Bi–C angles are 92 (1), 94 (1), and 96 (1)° and for $BiMe_3$ the Bi–C distance is 2.24 (2) Å and the C–Bi–C angle is 96.7 (10)°. In $Bi(mesityl)_3$ the average Bi–C distance is 2.28 Å, but the C–Bi–C angles are irregular, having values of 95.2, 105.4, and 107.4°.[4] These longer distances and the irregular C–Bi–C angles may be a consequence of the ligand–ligand interactions of the large mesityl group.

We attribute the larger angle and bond distances in our compound primarily to steric effects. This view is consistent with data from other structures involving this ligand.[8] However, the degree of deformation in the $CH(SiMe_3)_2$ ligand is severe and much greater than any previously reported, in either its transition-metal or its main-group derivatives. With the main-group metals the closest structure available for comparison is that of $SnClR_3$. If the angles around the carbon attached to bismuth are considered (i.e. the two Bi–C–Si and the Si–C–Si angles) the Si–C–Si angle is roughly constant and has a mean value of 115.2°. However, in each of the three ligands the two Bi–C–Si angles are remarkably dissimilar. The values for these three pairs of angles are (121.2, 106.4°), (120.7, 105.2°), and (119.9, 108.2°). This large deformation is thus quite regular and is intimately connected with the geometry of the molecule. Inspection of the molecular geometry given in Figure 1 and Table IV shows that the largest Bi–C–Si angle is always on the side of the ligand nearest the base of the trigonal pyramid. On this side of the molecule the steric strain is much greater, causing the Bi–C–Si angles to open out to ca. 120°. Conversely, toward the apex of the trigonal pyramid there is less strain and the Bi–C–Si angles may close slightly to ca. 106°. A similar type of strain is present in $SnClR_3$,[13] but the difference in angle is only about 2°, rather than the 12–14° seen here. This small difference is also consistent with the C–Sn–C angles being much wider,

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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.

Acknowledgment. We thank the Research Corp. and the National Science Foundation (Grant CHE-8116355) for generous support of this work.

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, $\beta = 102.47$ (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.
(2) Dewan, J. C.; Roberts, M. M.; Lippard, S. J. *Inorg. Chem.* **1983**, *22*, 1529.
(3) Ligand abbreviations: dppm = bis(diphenylphosphino)methane; dppe = bis(diphenylphosphino)ethane.
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(5) Dewan, J. C.; Wood, T. E.; Walton, R. A.; Lippard, S. J. *Inorg. Chem.* **1982**, *21*, 1854.
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(8) Wood, T. E.; Deaton, J. C.; Corning, J.; Wild, R. E.; Walton, R. A. *Inorg. Chem.* **1980**, *19*, 2614.
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