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Synthesis and Properties of Sulfur Dioxide Adducts of Organophosphinecopper(I) Iodides. Structures of the Dinuclear Compounds Tetrakis(methyldiphenylphosphine)di-μ-iodo-dicopper(I)–Sulfur Dioxide and Tris(triphenylphosphine)di-μ-iodo-dicopper(I)[1]

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Compounds of the general formula $Cu_mI_m(PR_3)_n\cdot xSO_2$, where PR_3 = PPh_3, PPh_2Me, $PBzl_3$, and PCy_3 (Bzl = benzyl; Cy = cyclohexyl), are formed by direct reaction of SO_2 with organophosphine copper(I) iodide complexes. The nature of the reaction solutions and isolated products has been elucidated by spectroscopic, tensimetric, and x-ray diffraction methods. Sulfur dioxide complexation occurs only at the coordinated halogen, even when three-coordinate copper(I) apparently is present in the complex. The strength of interaction is a strong function of both the specific phosphine and stoichiometry, and the bright yellow to orange crystalline complexes have SO_2 dissociation pressures of 2–70 Torr at ambient temperature. The crystal structure analysis of $Cu_2I_2(PPh_2Me)_4\cdot SO_2$ reveals a dimeric, di-μ-iodo-bridged structure involving pseudotetrahedral copper atoms and an SO_2 group bound weakly as a Lewis acid to one of the bridging iodides (I–S = 3.407 (5) Å and I–S–O = 98.1 (6), 114.5 (8)°). Additionally, we report the structure of the compound $Cu_2I_2(PPh_3)_3$ and its interaction with sulfur dioxide. X-ray structure determination reveals a dinuclear unit similar to that found in $Cu_2Cl_2(PPh_3)_3$ with μ-iodide bridges and both three-coordinate copper and four-coordinate copper. Pertinent crystallographic data are as follows: $Cu_2I_2(PPh_3)_3$, space group $P2_1$, a = 11.763 (4) Å, b = 20.682 (4) Å, c = 10.527 (3) Å, β = 105.66 (2)°, Z = 2, R = 0.047 for 4139 diffractometric reflections [with $I \geq 3\sigma(I)$ and $2\theta \leq 60°$]; $Cu_2I_2(PPh_2Me)_4SO_2$, space group $P\bar{1}$, a = 20.02 (2) Å, b = 12.062 (6) Å, c = 14.898 (7) Å, α = 116.30 (3)°, β = 68.44 (3)°, γ = 124.89 (2)°, Z = 2, R = 0.052 for 7112 diffractometric reflections [with $I \geq 3\sigma(I)$ and $2\theta \leq 50°$].

Introduction

Organophosphinecopper(I) halides have attracted much recent interest because their structures encompass a tremendous range of coordination types and polyhedral frameworks. For example, the 1:1:1 complexes $CuX(PR_3)$ have tetrameric structures which may be either of the cubane type (with all copper atoms pseudotetrahedral and all X atoms serving as μ_3 bridges) or of the step type (with the tetramer containing two pseudotetrahedral and two three-coordinate copper atoms and two μ_3- and two μ_2-iodides).[2,3] The 1:1:2 adducts $CuX(PR_3)_2$ may have either monomeric three-coordinate structures or dimeric pseudotetrahedral structures, whereas the 1:1:3 adducts all seem to have monomeric pseudotetrahedral solid-state structures.[4-7] A particularly interesting series which nicely illustrates the propensity of the organophosphinecopper(I) systems to form polynuclear complexes and the similar stabilities of the three- and four-coordinate species is formed by the 2:2:3 compounds $Cu_2X_2(PR_3)_3$.[8-14] Structure determinations for two crystalline modifications of $Cu_2Cl_2(PPh_3)_3$ revealed a dinuclear structure containing μ_2-bridging chlorides and both trigonal-planar and pseudotetrahedral copper atoms.[8,9]

We have been investigating the reactions of sulfur dioxide with transition metal substrates[15-18] and have examined the organophosphinecopper(I) iodide systems for several reasons. The tendency to form three-coordinate complexes, the general lability of many of these systems, and the affinity of copper(I) for sulfur-containing ligands provides the possibility for direct Cu–SO_2 adduct formation. Previous studies have shown that SO_2 interacts in aqueous media with chlorocopper(I) ions[19] and in liquid SO_2 with $CuX(PPh_3)_3$ (X = Cl, Br),[20] but no complexes were isolated. Interaction of SO_2 with the halide ligands is possible, SO_2 being known to form adducts with both coordinated and free iodide ions.[21,22]

In this paper we describe the preparation and characterization of a series of oligomeric complexes of the type $Cu_mI_m(PR_3)_n\cdot xSO_2$, where R_3 = Ph_3, Ph_2Me, Bzl_3 (Bzl = benzyl), and Cy_3 (Cy = cyclohexyl). Additionally, the x-ray crystal structures of $Cu_2I_2(PPh_2Me)_4\cdot SO_2$ and $Cu_2I_2(PPh_3)_3$ are described. Both complexes have dinuclear structures containing a central Cu_2I_2 ring, and in the former the SO_2 binds as a Lewis acid to a bridging iodide.

Experimental Section

Phosphines were purchased from Strem Chemical Co. and Pressure Chemical Co. and were used as received. Except when PPh_3 was used, reactions were carried out in a nitrogen atmosphere to minimize oxidation of the phosphine. The SO_2 was 99.98% pure (Matheson). Solvents were of the highest purity commerically available and were used without further purification.

Infrared spectra were recorded on a Perkin-Elmer 521 and UV–visible spectra on a Cary 14. Mass spectrometry was used to identify volatiles obtained upon heating the SO_2 adducts, thus identifying solvent that in some instances was present in the complexes. Elemental analyses were performed by Galbraith Laboratories, Inc. and by Group WX-2, Los Alamos Scientific Laboratory. A Mettler thermogravimetric analysis instrument was utilized.

Preparation of $Cu_2I_2(PPh_3)_3$. A 2:1 mole ratio of triphenylphosphine and CuI in chloroform was stirred at ambient temperature, with the intention of forming $CuI(PPh_3)_2$ for subsequent reaction with SO_2. The resulting colorless solution was filtered to remove trace insoluble matter and treated with SO_2 gas. The solution immediately became yellow, and heptane was added to decrease the solubility of the dissolved species. Large, well-formed, light yellow crystals developed when the stoppered solution was allowed to stand for several hours. Initially, we expected the product, because of its slight yellow color, to be an SO_2 adduct. The crystal structure determination and elemental analysis, however, showed the compound instead to be $Cu_2I_2(PPh_3)_3$: <0.05% S found; 0.0% S calculated. The compound may be prepared by the more direct methods reported by Costa and co-workers.[10,11] Melting point and infrared data show the material prepared by the two methods to be identical. Apparently a slight yellow color is characteristic of $Cu_2I_2(PPh_3)_3$ when prepared by the method described above.

Reaction of $Cu_2I_2(PPh_3)_3$ with Liquid SO_2. Prior to reaction with liquid SO_2, the 2:2:3 compound (prepared using Costa's procedure) was recrystallized from CH_2Cl_2–heptane to give slightly off-white crystals whose melting point and infrared spectrum agreed with those reported for $Cu_2I_2(PPh_3)_3$: mp 219–221 °C, lit.[10,11] mp 223–226 °C. The complex was finely ground, and 0.59 g was placed in a grease-free tensimeter[23] attached to a high-vacuum system. About 5 mL of SO_2 was distilled onto the solid and immediately a bright yellow solution and bright yellow solid resulted. After the mixture was kept for 1 h at −10 °C, unreacted SO_2 was removed at −63 °C, and the solid

Table I.[a] Cell Data for Some Methyldiphenylphosphinecopper(I) Iodide Complexes

Compd	Space group	Z	ρ_{obsd}	ρ_{calcd}	Lattice constants
$CuI(PPh_2Me)_3$[b]	$Pn2_1a$ or $Pnma$	4	1.41	1.40	$a = 20.4$, $b = 17.5$, $c = 10.6$ Å
$[CuI(PPh_2Me)_2]\cdot{}^1/_2CHCl_3$	Cc or $C2/c$	8	1.55	1.55	$a = 27.2$, $b = 12.8$, $c = 19.6$ Å; $\beta = 125.1°$
$CuI(PPh_2Me)$	Cc or $C2/c$	16	1.82	1.84	$a = 25.6$, $b = 11.9$, $c = 19.7$ Å; $\beta = 110.2°$

[a] Space groups and lattice parameters were determined by precession photography. Crystals were taken from the preparations described in the Experimental Section. Densities are in g/cm^3 and were determined by flotation in mixed organic solvents. [b] The analogous compound $CuCl(PPh_2Me)_3$ was refined successfully in $Pn2_1a$ with lattice constants $a = 20.229$, $b = 17.180$, $c = 10.309$ Å.[6] Thus, the compounds are probably isomorphous.

residue was warmed to 0 °C and maintained in an ice bath. A constant SO_2 dissociation pressure was reached within about 6 h. However, as SO_2 was removed incrementally from the system, the observed dissociation pressure decreased in a continuous fashion from ~25 to ~10 Torr (i.e., pressure decreased as the SO_2:dimer ratio was decreased). All SO_2 was readily removed at ambient temperature. The ratio of SO_2:$Cu_2I_2(PPh_3)_3$ was determined to be 1.98:1.00 using PVT measurements of the evolved SO_2. Elemental analysis (carbon and hydrogen), the melting point, and the infrared spectrum of the recovered white solid were identical with those of the starting material, $Cu_2I_2(PPh_3)_3$. Thus, the composition of the adduct (as isolated at −63 °C) is $Cu_2I_2(PPh_3)_3\cdot 2SO_2$. No evidence was observed for an intermediate 1:1 adduct, when volatiles were removed at temperatures between −63 and −10 °C.

Addition of gaseous SO_2 to solid $Cu_2I_2(PPh_3)_3$ in a 2:1 stoichiometry at 0 °C was also carried out. Formation of the bright yellow 2:1 adduct was slower (~1 h) and not quite as complete (80–90%) as in the liquid SO_2 reaction.

Preparation and Properties of $Cu_2I_2(PPh_2Me)_4\cdot SO_2$. PPh_2Me and CuI were mixed in a 2:1 molar ratio in a minimum quantity of $CHCl_3$ to give a colorless solution from which a solid could be crystallized by addition of hexane. A 1.71-g quantity of this mixture (primarily $Cu_2I_2(PPh_2Me)_4$, but also containing some $CuI(PPh_2Me)_3$) was dissolved in 40 mL of $CHCl_3$ and 100 mL of heptane was added. The solution was saturated with SO_2 to give a yellow color, stoppered, and allowed to stand for 2 days, during which time large, well-formed, red crystals of $Cu_2I_2(PPh_2Me)_4\cdot SO_2$ separated (0.87 g, 50% yield). If excess heptane (or other nonpolar solvent) is added too rapidly to the yellow solution, colorless crystals of $Cu_2I_2(PPh_2Me)_4$ form initially.

The SO_2 adduct is stable in the solid state for months if stored in a tightly capped vial with an atmosphere of SO_2. However, when it is dissolved in organic solvents, SO_2 immediately dissociates to give colorless solutions of the precursor complex. All SO_2 can be removed from the red crystals upon heating in air or in vacuo, with rapid loss occurring above ~120 °C. The ratio of SO_2:$Cu_2I_2(PPh_2Me)_4$ was determined to be 1.02:1.00. Red crystals of $Cu_2I_2(PPh_2Me)_4\cdot SO_2$ can be regenerated from $CHCl_3$–heptane solution or from liquid SO_2 solution using the white residue of $Cu_2I_2(PPh_2Me)_4$ obtained upon SO_2 removal from $Cu_2I_2(PPh_2Me)_4\cdot SO_2$.

Preparation and Properties of $Cu_2I_2(PBzl_3)_4\cdot 3SO_2$. The tribenzylphosphine analogue was prepared in a similar manner to that used to obtain $Cu_2I_2(PPh_2Me)_4\cdot SO_2$, except that the SO_2 adduct could be precipitated immediately from solution with a nonpolar solvent. The fluffy yellow crystals thus obtained possess similar properties to the PPh_2Me analogue, but lose SO_2 more readily.

Preparation and Properties of $[CuI(PPh_3)]_4\cdot 2SO_2$. When either a 1:1 or 2:1 mixture of PPh_3 and CuI was dissolved in $CHCl_3$, saturated with SO_2, and allowed to stand, yellow crystals of $[CuI(PPh_3)]_4\cdot 2SO_2$ formed. The complex is only sparingly soluble in chloroform and readily loses SO_2 at ambient temperature. The tetrameric formulation is tentatively assumed since the melting point (265–268 °C) of the white residue obtained upon SO_2 removal is nearly identical with the literature values[10] for $[CuI(PPh_3)]_4$ (265–267 °C).

Preparation and Properties of $[CuI(PCy_3)]_4\cdot{}^1/_2SO_2\cdot CHCl_3$. A solution (~$10^{-2}$ M) containing a 2:1 ratio of PCy_3:CuI was prepared by stirring these reactants together in $CHCl_3$ at ambient temperature. Unlike the cases where $PR_3 = PPh_2Me$ or $PBzl_3$, the addition of a large (>twofold) excess of heptane to the solution did not precipitate any solids. Therefore, the solution was saturated with SO_2 and cooled in the hope that an SO_2 adduct would precipitate. A yellow crystalline solid, which proved to be nearly insoluble in common organic solvents, slowly deposited in good yield (60–80%). The solid contained both SO_2 and chloroform, and elemental analysis (Table VII) indicated its composition to be $[CuI(PCy_3)]_4\cdot{}^1/_2SO_2\cdot CHCl_3$. Impurities were present, however, since the phosphorus:copper ratio was 1.2:1. The tetrameric formulation was assumed from comparison of the properties of the SO_2-and $CHCl_3$-free residue obtained on heating with those of $[CuI(PPh_3)]_4$ and $[CuI(PCy_3)]_4$ (see below). Unlike the PPh_3 analogue, $[CuI(PCy_3)]_4\cdot{}^1/_2SO_2\cdot CHCl_3$ did not lose SO_2 easily. A sample did not whiten upon standing for long periods of time in air and did not completely lose volatiles (SO_2 and $CHCl_3$) until heated to 190 °C in a melting point capillary, leaving a white residue (mp 218–223 °C).

When a 1:1 ratio of PCy_3 to CuI was dissolved in $CHCl_3$ (refluxing necessary), a colorless solution was obtained that became yellow upon saturation with SO_2. Addition of ethanol precipitated a nearly insoluble white solid that did not contain SO_2. On standing, the filtrate deposited only the white solid, elemental analysis of which indicated it to be $[CuI(PCy_3)]_4$. Anal. Calcd for $C_{72}H_{132}P_4Cu_4I_4$: C, 45.9; H, 7.1; P, 6.6; Cu, 13.5; I, 26.9. Found: C, 45.5; H, 7.3; P, 6.6; Cu, 13.3; I, 26.4. The melting points of the above (225–229 °C) and the white residue obtained on heating $[CuI(PCy_3)]_4\cdot{}^1/_2SO_2\cdot CHCl_3$ were similar, and a mixture melting point determination gave a 218–225 °C melting range, nearly identical with that of the residue alone.

Preparation of $CuI(PPh_2Me)_3$. The addition of *n*-heptane to a 3:1 molar mixture of methyldiphenylphosphine–cuprous iodide in chloroform solution produced a bulk product consisting of an approximate equimixture of well-formed $CuI(PPh_2Me)_3$ crystals and $Cu_2I_2(PPh_2Me)_4$ microcrystals (identification by x-ray diffraction, Table I).

Preparation of $[CuI(PPh_2Me)_2]_2\cdot CHCl_3$. Addition of heptane to a chloroform solution containing a 3:1 molar ratio of methyldiphenylphosphine:cuprous iodide produced a microcrystalline mixture of $CuI(PPh_2Me)_3$ and $[CuI(PPh_2Me)_2]_2\cdot CHCl_3$. Recrystallization from $CHCl_3$–*n*-heptane produced large crystals of $CuI(PPh_2Me)_3$ and $[CuI(PPh_2Me)_2]_2\cdot CHCl_3$ (identification by x-ray diffraction, Table I).

Preparation of $CuI(PPh_2Me)$. The compound was obtained in pure crystalline form as monoclinic-shaped platelets after two recrystallizations (from $CHCl_3$–*n*-heptane) of the colorless product formed when *n*-heptane was added to a 2:1 molar ratio of methyldiphenylphosphine:cuprous iodide in chloroform solution; mp 195–202 °C. Anal. Calcd for $CuIPC_{13}H_{13}$: C, 39.56; H, 3.35; I, 32.48. Found: C, 39.84; H, 3.37; I, 32.43.

X-Ray Data Collection, Structure Solution, and Refinement for $Cu_2I_2(PPh_2Me)_4\cdot SO_2$. Details of data collection and refinement are given in Table II. Unless otherwise noted, the structure analysis was as reported in earlier publications.[26] Crystals prepared as described above were examined optically and by precession photography and classed in the triclinic system. Satisfactory refinement in $P\bar{1}$ indicates this to be the proper space group choice. To inhibit SO_2 loss, the data crystal was coated with Duco cement. Corrections for Lp effects and absorption were made in the usual way.[26] A correction for a steady decrease of ca. 20% in the intensities of two standard reflections due to crystal decomposition was applied using a least-squares polynomial.

The structure was solved using direct methods and refined by standard least-squares/Fourier methods to an R factor of 0.046 for an anisotropic model for all atoms except carbon (no attempt was made to account for hydrogen atoms), using observed data with $2\theta \leq 40°$. An extinction parameter was refined.[27] Pronounced anisotropic thermal motion was evident in the SO_2 oxygen atoms, and the SO_2 group refined to abnormally short S–O distances (1.26 (1) and 1.36 (1) Å; cf. normally observed value of 1.44 ± 0.02 Å) and an overly large O–S–O angle (130 (1)°; cf. normal value of 114 ± 2°).[16,21,28] Difference Fourier syntheses in this region revealed only two elongated streaks of electron density. Therefore, the SO_2 was refined subsequently as a rigid body with parameters S–O = 1.445 Å and O–S–O = 114°. In final refinements all observed data were used ($2\theta \leq 50°$) and a final R factor of 0.052 was obtained. In the final refinement no atomic parameter shifted more than 0.1 esd. A final difference

Table II. X-Ray Data Collection Description

	$Cu_2I_2(PPh_2Me)_4 \cdot SO_2$	$Cu_2I_2(PPh_3)_3$
Space group	$P\bar{1}$	$P2_1$
ρ_{obsd}, g/cm^3 (flotation)	1.57	1.55
ρ_{calcd}, g/cm^3	1.58	1.57
a, Å	20.02 (2)	11.763 (4)
b, Å	12.062 (6)	20.682 (4)
c, Å	14.898 (7)	10.527 (3)
α, deg	116.30 (3)	
β, deg	68.44 (3)	105.66 (2)
γ, deg	124.89 (2)	
λ, Å	0.709 30	0.709 30
Z	2	2
Base scan width, deg	2	2
Scan rate, deg/min	2	2
θ_{min}, θ_{max}, deg	1, 50	1, 60
Takeoff angle, deg	3.5	3.5
Transmission coeff	0.63–0.68	0.67–0.85
No. of reflections collected	9577	7268
No. of reflections with $I \geqslant 3\sigma(I)$	7112	4139
μ, cm^{-1}	20.5	22.9
Crystal dimensions, mm	0.40 × 0.26 × 0.20	0.18 × 0.16 × 0.08
Crystal faces	{010}, {001}, {101}, $(2\bar{1}0)$, $(\bar{2}10)$	{100}, $(10\bar{1})$, {010}
Cell parameter refinement data	12 reflections, with $2\theta \geqslant 35°$	12 reflections, with $36 \leqslant 2\theta \leqslant 38°$
Diffractometer	Picker FACS-1	Picker FACS-1

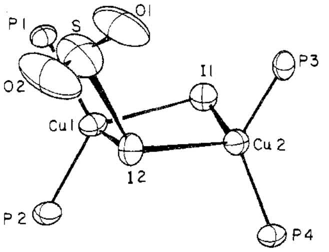

Figure 1. The central $CuI_2P_4 \cdot SO_2$ core of $Cu_2I_2(PPh_2Me)_4 \cdot SO_2$.

Fourier synthesis contained as the largest feature a peak of height 1.1 e/Å^3 near the iodine atoms.

A view of the $Cu_2I_2P_4 \cdot SO_2$ core is given in Figure 1 and a stereoview of the structure is presented in Figure 2. Final least-squares parameters and molecular dimensions are reported in Tables III and IV. A listing of observed and calculated structure factors is available.[29]

X-Ray Data Collection, Structure Solution, and Refinement for $Cu_2I_2(PPh_3)_3$. Unless noted otherwise, data collection and reduction for $Cu_2I_2(PPh_3)_3$ proceeded as for $Cu_2I_2(PPh_2Me)_4 \cdot SO_2$ (see Table II). Precession photographs were consistent with monoclinic space groups $P2_1$ and $P2_1/m$. Intensity distribution statistics and the successful refinement of the structure in the noncentric space group strongly support the selection of $P2_1$.

Data were collected in two shells ($0 < 2\theta \leq 45°$ and $45 < 2\theta \leq 60°$) in the quadrant ($\pm hkl$). The intensities of two standard reflections decreased by ca. 4% and 12% for the low- and high-angle data sets due to crystal decomposition, and appropriate corrections were applied by fitting the standards by least-squares to polynomial curves. For the low-angle data set, 3257 independent reflections were collected, of which 2897 satisfied the acceptance criterion $I \geq 3\sigma(I)$ and were used in the structure refinement. The corresponding numbers for the high-angle data set are 4011 and 1242.

A three-dimensional Patterson function was interpreted to give Cu and I positions, and subsequent atoms were located by standard Fourier methods. Attempts to refine any reasonable structural model in the centrosymmetric space group $P2_1/m$ never produced an R factor lower than 31%. Isotropic refinement of the 61 nonhydrogen atoms, plus a scale factor and extinction parameter, in $P2_1$ gave an R factor of 0.086. With refinement of the Cu, I, and P atoms anisotropically, R lowered to 0.043 and 0.040 before and after absorption corrections, respectively. In the final cycles of refinement hydrogen atoms were included but not refined in calculated positions with isotropic temperature factors of 6.0 Å^2. The hydrogen positions were defined by an idealized polyhedron with an origin at the center of each set of phenyl carbons, with origin–H distance of 1.38 Å and H–origin–H angles of 60° [resulting C–H distances 0.95 Å (average)].

In the final stages of refinement, the high- and low-angle data were combined and refined with two scale factors. A test refinement in which the signs of the $\Delta F''$ terms were reversed indicated the handedness initially chosen in this space group to be correct. For the final cycle (4139 reflections, 281 variables) the conventional R factor was 0.047, the maximum parameter shift was less than 0.1 esd, and the standard deviation in an observation of unit weight was 2.5. A final difference Fourier synthesis revealed as the largest features peaks of height 0.7–0.8 e Å^{-3} in the vicinity of the iodine atoms, compared to 4.0 e Å^{-3} for a typical carbon atom in this structure. A listing of observed and calculated structure factors is available.[29] Views of the molecular unit are presented in Figures 3 and 4. Final atomic parameters and selected distances and angles are given in Tables V and VI.

Structure of $Cu_2I_2(PPh_2Me)_4 \cdot SO_2$

The structure consists of a dinuclear $Cu_2I_2(PPh_2Me)_4$ molecule containing two μ_2-iodide bridges, with the SO_2 attached weakly to one of the bridging iodides (Figures 1 and 2). The I–S distance, 3.407 (5) Å, is very much longer than the sum of the respective covalent radii (2.36 Å) but shorter than the sum of the respective van der Waals radii (3.78 Å).[21] Furthermore, a weak Lewis acid–base interaction between the SO_2 and iodine is indicated by the pyramidal geometry at sulfur (I–S–O angles 114.5 (8) and 98.1 (6)°) and the red-orange color of the complex. A similar MI–SO_2 interaction was observed in *trans*-$Pt(PPh_3)_2(CH_3)I \cdot SO_2$, where the I–S distance was 3.391 (3) Å and the I–S–O angles were 104.7 (4) and 96.9 (3)°.[21] The angles between the I–S vector and the normal to the SO_2 planes are 32.4 and 21.3°, respectively, in the present and the earlier structure. Considering the weak nature of the I–SO_2 bonding, the difference in the metal coordination units, and the bridging vs. nonbridging nature of iodides, the agreement in the I–SO_2 geometries for the two structures is remarkable.

Each copper atom in $Cu_2I_2(PPh_2Me)_4 \cdot SO_2$ has a pseudotetrahedral environment with normal Cu–P distances,[6] 2.249–2.274 Å, and I–Cu–P angles in the range 100.29–110.33° (except for I1–Cu2–P4, 119.76°). The P–Cu–P angles, 122.85 and 127.89°, may be compared to the As–Cu–As angle of 118.0° found in $Cu_2Cl_2(AsPhMe_2)_4$ and to the P–Cu–P angle of 128.2° found in $Cu(PPh_2Me)_2(B_3H_8)$.[6]

The structure of $Cu_2I_2[(o\text{-}C_6H_4NH_2)AsMe_2]_4$ appears to be the only dinuclear structure previously reported containing a Cu_2I_2 core. The Cu_2I_2 core in this structure is centro-

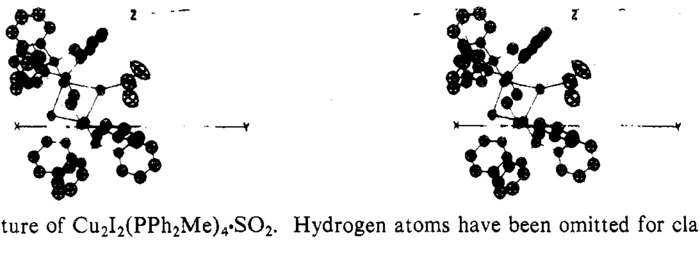

Figure 2. Stereoview of the structure of $Cu_2I_2(PPh_2Me)_4 \cdot SO_2$. Hydrogen atoms have been omitted for clarity.

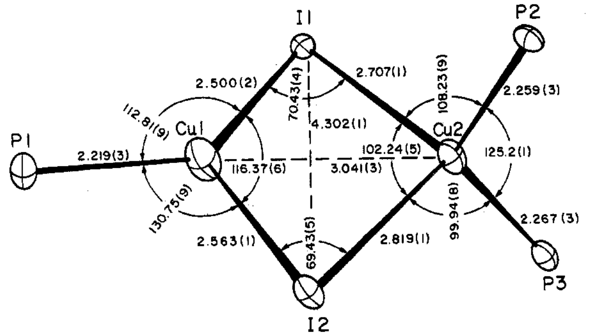

Figure 3. The central $Cu_2I_2P_3$ core of $Cu_2I_2(PPh_3)_3$.

symmetric and has Cu–I distances of 2.527 and 2.623 Å, an I–Cu–I angle of 116.1°, and a Cu–I–Cu angle of 63.9°. In the present compound the Cu_2I_2 core is asymmetric, due at least in part to the coordination of SO_2 to one iodine. A resulting expansion of *all* Cu–I distances to the range 2.650–2.848 Å is observed. The Cu–I–Cu angles, 79.99 and 83.40°, are also opened up from those found in the arsine compound. The dihedral angle between the CuI_2 planes, 15.3°, indicates a slight V shape for the Cu_2I_2 unit, as observed in several other structures with Cu_2I_2 units.[2a,8,9]

Structure of $Cu_2I_2(PPh_3)_3$

The structure of $Cu_2I_2(PPh_3)_3$ consists of discrete dinuclear units with a central four-member Cu_2I_2 ring containing μ_2-iodide bridges and both three- and four-coordinate copper atoms. The structure is thus analogous to that of the corresponding chloride compound $Cu_2Cl_2(PPh_3)_3$.[8,9] In the steplike tetramer $[CuI(PPh_3)]_4$, $Cu_2I_3(PPh_3)_2$ moieties with both three- and four-coordinate copper atoms are found, but these are terminal units additionally linked by iodide bridges to a central four-membered Cu_2I_2 ring in which *both* copper atoms are pseudotetrahedrally coordinated.[2a]

The geometry about Cu1 is distorted trigonal planar, with Cu1 lying 0.07 Å out of the I_2P coordination plane. The closest nonbonded contact involving Cu1 is ca. 3.0 Å to a phenyl hydrogen, and no additional interactions to P or I atoms are less than 4.4 Å. The Cu1–P distance, 2.219 (3) Å, and the Cu1–I distances, 2.500 (1) and 2.563 (1) Å, are normal for three-coordinate copper(I).[2-4,6,8] The P1–Cu1–I angles, 112.81 (9) and 130.75 (9)°, are quite interesting in that a similar pattern of angular distortions also occurs in $[CuI(PPh_3)]_4$ and in both the triclinic and monoclinic forms of $Cu_2Cl_2(PPh_3)_3$.[8,9] These distortions have previously been ascribed in $Cu_2Cl_2(PPh_3)_3$ to a packing arrangement producing intramolecular graphitelike phenyl–phenyl interactions, but a packing analysis fails to reveal analogous interactions in the present structure.

The environment of Cu2 is distorted tetrahedral with Cu2–P distances, 2.259 (3) and 2.267 (3) Å, and Cu2–I distances, 2.707 (1) and 2.819 (1) Å, which are longer on average than the corresponding values in $[CuI(PPh_3)]_4$, 2.228 (5)–2.242 (4) and 2.620 (2)–2.728 (2) Å. The I–Cu–P and P–Cu–P angles are distorted from the ideal tetrahedral values in a manner consistent with the strained nature of the Cu_2I_2 ring.

The four-membered Cu_2I_2 ring has a distinct V shape with the dihedral angle between the CuX_2 planes being 15.9°, compared to 12.7° in $[CuI(PPh_3)]_4$, 15.3° in $Cu_2I_2(PPh_2Me)_4 \cdot SO_2$, and 21.3 and 11.7° in the two forms of $Cu_2Cl_2(PPh_3)_3$.[8,9] The Cu–I–Cu values of 69.43 (5) and 70.43 (4)° are in the range 59–84° normally observed in Cu_2I_2 rings, while the I–Cu–I angles at the tetrahedral copper (102.24 (5)°) and the trigonal-planar copper (116.37 (6)°) are distorted in the expected direction from the idealized values by the nature of the Cu_2I_2 ring.[2-4,6,8] The Cu–Cu distance, 3.041 (3) Å, and the I–I distance, 4.302 (1) Å, are nonbonding. Indeed, the angles at the bridging halides in all the $Cu_2X_2(PPh_3)_3$ compounds appear to be determined by nonbonded interactions between the bridging halogens, since the X–X distances are close to the sum of the van der Waals radii (3.6 Å for Cl, 4.3 Å for I) while the Cu–Cu distances are longer than the sum of van der Waals radii. The constraints imposed by the Cu–X and X–X distances then produce the observed Cu–X–Cu and X–Cu–X angles. Similar conclusions have been reached by other authors.[3]

Discussion

We have been conducting a general investigation of the interaction of sulfur dioxide with organophosphinecopper(I) complexes containing large polarizable anionic ligands such as iodide and mercaptide.[17,31] The iodide ion is known to interact with sulfur dioxide both in the free form[22,32] and in the ligated form (as in $Pt(PPh_3)_2(CH_3)I \cdot SO_2$).[21] We find that SO_2 also binds to coordinated iodide in the $Cu_mI_m(PR_3)_n$ complexes described herein, in all cases, presumably, in a fashion as found in the structure described above. The SO_2 adducts (Table VII) are formed from solutions containing one or two PR_3 ligands per CuI and have stoichiometries which are highly dependent on the specific phosphine. This behavior undoubtedly is due to the complicated solution equilibria and oligomeric behavior generally exhibited by cuprous halide–phosphine systems.[5,6] The complexity, in turn, is due to the range of steric and electronic properties of the phosphines. The SO_2 is labile in all adducts, and removal of SO_2 from the solids at ambient or higher temperatures leaves pure, white residues of $Cu_mI_m(PR_3)_n$.

The similarity of the SO_2 infrared vibrations for the series of complexes (Table VII) seems to rule out direct Cu–SO_2 binding in any of the adducts; all apparently contain weak I–SO_2 interactions, as in the structure of $Cu_2I_2(PPh_2Me)_4 \cdot SO_2$. A good example of the nonaffinity of Cu(I) for SO_2 was shown in the CuI–PPh_3 system, which yielded $Cu_2I_2(PPh_3)_3$ devoid of any SO_2 from $CHCl_3$–heptane solution saturated with SO_2 at ambient temperature. The x-ray structure of this dinuclear species featured the presence of a three-coordinate copper atom, which could have incorporated SO_2 as a fourth ligand. Reaction of $Cu_2I_2(PPh_3)_3$ with liquid SO_2 did yield a weak, yellow bis-SO_2 adduct, with properties indicative of interaction of SO_2 with the bridging iodides. The known trigonal-planar

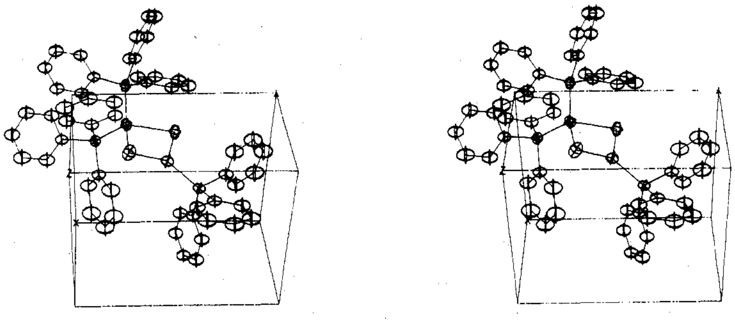

Figure 4. Stereoview of the structure of $Cu_2I_2(PPh_3)_3$. Hydrogen atoms have been omitted for clarity.

Table III. Final Least-Squares Parameters for $Cu_2I_2(PPh_2Me)_4 \cdot SO_2$[a]

A. Positional and Isotropic Thermal Parameters

	x	*y*	*z*	*B*, Å^2
Cu1	0.74637 (6)	−0.01248 (10)	0.02150 (7)	*b*
Cu2	0.74450 (6)	−0.5276 (10)	0.24635 (7)	*b*
I1	0.81666 (3)	−0.12369 (6)	0.05757 (4)	*b*
I2	0.64715 (3)	0.01497 (6)	0.20273 (4)	*b*
S	0.4443 (3)	−0.2224 (7)	0.2530 (6)	*b*
O1	0.3922 (5)	0.1592 (7)	0.3124 (6)	*b*
O2	0.4293 (6)	0.3035 (12)	0.1497 (6)	*b*
P1	0.6720 (1)	−0.1999 (1)	−0.0989 (2)	*b*
C1	0.5970 (5)	−0.3599 (9)	−0.0558 (7)	4.3 (2)
C2	0.7347 (5)	0.2588 (8)	−0.2111 (6)	3.5 (2)
C3	0.8171 (6)	−0.1638 (10)	−0.2297 (7)	4.1 (2)
C4	0.8678 (6)	−0.2050 (11)	−0.3167 (8)	5.9 (2)
C5	0.8335 (7)	−0.3405 (12)	−0.3808 (8)	6.5 (3)
C6	0.7517 (7)	−0.4361 (13)	−0.3652 (9)	7.1 (3)
C7	0.7001 (6)	−0.3966 (11)	−0.2793 (8)	5.8 (2)
C8	0.6068 (5)	−0.1878 (8)	−0.1505 (6)	3.0 (1)
C9	0.5431 (6)	−0.1637 (10)	−0.0825 (7)	5.0 (2)
C10	0.4919 (6)	−0.1529 (11)	−0.1185 (8)	5.9 (2)
C11	0.5058 (7)	−0.1609 (11)	−0.2193 (8)	6.2 (2)
C12	0.5701 (6)	−0.1843 (11)	−0.2869 (8)	5.7 (2)
C13	0.6204 (5)	−0.1967 (9)	−0.2512 (7)	4.5 (2)
P2	0.8408 (1)	0.2090 (2)	0.140 (2)	*b*
C14	0.8907 (6)	0.3327 (10)	0.1273 (7)	4.6 (2)
C15	0.9288 (5)	0.2210 (8)	−0.0857 (6)	2.9 (1)
C16	0.9753 (5)	0.1698 (9)	−0.0810 (6)	4.1 (2)
C17	1.0419 (6)	0.1679 (10)	−0.1598 (7)	4.7 (2)
C18	1.0593 (6)	0.2118 (10)	−0.2415 (7)	4.7 (2)
C19	1.0133 (6)	0.2614 (10)	−0.2456 (7)	4.6 (2)
C20	0.9466 (5)	0.2655 (8)	−0.1668 (6)	3.4 (2)
C21	0.8015 (4)	0.2968 (8)	−0.0103 (5)	2.8 (1)
C22	0.2671 (6)	−0.2129 (10)	0.0552 (7)	4.5 (2)
C23	0.2993 (6)	−0.2748 (11)	0.0770 (8)	5.8 (2)
C24	0.2605 (6)	0.5799 (10)	0.0520 (7)	5.0 (2)
C25	0.8081 (6)	0.5049 (10)	−0.0065 (7)	4.7 (2)
C26	0.8413 (5)	0.4457 (9)	0.0153 (6)	4.2 (2)
P3	0.6541 (1)	−0.2619 (2)	0.2817 (2)	*b*
C27	0.6013 (6)	−0.4042 (10)	0.1748 (7)	4.7 (2)
C28	0.6951 (5)	−0.3386 (8)	0.3151 (6)	3.0 (2)
C29	0.7249 (5)	−0.2679 (8)	0.4069 (6)	3.6 (2)
C30	0.7579 (5)	−0.3188 (10)	0.4369 (7)	4.6 (2)
C31	0.7605 (6)	−0.4432 (10)	0.3750 (7)	5.2 (2)
C32	0.7316 (6)	−0.5120 (10)	0.2843 (7)	4.9 (2)
C33	0.6986 (5)	−0.4613 (9)	0.2516 (7)	4.3 (2)
C34	0.5688 (4)	−0.2681 (8)	0.3852 (5)	2.9 (1)
C35	0.5597 (5)	−0.1487 (9)	0.4381 (6)	3.8 (2)
C36	0.4929 (5)	−0.1532 (9)	0.5175 (7)	4.4 (2)
C37	0.4365 (6)	−0.2804 (10)	0.5394 (7)	4.7 (2)
C38	0.4436 (6)	−0.4018 (11)	0.4882 (7)	5.3 (2)
C39	0.5116 (6)	−0.3958 (10)	0.4097 (7)	5.0 (2)
P4	0.8186 (1)	0.1491 (2)	0.3606 (2)	*b*
C40	0.7677 (6)	0.2611 (10)	0.4261 (7)	4.9 (2)
C41	0.9249 (5)	0.2746 (8)	0.3226 (6)	3.3 (2)
C42	0.9704 (5)	0.2214 (9)	0.2379 (7)	4.3 (2)
C43	1.0545 (6)	0.3163 (11)	0.2067 (8)	5.7 (2)
C44	1.0862 (7)	0.4587 (12)	0.2614 (9)	6.4 (3)
C45	1.0432 (7)	0.5121 (12)	0.3426 (9)	6.7 (3)
C46	0.9599 (6)	0.4191 (10)	0.3772 (7)	5.3 (2)
C47	0.8287 (5)	0.1219 (8)	0.4658 (6)	3.2 (2)
C48	0.8901 (6)	0.0951 (10)	0.4520 (7)	5.0 (2)
C49	0.8960 (7)	0.0618 (12)	0.5302 (9)	6.7 (3)
C50	0.8393 (7)	0.0645 (12)	0.6180 (9)	7.0 (3)
C51	0.7809 (7)	0.0900 (12)	0.6328 (9)	6.6 (3)
C52	0.7717 (6)	0.1205 (10)	0.5547 (7)	5.2 (2)

B. Anisotropic Thermal Parameters

	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
Cu1	0.00299 (4)	0.0069 (1)	0.00464 (6)	0.0039 (1)	−0.00143 (8)	0.0035 (1)
Cu2	0.00293 (4)	0.0074 (1)	0.00444 (6)	0.0036 (1)	−0.00103 (8)	0.0035 (1)
I1	0.00368 (3)	0.00980 (7)	0.00446 (4)	0.00831 (7)	−0.00034 (4)	0.00406 (8)
I2	0.00327 (2)	0.01330 (9)	0.00505 (4)	0.00879 (8)	0.00022 (5)	0.00560 (9)
P1	0.00292 (8)	0.0073 (3)	0.0045 (1)	0.0040 (3)	−0.0019 (2)	0.0028 (3)
P2	0.00270 (8)	0.0067 (2)	0.0045 (1)	0.0040 (2)	−0.0012 (2)	0.0036 (3)
P3	0.00259 (8)	−0.0074 (3)	0.0045 (1)	0.0034 (2)	−0.0008 (2)	0.0043 (3)

Table III (*Continued*)

B. Anisotropic Thermal Parameters (*Continued*)

	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
P4	0.00282 (9)	0.0071 (2)	0.0044 (1)	0.0045 (3)	−0.0012 (2)	0.0022 (3)
S	0.0054 (3)	0.0317 (12)	0.0196 (7)	0.0040 (9)	−0.0055 (7)	0.0100 (15)
O1	0.013 (1)	0.050 (4)	0.030 (3)	0.024 (4)	0.003 (3)	−0.013 (5)
O2	0.0073 (7)	0.035 (3)	0.022 (2)	0.010 (2)	−0.007 (2)	0.006 (4)

[a] Throughout this paper, standard deviations for the least significant digits are given in parentheses. [b] Refined anisotropically. The anisotropic thermal parameters are defined by the expression $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for $Cu_2I_2(PPh_2Me)_4 \cdot SO_2$[a, b]

Cu1		Cu2	
Cu1-P1	2.250 (2)	Cu2-P3	2.274 (2)
Cu1-P2	2.249 (2)	Cu2-P4	2.253 (2)
Cu1-I1	2.724 (1)	Cu2-I1	2.650 (1)
Cu1-I2	2.714 (1)	Cu2-I2	2.848 (1)
Cu1-Cu2	3.576 (2)	I2-S	3.407 (5)
I1-I2	4.109 (1)		
Cu1-I1-Cu2	83.40 (5)	Cu1-I2-Cu2	79.99 (5)
I2-S-O1	114.5 (8)	I2-S-O2	98.1 (6)
I1-Cu1-I2	98.16 (3)	I1-Cu2-I2	96.95 (3)
I1-Cu1-P1	100.29 (6)	I1-Cu2-P3	104.72 (6)
I1-Cu1-P2	109.80 (7)	I1-Cu2-P4	119.76 (7)
I2-Cu1-P1	110.33 (6)	I2-Cu2-P3	105.27 (6)
I2-Cu1-P2	106.34 (6)	I2-Cu2-P4	103.30 (6)
P1-Cu1-P2	127.89 (9)	P3-Cu2-P4	122.85 (9)
Phosphine 1		Phosphine 3	
P1-C1	1.861 (9)	P3-C27	1.827 (9)
P1-C2	1.817 (8)	P3-C28	1.831 (8)
P1-C8	1.837 (8)	P3-C34	1.823 (7)
Phosphine 2		Phosphine 4	
P2-C14	1.838 (9)	P4-C40	1.868 (10)
P2-C15	1.818 (7)	P4-C41	1.825 (8)
P2-C21	1.835 (8)	P4-C47	1.835 (8)
Cu1-P2-C14	115.1 (3)	Cu2-P4-C40	111.4 (3)
Cu1-P2-C15	114.5 (3)	Cu2-P4-C41	121.1 (3)
Cu1-P2-C21	114.4 (3)	Cu2-P4-C47	114.3 (3)

[a] C-C distances and C-C-C angles were in the ranges 1.29–1.46 Å (average 1.395 Å) and 116.8–124.4° (average 120.0°), respectively. [b] The SO_2 group was refined as a rigid body of C_{2v} symmetry with geometrical parameters S-O = 1.445 Å and O-S-O = 114.0°.

complex $[Cu(SPMe)_3]ClO_4$[33] failed to form a stable adduct with SO_2 in chloroform solution even at −63 °C.

It is of interest to note that the species $[CuI(PPh_3)]_4$, which is known to possess the step-type tetrameric solid-state geometry,[2a] forms a bis-SO_2 adduct. In this case it is possible that SO_2 attaches to each of the two μ_2-iodides rather than the two μ_3-iodides. The monomeric complex $CuI(PPh_2Me)_3$[5] gave a very weak 1:1 SO_2 adduct, perhaps as a result of the presence of three bulky phosphine ligands.

Infrared and Electronic Spectra. Spectral results for the SO_2 adducts are given in Table VII. The SO_2 symmetric and asymmetric stretching frequencies fall in the ranges 1128–1145 and 1312–1332 cm^{-1}, respectively, and are similar to those reported for $Pt(CH_3)(PPh_3)_2I \cdot SO_2$.[21] The S–O bending vibration occurs in the 516–523-cm^{-1} range. Strong UV absorptions are located near 380 nm for CH_3CN solutions, which also compare very well with values previously found for $Pt(CH_3)(PPh_3)_2I \cdot SO_2$ and $[(C_2H_5)_4N]I \cdot SO_2$ solutions in acetonitrile (378 nm, $\epsilon \sim 15\,000$). Chloroform solutions gave maxima at higher energy (~20-nm shift for the $PBzl_3$ complex), with much smaller molar extinction coefficients.

SO_2 Dissociation Pressures and Thermogravimetric Analyses. As can be seen clearly from SO_2 dissociation pressure data given in Table VIII, $Cu_2I_2(PPh_2Me)_4 \cdot SO_2$ is the most stable adduct studied tensimetrically. However, $[CuI(PCy_3)]_4 \cdot {}^1/_2SO_2 \cdot CHCl_3$, which was not studied because of the presence of $CHCl_3$, is even more stable since it does not lose SO_2 rapidly until heated to 190 °C. Although the data are quite fragmentary and the adduct stoichiometries are dissimilar, it appears that electronic effects of the phosphine ligands influence adduct stabilities. If one considers only the oligomeric complexes (i.e. excluding the $CuI(PPh_2Me)_3 \cdot SO_2$ adduct), the order of increasing stability parallels phosphine basicity: $PPh_3 < PBzl_3 \sim PPh_2Me < PCy_3$. This is reasonable since the SO_2 is acting as a Lewis acid, and increased electron density donation from the phosphine to copper should increase the basicity of the iodide, thus increasing the interaction strength with SO_2.

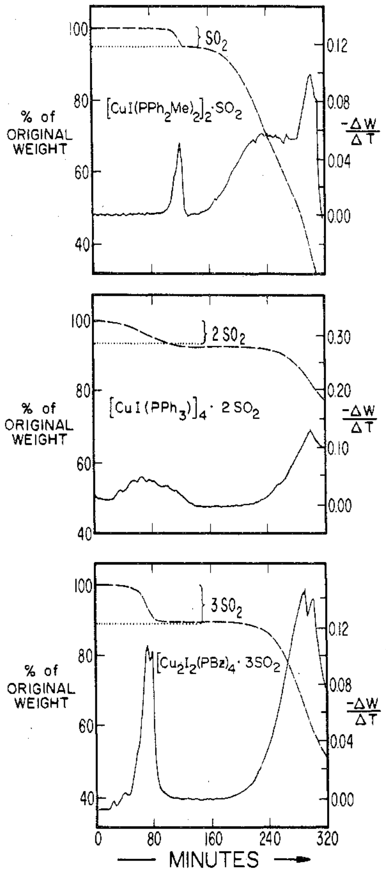

Figure 5. Thermogravimetric data for $Cu_2I_2(PPh_2Me)_4 \cdot SO_2$, $[CuI(PPh_3)]_4 \cdot 2SO_2$, and $Cu_2I_2(PBzl_3)_4 \cdot 3SO_2$. The dashed and solid curves represent respectively percent of original sample weight and rate of loss of volatiles as a function of time. Heating rate = 1 °C/min.

Thermogravimetric analyses of the adducts were performed in order to determine if the SO_2 dissociated in a stepwise fashion for adducts containing more than one SO_2 per oligomeric unit. However, as can be seen from Figure 5 no such behavior was observed. The curves also indicate that loss of phosphine occurs for the SO_2-free $Cu_mI_m(PR_3)_n$ residues, commencing near 150 °C for $Cu_2I_2(PPh_2Me)_4$, 200 °C for $Cu_2I_2(PBzl_3)_4$, and 250 °C for $[CuI(PPh_3)]_4$. For the PPh_2Me complex, the residue remaining at 300 °C corresponded closely in weight to CuI, but complete phosphine removal did not

Table V. Final Least-Squares Parameters for $Cu_2I_2(PPh_3)_3$[a]

A. Positional and Isotropic Thermal Parameters

	x	*y*	*z*	*B*, Å^2
Cu1	0.3272 (1)	0.2370 (2)	0.1611 (1)	*b*
Cu2	0.1369 (1)	0.1335 (1)	0.0857 (1)	*b*
I1	0.12080 (6)	0.25046 (8)	0.19516 (7)	*b*
I2	0.35564 (7)	0.14240 (8)	0.02493 (9)	*b*
P1	0.1438 (3)	0.0568 (2)	0.2404 (3)	*b*
C1	0.428 (1)	0.3469 (6)	0.406 (1)	4.4 (3)
C2	0.409 (1)	0.3014 (7)	0.495 (1)	5.7 (3)
C3	0.403 (1)	0.3196 (9)	0.622 (2)	7.3 (4)
C4	0.413 (2)	0.3833 (9)	0.646 (2)	7.8 (4)
C5	0.433 (2)	0.4266 (9)	0.568 (2)	7.6 (4)
C6	0.441 (1)	0.4122 (8)	0.438 (2)	6.3 (3)
C7	0.607 (1)	0.3024 (6)	0.297 (1)	4.0 (2)
C8	0.684 (1)	0.3212 (7)	0.415 (1)	5.2 (3)
C9	0.806 (1)	0.3098 (7)	0.445 (1)	5.7 (3)
C10	0.847 (1)	0.2810 (6)	0.349 (1)	4.8 (3)
C11	0.777 (1)	0.2636 (7)	0.230 (1)	5.4 (3)
C12	0.653 (1)	0.2735 (7)	0.204 (1)	5.3 (3)
C13	0.430 (1)	0.3868 (6)	0.144 (1)	4.9 (3)
C14	0.524 (1)	0.4168 (8)	0.112 (2)	7.0 (4)
C15	0.503 (2)	0.4686 (9)	0.023 (2)	8.4 (5)
C16	0.389 (2)	0.4883 (9)	−0.029 (2)	8.4 (5)
C17	0.296 (2)	0.456 (1)	−0.005 (2)	8.5 (5)
C18	0.318 (2)	0.4061 (9)	0.084 (2)	7.8 (4)
P2	0.4497 (3)	0.3162 (2)	0.2523 (3)	*b*
C19	0.163 (1)	−0.0251 (6)	0.187 (1)	3.9 (2)
C20	0.075 (1)	−0.0498 (7)	0.084 (1)	5.1 (3)
C21	0.084 (1)	−0.1128 (7)	0.037 (1)	5.8 (3)
C22	0.184 (1)	−0.1489 (8)	0.093 (1)	6.0 (3)
C23	0.268 (1)	−0.1247 (9)	0.197 (2)	7.1 (4)
C24	0.259 (1)	−0.0630 (7)	0.242 (1)	6.0 (3)
C25	0.259 (1)	0.0644 (6)	0.396 (1)	3.9 (2)
C26	0.361 (2)	0.0936 (9)	0.392 (2)	7.8 (4)
C27	0.453 (2)	0.0993 (9)	0.507 (2)	8.1 (4)
C28	0.435 (1)	0.0773 (8)	0.624 (2)	7.1 (4)
C29	0.343 (2)	0.0462 (9)	0.627 (2)	7.1 (4)
C30	0.248 (1)	0.0403 (7)	0.511 (1)	5.6 (3)
C31	0.011 (1)	0.0494 (6)	0.296 (1)	4.0 (2)
C32	−0.051 (1)	0.1040 (6)	0.310 (1)	4.6 (3)
C33	−0.151 (1)	0.1012 (7)	0.356 (1)	5.6 (3)
C34	−0.191 (1)	0.0424 (8)	0.384 (1)	6.4 (3)
C35	−0.132 (1)	−0.0119 (8)	0.372 (2)	6.3 (4)
C36	−0.032 (1)	−0.0097 (7)	0.325 (1)	5.1 (3)
P3	0.0128 (2)	0.1331 (2)	−0.1207 (3)	*b*
C37	−0.1408 (9)	0.1571 (6)	−0.139 (1)	3.6 (2)
C38	−0.209 (1)	0.1873 (6)	−0.253 (1)	4.6 (3)
C39	−0.327 (1)	0.2040 (7)	−0.263 (1)	5.7 (3)
C40	−0.374 (1)	0.1878 (7)	−0.157 (1)	5.5 (3)
C41	−0.308 (1)	0.1580 (7)	−0.050 (1)	4.9 (3)
C42	−0.189 (1)	0.1410 (7)	−0.034 (1)	4.2 (2)
C43	0.0582 (9)	0.1890 (6)	−0.232 (1)	3.5 (2)
C44	0.068 (1)	0.2525 (8)	−0.194 (1)	4.9 (2)
C45	0.105 (1)	0.2991 (8)	−0.277 (2)	6.2 (3)
C46	0.130 (1)	0.2769 (7)	−0.394 (1)	5.3 (3)
C47	0.122 (1)	0.2149 (8)	−0.427 (1)	5.8 (3)
C48	0.083 (1)	0.1692 (7)	−0.348 (1)	5.6 (3)
C49	0.000 (1)	0.0539 (6)	−0.200 (1)	3.8 (2)
C50	0.100 (1)	0.0220 (6)	−0.206 (1)	4.5 (2)
C51	0.097 (1)	−0.0402 (7)	−0.256 (1)	5.0 (3)
C52	−0.008 (1)	−0.0693 (7)	−0.303 (1)	5.2 (3)
C53	−0.110 (1)	−0.0403 (7)	−0.294 (1)	5.4 (3)
C54	−0.107 (1)	0.0216 (6)	−0.246 (1)	4.5 (2)

B. Anisotropic Thermal Parameters

	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
Cu1	0.0080 (1)	0.00230 (5)	0.0126 (2)	−0.0004 (1)	0.0057 (3)	−0.0011 (1)
Cu2	0.0079 (1)	0.00188 (4)	0.0089 (2)	−0.0007 (1)	0.0039 (2)	0.0007 (1)
I1	0.00735 (6)	0.00189 (2)	0.01081 (8)	−0.00009 (7)	0.0075 (1)	−0.00054 (8)
I2	0.00818 (8)	0.00295 (3)	0.0196 (1)	−0.00147 (8)	0.0131 (2)	−0.0053 (1)
P1	0.0072 (3)	0.00157 (7)	0.0078 (3)	0.0008 (2)	0.0016 (5)	−0.0005 (2)
P2	0.0056 (2)	0.00222 (8)	0.0128 (4)	0.0002 (2)	0.0037 (5)	−0.0016 (3)
P3	0.0073 (2)	0.00176 (7)	0.0073 (3)	−0.0003 (2)	0.0044 (4)	0.0002 (1)

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

Table VI. Selected Interatomic Distances (Å) and Angles (deg) for $Cu_2I_2(PPh_3)_3$[a]

Cu1		Cu2			
Cu1-P1	2.219 (3)	Cu2-P2	2.259 (3)	Cu1-I1-Cu2	70.43 (4)
		Cu2-P3	2.267 (3)	Cu1-I2-Cu2	69.43 (5)
Cu1-I1	2.500 (2)	Cu2-I1	2.707 (1)	CuI-Cu2	3.041 (3)
Cu1-I2	2.563 (1)	Cu2-I2	2.819 (1)	I1-I2	4.302 (1)
Phosphine 1		Phosphine 2		Phosphine 3	
P1-C1	1.82 (1)	P2-C19	1.82 (1)	P3-C37	1.83 (1)
P1-C7	1.87 (1)	P2-C25	1.83 (1)	P3-C43	1.82 (1)
P1-C13	1.83 (1)	P2-C31	1.82 (1)	P3-C49	1.82 (1)
I1-Cu1-P1	112.81 (9)	I1-Cu2-P2	108.23 (9)	I2-Cu2-P3	99.94 (8)
I2-Cu1-P1	130.75 (9)	I1-Cu2-P3	108.07 (9)	I1-Cu2-I2	102.24 (5)
I1-Cu1-I2	116.37 (6)	I2-Cu2-P2	110.66 (9)	P2-Cu2-P3	125.24 (11)
Cu1-P1-C1	114.3 (4)	Cu2-P2-C19	114.4 (4)	Cu2-P3-C37	117.5 (3)
Cu1-P1-C7	119.7 (4)	Cu2-P2-C25	117.3 (4)	Cu2-P3-C43	112.8 (4)
Cu1-P1-C13	111.1 (4)	Cu2-P2-C31	115.3 (4)	Cu2-P3-C49	113.1 (4)
C1-P1-C7	102.0 (5)	C19-P2-C25	103.5 (5)	C37-P3-C43	102.3 (5)
C1-P1-C13	104.6 (6)	C19-P2-C31	102.4 (5)	C37-P3-C49	103.7 (5)
C7-P1-C13	103.6 (6)	C25-P2-C31	102.0 (5)	C43-P3-C49	106.3 (5)

[a] The average C-C distances and C-C-C angles within individual phenyl rings were 1.37-1.39 Å and 119.6-121.3°, respectively. The average P-C-C angles were in the range 117.8-121.1° for individual phenyl groups.

Table VII. Characterization Data for $Cu_mI_m(PR_3)_n \cdot xSO_2$ Complexes

Compd	Color	SO_2:$Cu_mI_m(PR_3)_n$[a]	Mp,[b] °C	Elemental analyses,[c] %	$\nu(SO_2)$ cm^{-1}	UV max,[d] nm
$Cu_2I_2(PPh_2Me)_4 \cdot SO_2$	Red-orange	1.02	147-150	C, 50.4 (50.1); H, 4.3 (4.2); P, 10.0 (10.0); S, 2.6 (2.6); Cu, 10.3 (10.2); I, 20.7 (20.4)	1312, 1128, 518	374 (1360) 380 (11 000)
$Cu_2I_2(PBzl_3)_4 \cdot 3SO_2$	Yellow	2.92	166-168	C, 64.9 (63.1); H, 5.4 (5.3)[e]	1315, 1138, 516	361 (2400) 380 (11 000)
$[CuI(PPh_3)]_4 \cdot 2SO_2$	Pale yellow	1.98	264-268	C, 44.9 (44.6); H, 3.3 (3.1)	1332, 1145	
$[CuI(PCy_3)]_4 \cdot {}^1/_2SO_2 \cdot CHCl_3$	Yellow	0.52	218-223	C, 46.2 (43.1); H, 7.0 (6.6); P, 6.8 (6.1); S, 1.0 (0.8); Cu, 11.6 (12.5); I, 22.9 (24.9); Cl, 4.6 (5.2)	1326, 1135	
$Cu_2I_2(PPh_3)_3 \cdot 2SO_2$	Yellow	1.98				
$CuI(PPh_2Me)_3 \cdot SO_2$	Yellow	*f*	184-189			
$Pt(PPh_3)_2(CH_3)I \cdot SO_2$	Yellow				1322, 1138[g]	378 (15 000)[g]
$[PPh_3NPPh_3]I \cdot SO_2$	Yellow-orange		239-242		1277, 1093, 523[h]	

[a] Molar ratio determined experimentally by removing SO_2 from weighed adduct. Moles of SO_2 determined by PVT measurements on a calibrated vacuum line. [b] All adducts lose SO_2 before melting. Melting points were determined in open capillaries using heating rates of ca. 10° min^{-1}. [c] Calculated values in parentheses. [d] For $(1-5) \times 10^{-3}$ M solutions of adduct in SO_2-saturated $CHCl_3$ and in SO_2-saturated CH_3CN, respectively. Molar extinction coefficients are in parentheses. [e] Analysis was performed on $CuI(PBzl_3)_2$ residue obtained by complete removal of SO_2 from the adduct. [f] SO_2 labile at −63 °C. [g] Reference 21. UV spectrum obtained in acetonitrile solution. [h] Reference 31.

Table VIII. SO_2 Dissociation Pressures of the Complexes[a]

Compd	*P* (Torr) at various temperatures				
	0 °C	21 °C	50 °C	60 °C	72 °C
$[CuI(PCy_3)]_4 \cdot {}^1/_2SO_2 \cdot CHCl_3$		<1.0[b]			
$Cu_2I_2(PPh_2Me)_4 \cdot SO_2$		2.0	9.4		19.2
$Cu_2I_2(PBzl_3)_4 \cdot 3SO_2$	5.6	18.0		190	
$[CuI(PPh_3)]_4 \cdot 2SO_2$		60		130	
$Cu_2I_2(PPh_3)_3 \cdot 2SO_2$	25				
$CuI(PPh_2Me)_3 \cdot SO_2$		304			

[a] Measured by placing solid adduct in an evacuated grease-free tensimeter[23] and allowing pressure to equilibrate. For adducts isolated from $CHCl_3$ solution, true equilibrium often was not attained, possibly because of phase-mixture problems. In these cases, the dissociation pressure was taken to be the pressure recorded after a 3-day period. [b] Estimate based on long-term stability of the complex to atmospheric exposure at ambient temperature.

occur for the others over the specified time interval.

Conclusions

The synthetic, spectroscopic, and structural results reported herein indicate that organophosphinecopper(I) iodides interact with SO_2 to form weak adducts with SO_2 attached to the iodide ligand. No evidence is found for direct Cu–SO_2 binding. Stoichiometries of the resulting adducts vary widely and are a complicated function of the steric and electronic nature of the phosphine. Adduct stabilities appear to increase with phosphine basicity.

Registry No. $Cu_2I_2(PPh_3)_3$, 60819-05-8; $Cu_2I_2(PPh_3)_3 \cdot 2SO_2$, 62743-85-5; $Cu_2I_2(PPh_2Me)_4 \cdot SO_2$, 62743-84-4; $Cu_2I_2(PBzl_3)_4 \cdot 3SO_2$, 62743-83-3; $[CuI(PPh_3)]_4 \cdot 2SO_2$, 62743-81-1; $[CuI(PCy_3)]_4 \cdot {}^1/_2SO_2$, 62743-80-0; $[CuI(PCy_3)]_4$, 62743-79-7; $CuI(PPh_2Me)_3$, 36386-12-6; $[CuI(PPh_2Me)_2]_2$, 62743-78-6; $CuI(PPh_2Me)$, 62743-77-5; $CuI(PPh_2Me)_3 \cdot SO_2$, 62743-76-4; $Pt(PPh_3)_2(CH_3)I \cdot SO_2$, 36182-31-7; $[PPh_3NPPh_3]I \cdot SO_2$, 62726-55-0.

Supplementary Material Available: Listings of structure factor amplitudes (103 pages). Ordering information is given on any current masthead page.

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Aryldiazenido, Aryldiazene, and Arylhydrazido Complexes. Reaction of Diazonium Ions with Carbonylhydridotris(triphenylphosphine)iridium(I) and the X-Ray Structures of Iridium Complexes Containing Singly and Doubly Protonated Orthometalated Aryldiazenido Ligands

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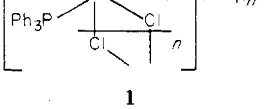
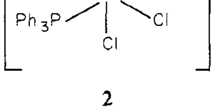
Reaction of substituted benzenediazonium tetrafluoroborates with $IrH(CO)\{P(C_6H_5)_3\}_3$ gives orthometalated arylhydrazido complexes, $[Ir(NHNHC_6H_3R)(CO)(PPh_3)_2]BF_4$, which convert readily to the analogous diazenes, $[Ir(NHNC_6H_3R)(X)(CO)(PPh_3)_2]BF_4$ with X = F or BF_4. Each type has been structurally characterized by x-ray crystallography. $[Ir(NHNHC_6H_3\text{-}2\text{-}NO_2)(CO)(PPh_3)_2]BF_4$ crystallizes in the monoclinic space group $P2_1/c$ with a = 10.921 (3) Å, b = 20.125 (7) Å, c = 18.061 (5) Å, and β = 97.78 (2)°, Z = 4; 2069 reflections having $I > 2.3\sigma(I)$ were used for structure solution and refinement to R = 0.042. Two weak N—H···F hydrogen bonds connect the BF_4^- anions to the iridium complex, which has an irregular square-based pyramidal geometry with phosphines on the axis and trans to the Ir–aryl bond. The bond lengths N(1)–N(2) = 1.388 (13) Å and Ir–N(1) = 1.912 (10) Å. The solvated complex $[Ir(NHNC_6H_3\text{-}2\text{-}CF_3)(F)(CO)(PPh_3)_2]BF_4{\cdot}2CH_3OH$ crystallizes in the orthorhombic space group $Pnma$ with a = 14.61 (2), b = 15.80 (1), and c = 20.16 (2) Å, Z = 4; 624 reflections for which $I > 2.3\sigma(I)$ allowed solution of the structure and refinement to R = 0.085. The pseudooctahedral iridium complex contains trans phosphines related by a crystallographic mirror plane, and a fluorine ligand trans to the Ir–aryl bond of the aryldiazene chelate.

Introduction

The coordination chemistry of the diazonium ion and the chemistry of the aryldiazenido (MNNR), aryldiazene (MNHNR), and related complexes thereby obtained are currently the subject of considerable interest and activity.[1] We have previously established that reactions of diazonium ions with $IrCl(CO)(PPh_3)_2$ are dependent upon various factors including the solvent and temperature. Products include[2] aryldiazenido complexes of iridium(III) from the oxidative addition of RN_2BF_4 or RN_2Cl to give **1** or **2** as well as **3**, which is an isomer of **1**. Formally the latter can be derived from **1** by cyclometalation of the aryldiazenido group and protonation of the nitrogen atom N(1), but in fact the reaction mechanism is much more complicated than this.[3]



1



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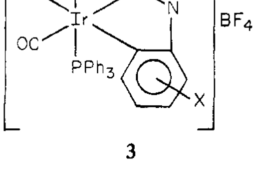

3

We now have obtained results on the reaction of the hydrido complex $IrH(CO)(PPh_3)_3$ with diazonium ions. Our interest here, apart from the obvious extension of the previous work, was to test the possibility that a hydrido(aryldiazenido)iridium(III) or aryldiazeneiridium(I) complex intermediate in the formation of the orthometalated complex **3** could be isolated. If coordination alone occurred, a hydrido(aryldiazenido) complex would result, and such complexes are scarce. If, as frequently happens for hydrido complexes, including some iridium(III) ones,[1] migration of the hydride ligand followed, the diazonium ion will have "inserted" into the Ir–H bond, to yield new aryldiazene (**4**) and aryldiazenido (**5**) complexes (eq 1).

$$IrH(CO)(PPh_3)_3 \xrightarrow[\text{insertion}]{RN_2^+} \underset{\mathbf{4}}{[Ir(NHNR)(CO)(PPh_3)_2]^+} \xrightarrow{-H^+} \underset{\mathbf{5}}{[Ir(NNR)(CO)(PPh_3)_2]} \qquad (1)$$

In actuality, our results indicate that, while such an aryldiazene may be an intermediate, the aryl group of the diazonium ion is orthometalated in the products isolated, resulting in complexes of the hitherto unobserved type **6**, which