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Molecules with an M_4X_4 Core. 9.[1-8] Crystal Structure and Molecular Geometry of Tetrameric (Methyldiphenylphosphine)copper(I) Iodide, $[(PMePh_2)CuI]_4$

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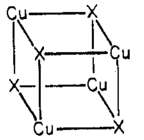
The tetrameric species (methyldiphenylphosphine)copper(I) iodide, $[(PMePh_2)CuI]_4$, has been synthesized and investigated via a full three-dimensional x-ray structural analysis. The complex crystallizes in the centrosymmetric monoclinic space group $C2/c$ [C_{2h}^6; No. 15] with a = 25.704 (5) Å, b = 11.971 (2) Å, c = 19.631 (4) Å, β = 110.70 (1)°, V = 5651 (4) Å^3, ρ(obsd) = 1.83 (3) g cm^{-3}, and ρ(calcd) = 1.84 g cm^{-3} for molecular weight = 1562.67 and Z = 4. Diffraction data were collected with a Picker FACS-1 four-circle automated diffractometer using Nb-filtered Mo Kα radiation. The structure was solved by symbolic addition and refined via a combination of difference-Fourier and least-squares techniques. The resulting discrepancy indices are R_F = 5.1% and R_{wF} = 4.4% for 3701 independent reflections with $2\theta \leq 45°$. The $[(PMePh_2)CuI]_4$ molecule lies on a site of crystallographic C_2 symmetry, the Cu_4I_4 core consisting of a "cubane-like" skeleton of alternating copper(I) and iodide ions. Copper···copper distances range from 2.8395 (13) to 3.0095 (13) Å (average = 2.9300 Å), iodine···iodine contacts range from 4.2973 (12) to 4.4883 (8) Å (average = 4.4061 Å), and copper–iodine bond lengths range from 2.6108 (11) to 2.7591 (11) Å (average = 2.6982 Å). These results are discussed in relation to previous studies on $[(PEt_3)CuI]_4$ (which has a regular "cubane-like" Cu_4I_4 core of precise T_d symmetry) and $[(PPh_3)CuI]_4$ (which has a "step-like" core of crystallographic C_i symmetry).

Introduction

We have recently completed x-ray structural analyses of three complete series of tetrameric phosphinecopper(I) and phosphinesilver(I) halides, viz., $[(PPh_3)CuX]_4$ (X = Cl,[1] Br,[2] I[4]), $[(PEt_3)CuX]_4$ (X = Cl,[5] Br,[5] I[3]), and $[(PEt_3)AgX]_4$ (X = Cl,[8] Br,[8] I[7]). Related studies of the species $[(PPh_3)AgX]_4$ (X = Cl,[9] Br,[10] I[11]) have been carried out by Teo and Calabrese. It is established that for copper, the familiar and ubiquitous "cubane" structure (I) is destabilized relative to the "step" structure (II) when large halogen atoms (X) are accompanied by bulky ligands on the metal atom.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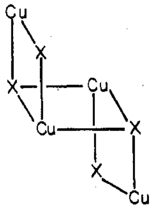
II

The species $[(PPh_3)CuI]_4$ has previously been shown to possess a "step structure",[4] whereas $[(PEt_3)CuI]_4$ has a "cubane structure".[3] We now report the results of a structural study on a copper(I) iodide complex of a trisubstituted phosphine ligand of intermediate bulk, i.e., the species $[(PMePh_2)CuI]_4$.

Experimental Section

Synthesis of $[(PMePh_2)CuI]_4$. Approximately 3 mL of $PMePh_2$ (ca. 3 g, 14 mmol) was injected into a slurry of CuI (4.3 g, 22.5 mmol) in toluene (50 mL) under a positive pressure of nitrogen. The solution was stirred for 24 h at 80–90 °C and excess CuI removed by filtration. Cooling of the filtrate yielded crystals of $[(PMePh_2)CuI]_4$ which were collected and recrystallized from toluene. Anal. Calcd for $C_{52}H_{52}Cu_4I_4P_4$: C, 39.97; H, 3.35; Cu, 16.26; I, 32.48; P, 7.93. Found (Galbraith Laboratories, Knoxville, Tenn.): C, 40.03; H, 3.25; Cu, 16.12; I, 32.57; P, 7.79.

Collection of X-Ray Diffraction Data. The crystal selected for the structural analysis *approximated* to a block extended in the [010] direction and with pointed ends. The crystal was bounded by nine discernible faces [(100), ($\bar{1}$00), (001), (00$\bar{1}$), and ($\bar{1}$01) defining the sides, ($\bar{1}$11) and (11$\bar{1}$) defining one end, and (1$\bar{3}\bar{2}$) and (0$\bar{1}$1) defining the other end]. The approximate dimensions of the crystal were 0.50 × 0.23 × 0.22 mm. The crystal was inserted into a thin-walled capillary, which was flushed with nitrogen, flame sealed, fixed with beeswax into a brass pin, and set in a eucentric goniometer head.

Preliminary Weissenberg, rotation, precession, and cone-axis photographs provided preliminary unit cell parameters, indicated C_{2h} ($2/m$) Laue symmetry, and revealed the systematic absences hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$. Possible space groups for the monoclinic crystal are the centrosymmetric space group $C2/c$ [C_{2h}^6; No. 15] and the noncentrosymmetric space group Cc [C_s^4; No. 9].

Based upon unit cell and density measurements (see Table I), there are four tetrameric molecules in the unit cell. In the absence of gross disorder, the crystallographic asymmetric unit is therefore half of the molecule in space group $C2/c$ or one entire tetrameric unit in space group Cc. The space group $C2/c$ allows the tetrameric unit to possess either an inversion center (possible for the "step" structure) or a C_2 axis (possible for a "cubane-like" geometry).

Data collection was carried out at the University of Illinois at Chicago Circle. The crystal was mounted on a Picker FACS-1 four-circle automated diffractometer, was accurately centered, and was aligned with b^* coincident with the instrumental ϕ axis. X-ray diffraction data were collected as described previously;[12] details of the present study are listed in Table I.

The effects of absorption were investigated by measuring (via θ–2θ scans) the 040 reflection (2θ = 13.61°) at χ = 90° and at 10° intervals of ϕ from 0 to 350°. The observed variation was ~6%. While we had intended to make an absorption correction, the crystal was unfortunately lost during the move of our research group from Chicago

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Table I. Experimental Data for the X-Ray Diffraction Study of $[(PMePh_2)CuI]_4$

(A) Crystal Parameters[a]

Crystal system	Monoclinic	cos β	−0.3534 (2)
Space group	$C2/c$	β, deg	110.70 (1)
Temp, °C	21.1 (2)	V, Å^3	5651 (4)
a, Å	25.704 (5)	Z	4
b, Å	11.971 (2)	Mol wt	1562.67
c, Å	19.631 (4)	ρ(calcd),[b] g cm^{-3}	1.84
		ρ(obsd),[b] g cm^{-3}	1.83 (3)

(B) Measurement of Intensity Data

Radiation	Mo Kα
Filter(s)	Nb foil at counter aperture (~47% transmission of Mo Kα)
Attenuators	Cu foil, used if $I > 10^4$ counts/s
Takeoff angle, deg	3.0
Detector aperture	3-mm wide (in 2θ) × 4-mm tall (in χ)
Crystal–detector dist, mm	330
Crystal orientation	b^* coincident with diffractometer ϕ axis
Reflections measd	$+h, +k, \pm l$, except for $0kl$ ($l \geqslant 0$ only)
Scan type	Coupled θ(crystal)–2θ(counter)
Scan speed	2.0°/min
Scan length	$\Delta(2\theta) = (1.50 + 0.692 \tan \theta)°$ starting 0.75° below the Mo Kα_1 peak
Max value of 2θ, deg	45
Background measurement	Stationary-crystal, stationary-counter; 20 s each at beginning and end of 2θ scan
Std reflections	Three remeasured after every 49 reflections; rms deviations (after application of an anisotropic linear decay correction):[c] 406, 0.79%; $10,0,\bar{8}$, 0.64%; 040, 0.97%
Reflections collected:	3708 independent measurements, plus 6 duplicate measurements (averaged into primary data set) and 217 systematic absences

(C) Treatment of Intensity Data

Conversion[c] to $\lvert F_o\rvert$ and $\sigma(\lvert F_o\rvert)$	As in ref 12, using an "ignorance factor" of $p = 0.03$
Absorption coeff	μ(Mo Kα) = 38.0 cm^{-1}; no correction made (see text)

[a] Unit cell parameters are from a least-squares fit to the setting angles of the resolved Mo Kα_1 peaks of 12 reflections in the 2θ range 36.7–46.0° and widely dispersed in reciprocal space. The maximum and root-mean-square angular disagreements were 0.010 and 0.018°, respectively (λ (Mo Kα_1) = 0.70930 Å). [b] Density measured by neutral buoyancy in aqueous barium iodide. [c] Data reduction and analysis, including decay correction, were performed using the Fortran IV program RDUS2, by B. G. DeBoer.

Table II. Statistics for Intensity Distribution for $[(PMePh_2)CuI]_4$

		Theoretical[a]	
Quantity	Obsd	Centrosym	Noncentrosym
$\langle \lvert E\rvert^2 \rangle$	1.000	1.000	1.000
$\langle \lvert E\rvert \rangle$	0.808	0.798	0.886
$\langle \lvert E^2 - 1\rvert \rangle$	0.940	0.968	0.736
$\lvert E\rvert > 1.0$, %	33.16	32.0	37.0
$\lvert E\rvert > 2.0$, %	3.88	5.00	1.80
$\lvert E\rvert > 3.0$, %	0.05	0.30	0.01

[a] I. L. Karle, K. S. Dragonette, and S. A. Brenner, *Acta Crystallogr.*, 19, 713 (1965).

to Buffalo, and no such correction was then possible. However, the maximum systematic error due to neglect of absorption is estimated as about 3% in $|F_o|$. Our experience suggests that this will lead to no significant errors in positional parameters and to systematic errors of less than 1.0 σ in thermal parameters.

Solution and Refinement of the Structure. All calculations were performed using the CDC 6600 Cyber 173 computer system at the State University of New York at Buffalo. The structure solution package consisted of the following programs: RDUS 2 (data reduction and analysis, including anisotropic decay correction) by B. G. DeBoer; FAME (Wilson plot and generation of $|E|$ values) and MAGIC (phase generation from $|E|$ values via symbolic addition) by R. B. K. Dewar and A. L. Stone; JIMDAP (Fourier synthesis, derived from A. Zalkin's FORDAP) by J. A. Ibers and co-workers; LSHF (structure factor calculations and full-matrix least-squares refinement), STAN1 (distances and angles and their esd's), and PLOD (least-squares planes) all by B. G. DeBoer; and ORTEP-II (thermal ellipsoid plots) by C. K. Johnson.

Analytical scattering factors[13a] were used for all atoms; both the real and the imaginary components of anomalous dispersion[13b] were included for all nonhydrogen atoms. The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma(|F_o|)]^{-2}$. Discrepancy indices used below are defined as follows

$$R_F = \left[\frac{\Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert}{\Sigma \lvert F_o\rvert}\right] \times 100\ (\%)$$

$$R_{wF} = \left[\frac{\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2}{\Sigma w \lvert F_o\rvert^2}\right]^{1/2} \times 100\ (\%)$$

All data with $(\sin \theta/\lambda) < 0.15$ were corrected for "β-filter absorption", as described previously by Churchill and DeBoer.[12] The statistics for intensity distribution in $[(PMePh_2)CuI]_4$ (see Table II) suggested that the correct space group was the centrosymmetric $C2/c$. The structure was solved by the method of symbolic addition.[14] The origin of the unit cell was defined by assigning positive phases to the reflections 393 ($|E|$ = 3.77) and $66\bar{3}$ ($|E|$ = 2.47), and symbols were assigned to a further three strong reflections (13,3,6, $|E|$ = 2.52; $10,2,\bar{1}\bar{6}$, $|E|$ = 2.67; $59\bar{3}$, $|E|$ = 3.83) which each had many $\sum_2$ interactions. Application of the symbolic addition procedure to the 346 reflections with $|E| > 1.4$ generated symbolic signs to all reflections. Assignment of real (+ or −) signs to the three symbols gave eight possible solutions. That of lowest "contradiction index" (C = 0.0) led to an E map from which could be seen a cubic arrangement of Cu and I atoms about the crystallographic C_2 axis. Two cycles of least-squares refinement of the scale factor and positional and isotropic thermal parameters of the Cu_2I_2 portion of the crystallographic asymmetric unit resulted in R_F = 28.3% and R_{wF} = 34.1%. A Fourier synthesis now led to the location of both phosphorus atoms, the two methyl carbons, and three of the four phenyl rings. Full-matrix least-squares refinement of positional and isotropic thermal parameters for these atoms (105 parameters in all) led to convergence with R_F = 12.98% and R_{wF} = 14.89%. A difference Fourier map now revealed the positions of the carbon atoms associated with the fourth phenyl ring. (Peak heights were 3.62 e Å^{-3} for the carbon atom linked to phosphorus but only 1.40–1.99 e Å^{-3} for the other five carbon atoms.) Six cycles of full-matrix least-squares refinement of positional parameters, anisotropic thermal parameters for copper, iodine, and phosphorus atoms, and isotropic thermal parameters for carbon atoms (159 parameters in all) led to convergence with R_F = 6.33%, R_{wF} = 6.60%, and a "goodness-of-fit" (GOF) of 2.66. However, all was not well—isotropic thermal parameters for atoms in the last-found phenyl ring were (in Å^2) 7.3 for C(27), 16.4 for C(28), 21.2 for C(29), 19.3 for C(210), 23.0 for C(211), and 23.1 for C(212). Removal of these six atoms and continued refinement led to increases in the discrepancy indices to R_F = 7.60% and R_{wF} = 11.10%. Following a number of fruitless attempts at solving the problem, we realized that the phenyl group suffered some form of disorder. The two most probable forms of disorder were (i) site disorder of the methyl group centered on C(2) and the phenyl group centered on C(27) or (ii) some form of rotational disorder (i.e., two or more rotational orientations) of the phenyl group in its known site. This problem was resolved by refining independently the occupancies of all carbon atoms of the current phenyl group. Resulting values for the occupancies were 1.01 for C(27), 0.58 for C(28), 0.63 for C(29), 0.89 for C(210), 0.62 for C(211), and 0.52 for C(212). The similar high values for the P-bonded C(27) and the para carbon [C(210)] indicated that the disorder was of the rotational variety (ii, above). A difference-Fourier synthesis now led to location of four features [termed C(28)D, C(29)D, C(211)D, and C(212)D and of peak heights 0.75, 0.87, 0.83, and 0.98 e Å^{-3}] which, taken in conjunction with C(27) and C(210), defined a second six-membered ring. Refinement was now continued using coupled occupancies of α for C(28), C(29), C(211), and C(212) and 1-α for C(28)D, C(29)D, C(211)D, and C(212)D, with α being given an initial value of 0.6. Anisotropic thermal parameters were assigned to all nonhydrogen atoms other than those involved in the disorder problem, and isotropic thermal parameters were used for the disordered carbon atoms.

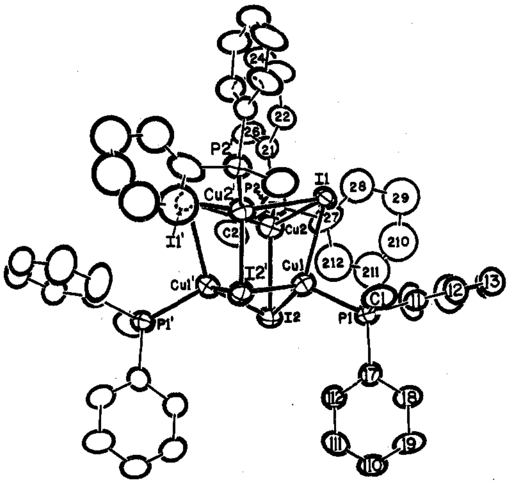

Figure 1. Geometry of the [(PMePh$_2$)CuI]$_4$ molecule, showing the labeling of atoms. Hydrogen atoms are omitted for the sake of clarity. Only the major component of the disordered phenyl ring is shown. [ORTEP diagram, 30% probability ellipsoids.]

Hydrogen atoms were fixed in idealized positions with d(C–H) = 0.95 Å.[15] Phenyl hydrogens were defined outward from the centroid-of-ring to carbon vectors, and methyl hydrogens were placed in idealized conformations staggered relative to the Cu(2)–P(2) vector. All [C–H] and CH_3 groups were constrained as nonrotating rigid bodies with B(H) = [1.25 × B(C) + 1.0] Å^2; other positional parameters were refined independently.

Several cycles of refinement (each cycle consisting of two "blocks" due to core limitations of the computer) led to final convergence $[(\Delta/\sigma)_{\max} = 0.08]$ with $R_F = 5.05\%$, $R_{wF} = 4.35\%$, and GOF = 1.74 for the 3701 reliable reflections with $\Delta F/\sigma(F) < 10.0$ or $R_F = 5.12\%$ and $R_{wF} = 5.05\%$ for all 3708 crystallographically independent reflections. (No reflections were rejected as "not significantly above background".) During the last two cycles of refinement, positional parameters (only) for all atoms were varied. A final difference-Fourier synthesis had, as its largest feature, a peak height 1.23 e Å^{-3} at 0.02, 0.035, 0.155—i.e., close to I(2). Peaks of height up to 1.0 e Å^{-3} were visible in the vicinity of the disordered phenyl ring. This suggests that there is a third orientation of this system or that it is subject to disorder over a considerable angular range, possibly with favored minima. No attempts were made to clarify (?) further this problem and the structural investigation was declared complete.

Positional parameters are collected in Table III; thermal parameters are listed in Table IV.

Discussion

The crystal consists of discrete molecular units of the tetramer, [(PMePh$_2$)CuI]$_4$, the molecules being separated by normal van der Waals distances; there are no abnormally short intermolecular contacts. Each [(PMePh$_2$)CuI]$_4$ molecule lies on a site of crystallographic C_2 symmetry. The molecular geometry and the labeling of atoms are illustrated in Figure 1. Atoms of the basic asymmetric unit are labeled normally. Atoms in the "remaining half" of the tetrameric molecule are related to the basic unit via rotation about the crystallographic C_2 axis at (0, y, $^1/_4$) and are labeled with a prime. Coordinates of the two halves of the molecule are interrelated via the transformation $[x', y', z'] = [-x, y, {}^1/_2 - z]$. Intramolecular distances and angles are given in Tables V and VI.

The stereochemistry of the heavy-atom (i.e., $P_4Cu_4I_4$) core of the molecule is illustrated in Figures 2 and 3. The Cu_4I_4 moiety defines a slightly irregular "cubane-like" arrangement of alterating copper(I) and iodide ions. Each copper(I) ion is in a distorted tetrahedral coordination environment, being linked to three iodide ions and one methyldiphenylphosphine ligand. The I–Cu–I angles about Cu(1) range from 107.60 (4) to 113.39 (3)°; those centered on Cu(2) range from 107.03 (4) to 113.38 (3)°. P–Cu–I angles are appreciably less regular, ranging from 101.94 (6) to 115.41 (6)° about Cu(1) and from 101.62 (6) to 121.77 (6)° about Cu(2).

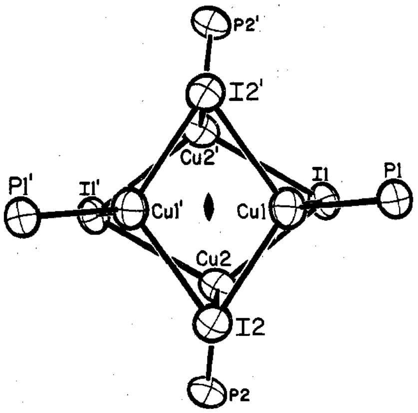

Figure 2. The $P_4Cu_4I_4$ core of the [(PMePh$_2$)CuI]$_4$ molecule, viewed down the crystallographic C_2 axis.

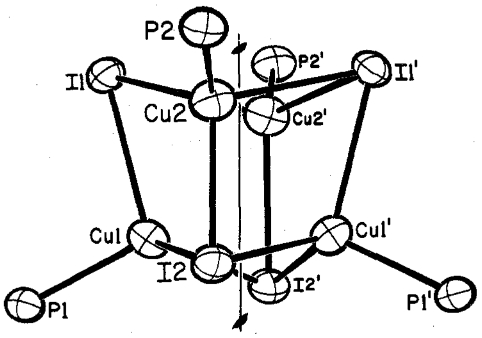

Figure 3. A general view of the $P_4Cu_4I_4$ core of the [(PMePh$_2$)CuI]$_4$ molecule showing the crystallographic C_2 axis.

The copper–iodine bond lengths show significant variations—from 2.6440 (11) to 2.7262 (11) Å about Cu(1) and from 2.6108 (11) to 2.7591 (11) Å about Cu(2). The average of the six crystallographically independent copper–iodine bond lengths is 2.6982 Å—a value in surprisingly good agreement with the Cu–I bond lengths of 2.6837 (13) and 2.6767 (15) Å in the Cu_4I_4 cores of the regular (T_d symmetry) "cubane-like" species [(PEt$_3$)CuI]$_4$ and [(AsEt$_3$)CuI]$_4$.[3]

The six nonbonding copper···copper distances, in order of increasing length, are Cu(1)···Cu(2) = Cu(1)'···Cu(2)' = 2.8395 (13) Å, Cu(1)···Cu(1)' = 2.9202 (18) Å, Cu(2)···Cu(2)' = 2.9620 (18) Å, and Cu(1)···Cu(2)' = Cu(1)'···Cu(2) = 3.0095 (13) Å. The average copper···copper distance of 2.9300 Å is, again, almost indistinguishable from that of 2.9272 (20) Å found in the far-less sterically restricted symmetrical species [(PEt$_3$)CuI]$_4$.[3] This last result is somewhat surprising, especially when considered in association with the observation that the Cu···Cu distance in [(AsEt$_3$)CuI]$_4$ is only 2.7826 (24) Å—i.e., is contracted by 0.1446 Å relative to the analogous contacts in [(PEt$_3$)CuI]$_4$.[3]

Iodine···iodine distances within the [(PMePh$_2$)CuI]$_4$ molecule spread over a slightly larger range than the copper···copper distances. The shortest is I(1)···I(1)' = 4.2973 (12) Å and the longest are I(1)···I(2) and I(1)'···I(2)' with values of 4.4883 (8) Å. The mean of 4.4061 Å is close to the predicted van der Waals contact of ~4.3 Å for I···I[16] and may be compared with values of 4.3800 (11) Å in [(PEt$_3$)CuI]$_4$ and 4.4237 (15) Å in [(AsEt$_3$)CuI]$_4$.[3]

van der Waals repulsive forces are, presumably, a principal component of the distortion of the six faces of the "cubane" moiety from a square-planar geometry. This distortion manifests itself in small Cu–I–Cu angles (individual values ranging from 63.37 (3) to 67.27 (4)°, and averaging 65.75°) and in marked nonplanarity of the four-membered systems defining the cube faces. Thus, as shown in Table VII, fold

Table III. Positional Parameters for $[(PMePh_2)CuI]_4$ (with Esd's)[a] and Isotropic Thermal Parameters[b]

Atom	x	y	z	B,[b] Å^2
Cu(1)	0.04662 (4)	0.08458 (7)	0.31923 (5)	5.26
Cu(2)	0.04464 (4)	0.25649 (8)	0.21867 (5)	5.25
I(1)	0.06482 (2)	0.30474 (4)	0.35533 (2)	4.25
I(2)	0.05970 (2)	0.03350 (4)	0.19523 (3)	4.86
P(1)	0.10592 (8)	0.00017 (14)	0.41886 (10)	4.50
P(2)	0.09088 (8)	0.33967 (15)	0.15432 (10)	4.73
C(1)	0.0826 (4)	0.0191 (7)	0.4953 (5)	7.7
C(11)	0.1771 (3)	0.0512 (5)	0.4504 (4)	5.4
C(12)	0.2002 (4)	0.0673 (10)	0.3981 (6)	9.6
C(13)	0.2563 (4)	0.1001 (10)	0.4187 (7)	11.2
C(14)	0.2860 (4)	0.1177 (8)	0.4893 (7)	10.0
C(15)	0.2628 (4)	0.1049 (8)	0.5414 (6)	9.0
C(16)	0.2088 (4)	0.0708 (7)	0.5193 (5)	7.8
C(17)	0.1146 (3)	−0.1513 (6)	0.4157 (4)	4.6
C(18)	0.1629 (4)	−0.2043 (7)	0.4506 (6)	9.5
C(19)	0.1671 (4)	−0.3208 (7)	0.4488 (7)	10.2
C(110)	0.1230 (3)	−0.3824 (6)	0.4095 (5)	6.8
C(111)	0.0744 (3)	−0.3306 (6)	0.3765 (4)	6.2
C(112)	0.0692 (3)	−0.2149 (6)	0.3790 (4)	5.4
C(2)	0.0664 (4)	0.2836 (7)	0.0631 (4)	8.1
C(21)	0.0844 (3)	0.4893 (5)	0.1417 (3)	4.2
C(22)	0.0791 (3)	0.5549 (6)	0.1958 (4)	5.6
C(23)	0.0768 (4)	0.6727 (6)	0.1890 (4)	6.7
C(24)	0.0780 (4)	0.7217 (6)	0.1282 (4)	6.6
C(25)	0.0819 (4)	0.6565 (7)	0.0741 (5)	7.7
C(26)	0.0859 (4)	0.5433 (6)	0.0794 (4)	7.2
C(27)	0.1666 (4)	0.3214 (8)	0.1852 (6)	7.9
C(28)[c]	0.2015 (8)	0.4077 (17)	0.2237 (10)	11.2 (6)
C(29)[c]	0.2651 (10)	0.3923 (21)	0.2527 (13)	14.3 (8)
C(210)	0.2751 (8)	0.2852 (16)	0.2270 (11)	15.9 (6)
C(211)[c]	0.2495 (10)	0.2125 (20)	0.1894 (12)	13.5 (8)
C(212)[c]	0.1864 (10)	0.2188 (21)	0.1771 (14)	14.3 (7)
C(28)D[d]	0.1866 (20)	0.2616 (44)	0.1258 (27)	14.2 (16)
C(29)D[d]	0.2144 (37)	0.3629 (68)	0.1582 (50)	26.1 (33)
C(211)D[d]	0.2565 (24)	0.2748 (45)	0.2821 (28)	16.1 (18)
C(212)D[d]	0.1946 (19)	0.2656 (37)	0.2469 (25)	13.2 (14)
H(1A)[e]	0.1079	−0.0170	0.5370	9.9
H(1B)	0.0810	0.0965	0.5051	9.9
H(1C)	0.0466	−0.0128	0.4840	9.9
H(12)	0.1775	0.0540	0.3489	13.1
H(13)	0.2725	0.1091	0.3825	15.1
H(14)	0.3236	0.1410	0.5035	13.5
H(15)	0.2858	0.1205	0.5902	11.9
H(16)	0.1930	0.0605	0.5560	10.5
H(18)	0.1940	−0.1597	0.4774	12.7
H(19)	0.2013	−0.3577	0.4735	13.9
H(110)	0.1257	−0.4612	0.4061	9.9
H(111)	0.0429	−0.3748	0.3507	8.9
H(112)	0.0349	−0.1778	0.3553	7.4
H(2A)	0.0857	0.3182	0.0354	11.7
H(2B)	0.0729	0.2053	0.0651	11.7
H(2C)	0.0277	0.2976	0.0409	11.7
H(22)	0.0783	0.5187	0.2385	7.7
H(23)	0.0730	0.7186	0.2264	9.4
H(24)	0.0760	0.8008	0.1240	9.3
H(25)	0.0822	0.6915	0.0308	11.0
H(26)	0.0899	0.4991	0.0414	9.6
H(28)[c]	0.1847	0.4753	0.2306	15.7
H(29)[c]	0.2940	0.4423	0.2785	20.5
H(210)	0.3139	0.2697	0.2446	21.1
H(211)[c]	0.2688	0.1511	0.1788	18.4
H(212)[c]	0.1597	0.1629	0.1541	19.1
H(28)D[d]	0.1669	0.3196	0.0941	19.7
H(29)D[d]	0.2384	0.4070	0.1418	30.7
H(211)D[d]	0.2737	0.2081	0.3057	21.0
H(212)D[d]	0.1720	0.2176	0.2632	18.5

[a] Esd's, shown in parentheses, are right adjusted to the last digit of the preceding number. [b] "Equivalent isotropic" thermal parameters, shown without esd's for nonhydrogen atoms, correspond to the average of the rms displacements along the three principal axis of the vibration ellipsoid. For the full anisotropic form, see Table III. [c] These positions represent the major configuration of the disordered phenyl ring, having occupancies of 0.664 (9). [d] These positions represent the minor configuration of the disordered ring, having occupancies of 0.336 (9). [e] Hydrogen atoms are in calculated positions—see text.

angles across the I···I diagonals of the cubane faces are 146.09° for the I(1)–Cu(1)–I(2)–Cu(2) face, 139.15° for the I(1)′–Cu(2)′–I(1)–Cu(2) face, 139.95° for the I(2)′–Cu(1)–I(1)–Cu(2)′ face, and 135.63° for the I(2)–Cu(1)–I(2)′–Cu(1)′ face. Dihedral angles about the Cu···Cu diagonals are less acute, ranging from 149.67 to 158.16°.

Copper–phosphorus distances are Cu(1)–P(1) = 2.2500 (20) Å and Cu(2)–P(2) = 2.2498 (20) Å (average = 2.2499 Å)

Table IV. Anisotropic Thermal Parameters for $[(PMePh_2)CuI]_4$ with Esd's[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U\rangle$[b]
Cu(1)	5.55 (5)	4.41 (4)	5.26 (4)	0.39 (4)	1.22 (4)	0.76 (4)	0.221,0.261,0.287
Cu(2)	6.30 (5)	5.02 (5)	4.95 (4)	−0.42 (4)	2.65 (4)	−0.08 (4)	0.233,0.251,0.287
I(1)	4.96 (2)	3.57 (2)	3.81 (2)	−0.62 (2)	1.05 (2)	−0.47 (2)	0.197,0.230,0.264
I(2)	5.09 (3)	3.89 (2)	5.57 (3)	0.41 (2)	1.84 (2)	−0.95 (2)	0.202,0.255,0.280
P(1)	5.16 (9)	3.38 (8)	4.53 (9)	0.45 (7)	1.18 (7)	0.14 (7)	0.203,0.237,0.271
P(2)	5.92 (10)	4.25 (9)	4.72 (9)	0.33 (8)	2.75 (8)	−0.04 (7)	0.215,0.234,0.280
C(1)	11.4 (7)	5.4 (4)	7.2 (5)	2.2 (4)	4.3 (5)	0.3 (4)	0.24,0.29,0.39
C(11)	5.6 (4)	3.4 (3)	5.9 (4)	0.7 (3)	0.3 (4)	−0.3 (3)	0.20,0.24,0.33
C(12)	5.8 (5)	13.2 (9)	8.9 (7)	−1.7 (5)	1.2 (5)	−1.5 (6)	0.25,0.36,0.42
C(13)	5.5 (6)	14.1 (10)	13.8 (10)	−1.5 (6)	3.2 (6)	−0.9 (8)	0.25,0.41,0.43
C(14)	6.6 (6)	5.9 (5)	13.1 (10)	0.4 (4)	−2.0 (7)	−1.5 (6)	0.25,0.27,0.50
C(15)	8.0 (7)	6.5 (6)	9.3 (7)	0.1 (5)	−0.9 (6)	−0.9 (5)	0.26,0.29,0.43
C(16)	7.4 (5)	5.6 (4)	7.5 (5)	−0.6 (4)	−0.9 (4)	−0.3 (4)	0.24,0.27,0.40
C(17)	4.7 (4)	4.3 (3)	4.4 (3)	0.5 (3)	0.9 (3)	0.2 (3)	0.22,0.24,0.27
C(18)	5.5 (5)	4.1 (4)	15.8 (9)	0.3 (4)	0.0 (5)	−0.9 (5)	0.22,0.26,0.49
C(19)	6.1 (5)	4.0 (4)	18.2 (10)	1.0 (4)	1.6 (6)	−0.7 (5)	0.21,0.29,0.51
C(110)	6.8 (5)	3.7 (4)	9.3 (6)	0.4 (4)	2.1 (4)	−0.5 (4)	0.21,0.29,0.37
C(111)	7.6 (5)	4.5 (4)	5.8 (4)	−0.8 (4)	1.4 (4)	−0.9 (3)	0.22,0.28,0.33
C(112)	5.8 (4)	4.4 (4)	5.0 (4)	0.2 (3)	0.7 (3)	−0.2 (3)	0.23,0.24,0.31
C(2)	13.2 (7)	6.9 (5)	5.4 (4)	−0.8 (5)	4.7 (5)	−1.6 (4)	0.21,0.31,0.41
C(21)	4.6 (3)	4.5 (3)	3.8 (3)	0.1 (3)	1.8 (3)	0.3 (3)	0.21,0.24,0.25
C(22)	7.4 (5)	5.3 (4)	4.7 (4)	−0.5 (3)	3.1 (3)	−0.5 (3)	0.22,0.26,0.31
C(23)	9.8 (6)	4.3 (4)	6.9 (5)	−0.4 (4)	4.2 (4)	−1.3 (4)	0.21,0.28,0.36
C(24)	9.2 (6)	4.2 (4)	7.0 (5)	0.0 (4)	3.8 (4)	−0.1 (4)	0.23,0.28,0.34
C(25)	12.0 (7)	5.7 (5)	6.9 (5)	2.7 (5)	5.1 (5)	2.6 (4)	0.21,0.28,0.41
C(26)	11.9 (7)	5.3 (5)	5.2 (4)	2.6 (4)	4.0 (4)	0.7 (3)	0.23,0.24,0.40
C(27)	7.7 (5)	6.7 (5)	11.3 (7)	3.0 (5)	5.9 (5)	3.5 (5)	0.23,0.26,0.42

[a] The anisotropic temperature factors (units Å^2) enter the equation for the calculated structure factor in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] These are the root-mean-square amplitudes of vibration (in Å) along the principal axis of the vibrations ellipsoid. For relative orientations, see the figures.

Table V. *Interatomic Distances (A), with Esd's,*[a] *for* $[(PMePh_2)CuI]_4$

	A. Copper–Copper Distances		
Cu(1)···Cu(1)′	2.9202 (18)	Cu(2)···Cu(2)′	2.9620 (18)
Cu(1)···Cu(2)	2.8395 (13)	Cu(2)′···Cu(1)′	2.8395 (13)
Cu(1)···Cu(2)′	3.0095 (13)	Cu(2)···Cu(1)′	3.0095 (13)
	Cu–Cu(av) = 2.9300 ± 0.0776 A[b]		
	B. Copper–Iodine Bond Lengths		
Cu(1)–I(1)	2.7262 (11)	Cu(2)–I(2)	2.7591 (11)
Cu(1)–I(2)	2.6440 (11)	Cu(2)–I(1)	2.6108 (11)
Cu(1)–I(2)′	2.7157 (12)	Cu(2)–I(1)′	2.7333 (12)
	Cu–I(av) = 2.6982 ± 0.0576 A[b]		
	C. Copper–Phosphorus Distances		
Cu(1)–P(1)	2.2500 (20)	Cu(2)–P(2)	2.2498 (20)
	Cu–P(av) = 2.2499 ± 0.0001 A[b]		
	D. Iodine–Iodine Contacts		
I(1)···I(1)′	4.2973 (12)	I(2)···I(2)′	4.3253 (12)
I(1)···I(2)	4.4883 (8)	I(2)′···I(1)′	4.4883 (8)
I(1)···I(2)′	4.4188 (9)	I(2)···I(1)′	4.4188 (9)
	I···I(av) = 4.4061 ± 0.0802 A[b]		
	E. Phosphorus–Carbon Distances		
P(1)–C(1)	1.817 (8)	P(2)–C(2)	1.805 (7)
P(1)–C(11)	1.817 (8)	P(2)–C(21)	1.808 (7)
P(1)–C(17)	1.831 (7)	P(2)–C(27)	1.834 (9)
	P–C(av) = 1.819 ± 0.012 A[b]		
	F. Carbon–Carbon Bond Length		
C(11)–C(12)	1.369 (12)	C(17)–C(18)	1.346 (10)
C(12)–C(13)	1.408 (12)	C(18)–C(19)	1.399 (11)
C(13)–C(14)	1.341 (13)	C(19)–C(110)	1.344 (11)
C(14)–C(15)	1.361 (14)	C(110)–C(111)	1.339 (10)
C(15)–C(16)	1.362 (12)	C(111)–C(112)	1.393 (10)
C(16)–C(11)	1.332 (10)	C(112)–C(17)	1.367 (9)
C(21)–C(22)	1.366 (9)	C(24)–C(25)	1.350 (10)
C(22)–C(23)	1.417 (10)	C(25)–C(26)	1.360 (11)
C(23)–C(24)	1.340 (10)	C(26)–C(21)	1.396 (10)
C(27)–C(28)	1.401 (19)	C(27)–C(28)D	1.601 (47)
C(28)–C(29)	1.539 (26)	C(28)D–C(29)D	1.437 (85)
C(29)–C(210)	1.434 (26)	C(29)D–C(210)	1.907 (81)
C(210)–C(211)	1.181 (23)	C(210)–C(211)D	1.334 (49)
C(211)–C(212)	1.555 (29)	C(211)D–C(212)D	1.499 (60)
C(212)–C(27)	1.361 (25)	C(212)D–C(27)	1.347 (44)
	C–C(av) = 1.366 ± 0.026 A[b,c]		

[a] Esd's were calculated from the full *positional* covariance matrix generated in the final cycle of least-squares refinement. Contributions from the uncertainty in unit cell parameters are included. No corrections have been applied for possible systematic errors caused by thermal motion of the atoms. [b] *Esd's on average distances are calculated via the scatter formula, viz.,* $\sigma(\text{av}) = [\Sigma_i(d_i - \bar{d})^2/(N-1)]^{1/2}$, *where* d_i *is the* ith distance and $\bar{d}$ is the average of N such distances. [c] Values for the disordered rings [C(27)–C(28)–C(29)–C(210)–C(211)–C(212) and C(27)–C(28)D–C(29)D–C(210)–C(211)D–C(212)D] are not included in this calculation.

as compared to 2.2538 (27) Å in $[(PEt_3)CuI]_4$.[3]

Phosphorus–carbon distances are normal, with values of 1.805 (7) and 1.817 (18) Å for the P–Me vectors and 1.808 (7)–1.834 (9) Å for the P–Ph bond lengths. Carbon–carbon distances within the ordered phenyl rings average 1.366 ± 0.026 Å. There are, however, considerable variations in C–C distances determined for the disordered phenyl fragment; these variations (from 1.18 to 1.91 Å) are an artifact of our nonideal model and should be ignored.

Conclusion

Three simple tetrameric phosphine–copper(I)–iodide structures have now been investigated—$[(PEt_3)CuI]_4$,[3] $[(PMePh_2)CuI]_4$, and $[(PPh_3)CuI]_4$.[4] The first of these has

Table VI. Selected Intramolecular Angles (deg), with Esd's, for $[(\mathrm{PMePh_2})\mathrm{CuI}]_4$

	(A) $\mathrm{Cu_4I_4}$ "Cube" Angles		
I(1)-Cu(1)-I(2)	113.39 (3)	Cu(1)-I(1)-Cu(2)	64.24 (3)
I(1)-Cu(1)-I(2)′	108.58 (3)	Cu(1)-I(1)-Cu(2)′	66.90 (3)
I(2)-Cu(1)-I(2)′	107.60 (4)	Cu(2)-I(1)-Cu(2)′	67.27 (4)
I(1)-Cu(2)-I(2)	113.38 (3)	Cu(1)-I(2)-Cu(2)	63.37 (3)
I(1)-Cu(2)-I(1)′	107.03 (4)	Cu(1)-I(2)-Cu(1)′	66.01 (3)
I(2)-Cu(2)-I(1)′	107.13 (3)	Cu(2)-I(2)-Cu(1)′	66.69 (3)
Mean	109.52 ± 3.04	Mean	65.75 ± 1.58
	(B) Phosphorus-Copper-Iodine Angles		
P(1)-Cu(1)-I(1)	101.94 (6)	P(2)-Cu(2)-I(2)	101.62 (6)
P(1)-Cu(1)-I(2)	115.41 (6)	P(2)-Cu(2)-I(1)	121.77 (6)
P(1)-Cu(1)-I(2)′	109.71 (6)	P(2)-Cu(2)-I(1)′	104.89 (6)
	Mean = 109.22 ± 8.07		
	(C) Copper-Phosphorus-Carbon Angles		
Cu(1)-P(1)-C(1)	110.0 (3)	Cu(2)-P(2)-C(2)	109.0 (3)
Cu(1)-P(1)-C(11)	115.9 (2)	Cu(2)-P(2)-C(21)	118.3 (2)
Cu(1)-P(1)-C(17)	118.0 (2)	Cu(2)-P(2)-C(27)	118.1 (3)
	Mean = 114.9 ± 4.3		
	(D) Carbon-Phosphorus-Carbon Angles		
C(1)-P(1)-C(11)	105.3 (4)	C(2)-P(2)-C(21)	104.5 (4)
C(1)-P(1)-C(17)	103.4 (4)	C(2)-P(2)-C(27)	103.9 (5)
C(11)-P(1)-C(17)	102.9 (3)	C(21)-P(2)-C(27)	101.5 (4)
	Mean = 103.6 ± 1.3		
	(E) Phosphorus-Carbon-Carbon Angles		
P(1)-C(11)-C(12)	116.4 (6)	P(2)-C(21)-C(22)	119.5 (5)
P(1)-C(11)-C(16)	125.9 (8)	P(2)-C(21)-C(26)	123.3 (5)
P(1)-C(17)-C(18)	123.5 (6)	P(2)-C(27)-C(28)	119.6 (10)
P(1)-C(17)-C(112)	118.5 (5)	P(2)-C(27)-C(212)	117.8 (13)
		P(2)-C(27)-C(28)D	112.8 (19)
		P(2)-C(27)-C(212)D	121.6 (21)

Table VII. Equations of Planes and Important Dihedral Angles within the $\mathrm{Cu_4I_4}$ Core of $[(\mathrm{PMePh_2})\mathrm{CuI}]_4$

Plane	Atoms	Equations[a]
Ia	I(1), Cu(1), I(2)	$0.8375X - 0.2078Y + 0.5054Z = 1.980$
Ib	Cu(1), I(2), Cu(2)	$0.8878X + 0.1213Y + 0.4441Z = 1.907$
Ic	I(2), Cu(2), I(1)	$0.9751X + 0.1947Y + 0.1063Z = 0.751$
Id	Cu(2), I(1), Cu(1)	$0.9731X - 0.1397Y + 0.1830Z = 0.033$
IIa	I(1)′, Cu(2)′, I(1)	$-0.3057X + 0.9371Y + 0.1683Z = 4.721$
IIb	Cu(2)′, I(1), Cu(2)	$-0.0938X + 0.9670Y - 0.2371Z = 2.043$
IIc	I(1), Cu(2), I(1)′	$0.3057X + 0.9371Y - 0.1683Z = 2.116$
IId	Cu(2), I(1)′, Cu(2)′	$0.0938X + 0.9670Y + 0.2371Z = 3.894$
IIIa	I(2)′, Cu(1), I(1)	$-0.0389X - 0.2403Y + 0.9699Z = 5.479$
IIIb	Cu(1), I(1), Cu(2)′	$-0.4347X - 0.1801Y + 0.8824Z = 5.392$
IIIc	I(1), Cu(2)′, I(2)′	$-0.5032X + 0.2431Y + 0.8293Z = 6.635$
IIId	Cu(2)′, I(2)′, Cu(1)	$-0.1307X + 0.1855Y + 0.9739Z = 6.018$
IVa	I(2), Cu(1)′, I(2)′	$0.1674X + 0.9260Y + 0.3385Z = 1.635$
IVb	Cu(1)′, I(2)′, Cu(1)	$-0.2205X + 0.9652Y + 0.1407Z = 2.006$
IVc	I(2)′, Cu(1), I(2)	$-0.1674X + 0.9260Y - 0.3385Z = -0.892$
IVd	Cu(1), I(2), Cu(1)′	$0.2205X + 0.9652Y - 0.1407Z = -0.052$

Planes	Dihedral angle, deg	Planes	Dihedral angle, deg
Ia-Ic	146.09	IIIa-IIIc	139.95
Ib-Id	158.16	IIIb-IIId	151.98
IIa-IIc	139.15	IVa-IVc	135.63
IIb-IId	150.46	IVb-IVd	149.67

[a] Cartesian (Å) coordinates (X, Y, Z) are related to the fractional coordinates by $X = ax + zc \cos \beta$, $Y = yb$, and $Z = ac \sin \beta$.

a cubane-like $\mathrm{Cu_4I_4}$ core of regular T_d symmetry; the present $[(\mathrm{PMePh_2})\mathrm{CuI}]_4$ molecule has a cubane-like $\mathrm{Cu_4I_4}$ core of C_2 symmetry which is distorted from T_d symmetry by atomic shifts of little more than 0.1 Å, while the $[(\mathrm{PPh_3})\mathrm{CuI}]_4$ molecule takes up a "step-like" or "chair"[11] geometry of C_i symmetry.

An interesting result is that *average* dimensions within the slightly distorted cubane-like $\mathrm{Cu_4I_4}$ core of $[(\mathrm{PMePh_2})\mathrm{CuI}]_4$ are almost indistinguishable from the sharply defined bond lengths and angles within the regular $[(\mathrm{PEt_3})\mathrm{CuI}]_4$ system.

Finally, we note that the observation of distortion within the core of the $[(\mathrm{PMePh_2})\mathrm{CuI}]_4$ molecule is consistent with the analysis of $\mathrm{L_4M_4X_4}$ tetramers by Teo and Calabrese,[11] who conclude that "as steric hindrance among the ligands increases, the following stereochemical variation inevitably occurs: symmetrical "cubane" → distorted "cubane" → ("cubane" ⇄ "chair" isomerization) → "chair".

We herein have discussed phosphine–copper–iodide species covering the first two and last of these possibilities. "Cubane" ⇄ "chair" isomerization in this system should, therefore, be observable with a phosphine ligand intermediate in bulk between $\mathrm{PMePh_2}$ and $\mathrm{PPh_3}$.

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Registry No. $[(PMePh_2)CuI]_4$, 64024-83-5.

Supplementary Material Available: A listing of structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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Structure of Hydrido(dithiomethyl ester)bis(carbonyl)bis(triphenylphosphine)osmium–Hemibenzene, $OsH(CS_2(CH_3))(CO)_2(P(C_6H_5)_3)_2\cdot{}^1/_2C_6H_6$

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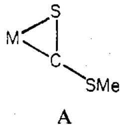
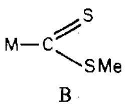
The structure of $OsH(CS_2Me)(CO)_2(PPh_3)_2\cdot{}^1/_2C_6H_6$ has been determined by single-crystal x-ray methods. The compound crystallizes with two formula units in space group C_i^1-$P\bar{1}$ of the triclinic system in a cell of dimensions $a = 12.217$ (4) Å, $b = 15.129$ (9) Å, $c = 11.241$ (4) Å, $\alpha = 106.23$ (3)°, $\beta = 93.97$ (3)°, $\gamma = 101.57$ (3)°, $V = 1936.9$ Å^3, $\rho_{calcd} = 1.546$ g/cm^3, and $\rho_{obsd} = 1.56$ (2) g/cm^3. The structure has been refined by least-squares methods to a final R index on F of 0.036 for the 182 variables and 7005 data. Included in the refinement was the hydrido ligand. The coordination about the Os atom is approximately octahedral with trans phosphine groups and with the dithiomethyl ester group trans to a carbonyl and the hydrido ligand trans to the other carbonyl group. The Os–H distance is 1.64 (6) Å. The dithiomethyl ester ligand is bound in a monodentate fashion through the C atom. The Os–C(3), C(3)–S(1), and C(3)–S(2) bond lengths of 2.137 (5), 1.724 (5), and 1.648 (4) Å, respectively, suggest that stabilization of the donor C atom is by π interaction between it and the two adjacent sulfur atoms and not with the metal.

Introduction

Recent reports describe the preparation of complexes involving the dithiomethyl ester group (SCSMe) as a ligand.[3,4] On the basis of IR evidence, two coordination modes are suggested for it. The group can either behave in a bidentate fashion with carbon and sulfur atoms acting as donors (A) or, alternatively, a monodentate attachment is possible with coordination occurring via the central carbon atom (B).



A



B

The first bonding mode is found in the complexes $Os(SCSMe)(CO)_2(PPh_3)_2^+$ and $Ru(SCSMe)(CO)_2(PPh_3)_2^+$ for which IR bands, attributed to ν_{CS}, have been observed at 1070 and 1115 cm^{-1}, respectively.[3,5] Confirmation of such an arrangement has been obtained from a crystal-structure analysis of the latter compound.[5] For the complexes $OsH(CS_2Me)(CO)_2(PPh_3)_2$ and $IrHCl(CS_2Me)(CO)(PPh_3)_2$,[4] however, bidentate coordination is not possible if octahedral geometry is to be maintained. The shift in the ν_{CS} bands to 1005 and 985 cm^{-1}, respectively, is consistent with the alternative monodentate attachment. The present crystal structure of $OsH(CS_2Me)(CO)_2(PPh_3)_2$ confirms this mode of attachment and provides insight into the stabilization of this ligand.

Experimental Details

The compound $OsH(CS_2Me)(CO)_2(PPh_3)_2$ was prepared as described previously.[4] Suitable crystals as the hemibenzene solvate were obtained by recrystallization from benzene.

On the basis of morphology and an extensive series of photographs the material was assigned to the triclinic system. Cell dimensions, obtained by hand centering[6] of 11 reflections in the region $75 \leq 2\theta$(Cu Kα_1) $\leq 90°$ on a Picker FACS-I diffractometer, are $a = 12.217$ (4) Å, $b = 15.129$ (9) Å, $c = 11.241$ (4) Å, $\alpha = 106.23$ (3)°, $\beta = 93.97$ (3)°, and $\gamma = 101.57$ (3)° ($t = 23.5$ °C, λ(Cu Kα_1) 1.540 562 Å). For a cell volume of 1936.9 Å^3 and a molecular weight of 902.95 amu ($C_{43}H_{37}O_2OsP_2S_2$) the density of 1.546 g/cm^3 calculated for two formula units in the cell agrees well with that of 1.56 (2) g/cm^3 measured by flotation methods. A Delaunay reduction failed to reveal any hidden symmetry in the cell. Space group C_i^1-$P\bar{1}$ was assumed and was ultimately shown to be correct on the basis of the excellent agreement between observation and model.

A crystal of prismatic habit was mounted in air roughly along [010]. The crystal, which displayed faces of the forms {010}, {100}, {001}, and {01$\bar{1}$}, had a calculated volume of 0.00662 mm^3 and was approximately 0.37-mm long and of cross section 0.18 × 0.12 mm. Data were collected in shells of 2θ by methods standard in this laboratory.[6,7] The scan speed was 2°/min from 0.75° below the Cu Kα_1 peak to 0.75° above the Cu Kα_2 peak. The takeoff angle was 4.5° and the