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**Supplementary Material Available:** A table containing the titration data for these cryptates (2 pages). Ordering information is given on any current masthead page.

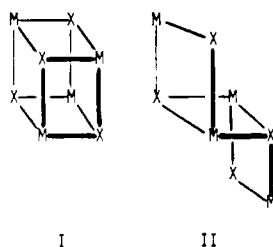
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### Molecules with an $M_4X_4$ Core. 12.<sup>1</sup> Disruption of Tetrameric (Triphenylarsine)copper(I) Iodide in Acetonitrile Solution. Crystal Structure of $[(AsPh_3)(MeCN)CuI]_2$

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The complex  $[(PPh_3)AgI]_4$  may be isolated as the "cubane-like" isomer (I) from chloroform/ether or as a steplike



or "chair" structure (II) from methylene chloride/ether.<sup>2</sup> To the best of our knowledge, this is the only reported case in which each of the skeletal forms has been confirmed structurally for a given  $L_4M_4X_4$  species.

Far-infrared spectroscopic studies of  $(Ph_3As)_4Cu_4X_4$  ( $X = Br, I$ ) indicated that the samples studied had a *chairlike* configuration.<sup>3</sup> Unfortunately, the solvent from which they were crystallized was not explicitly stated. We later found<sup>1</sup> that crystallization of  $[(AsPh_3)CuI]_4$  from benzene led to the formation of a *cubanelike*  $Cu_4I_4$  core in crystals of stoichiometry  $[(AsPh_3)CuI]_4 \cdot C_6H_6$ . It seems probable, therefore, that  $[(AsPh_3)CuI]_4$  also exists in both the cubanelike and steplike form.

In the course of recrystallizing  $[(AsPh_3)CuI]_4$  from various solvents we have found that acetonitrile cleaves the tetrameric unit to form dimeric  $[(AsPh_3)(MeCN)CuI]_2$ , which has been characterized via a complete single-crystal X-ray diffraction study.

#### Experimental Section

$[(AsPh_3)(MeCN)CuI]_2$  can be prepared by dissolving  $[(AsPh_3)CuI]_4 \cdot C_6H_6$  in hot acetonitrile and slowly evaporating the resulting solution. A more efficient synthesis is as follows.

**Table I.** Experimental Data for the X-ray Diffraction Study of  $[(AsPh_3)(MeCN)CuI]_2$

A. Crystal Parameters at 24 °C <sup>a</sup>	
cryst system: triclinic	$\beta = 101.78 (2)^\circ$
space group: $P\bar{1}$	$\gamma = 98.52 (1)^\circ$
$a = 9.437 (2) \text{ \AA}$	$V = 1001.2 (3) \text{ \AA}^3$
$b = 9.500 (2) \text{ \AA}$	$Z = 1$ (dimeric unit)
$c = 12.136 (3) \text{ \AA}$	$fw = 1075.5$
$\alpha = 105.69 (2)^\circ$	$\rho_{\text{calcd}} = 1.78 \text{ g cm}^{-3}$

B. Collection of Intensity Data	
diffractometer: Syntex P2 <sub>1</sub>	
radiation: Mo $K\alpha$ ( $\lambda$ 0.710 730 $\text{ \AA}$ )	
monochromator: highly ordered graphite, equatorial geometry	
rflectns measd: $\pm h, \pm k, \pm l$	
scan type: $\theta(\text{cryst})-2\theta(\text{counter})$	
$2\theta$ range: 3–50°	
scan speed: 2.0°/min	
scan width: $[2.0 + \Delta(\alpha_2 - \alpha_1)]^\circ$	
rflectns collected: 3888 total data, 3553 independent data	
stds: 3 collected every 97 data; no significant variations	
abs coeff: $\mu = 44.2 \text{ cm}^{-1}$	

<sup>a</sup> Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo  $K\alpha$  components of the 24 reflections of the forms  $\{172\}$ ,  $\{117\}$ ,  $\{721\}$ ,  $\{161\}$ ,  $\{218\}$ ,  $\{611\}$ ,  $\{272\}$ ,  $\{237\}$ ,  $\{621\}$ ,  $\{361\}$ ,  $\{317\}$ , and  $\{522\}$ .

**Table II.** Positional Parameters, with Esd's, for  $[(AsPh_3)(MeCN)CuI]_2$ <sup>a</sup>

atom	x	y	z
Cu	0.00062 (5)	0.12927 (5)	0.08782 (4)
I	0.11131 (3)	0.13664 (3)	-0.09850 (2)
As	0.20619 (3)	0.25969 (4)	0.25285 (3)
N	-0.16294 (34)	0.24402 (36)	0.07422 (27)
C(1)	-0.25022 (45)	0.31144 (47)	0.06255 (34)
C(2)	-0.36568 (59)	0.39909 (65)	0.04688 (48)
C(11)	0.28303 (36)	0.46144 (36)	0.25390 (27)
C(12)	0.43140 (37)	0.53247 (39)	0.29434 (31)
C(13)	0.47717 (44)	0.67791 (45)	0.29691 (36)
C(14)	0.37278 (53)	0.75628 (45)	0.26084 (40)
C(15)	0.22660 (50)	0.68710 (49)	0.21933 (44)
C(16)	0.18125 (41)	0.53980 (44)	0.21440 (36)
C(21)	0.38773 (35)	0.18464 (34)	0.27490 (29)
C(22)	0.47661 (43)	0.20298 (44)	0.38513 (32)
C(23)	0.60947 (45)	0.15528 (47)	0.39473 (37)
C(24)	0.65303 (43)	0.08917 (46)	0.29535 (41)
C(25)	0.56428 (45)	0.06984 (47)	0.18694 (37)
C(26)	0.43127 (41)	0.11569 (43)	0.17505 (31)
C(31)	0.17190 (35)	0.30020 (38)	0.41017 (28)
C(32)	0.11839 (59)	0.18034 (50)	0.44432 (39)
C(33)	0.08910 (68)	0.20333 (61)	0.55432 (43)
C(34)	0.11078 (48)	0.34543 (60)	0.62977 (36)
C(35)	0.16259 (50)	0.46382 (51)	0.59682 (35)
C(36)	0.19529 (45)	0.44294 (42)	0.48780 (33)
H(12)	0.5026	0.4799	0.3207
H(13)	0.5795	0.7246	0.3231
H(14)	0.4033	0.8579	0.2651
H(15)	0.1555	0.7403	0.1936
H(16)	0.0794	0.4918	0.1836
H(22)	0.4471	0.2480	0.4543
H(23)	0.6709	0.1685	0.4708
H(24)	0.7443	0.0573	0.3024
H(25)	0.5940	0.0240	0.1180
H(26)	0.3696	0.0999	0.0984
H(32)	0.1014	0.0813	0.3921
H(33)	0.0536	0.1198	0.5776
H(34)	0.0895	0.3606	0.7048
H(35)	0.1768	0.5624	0.6488
H(36)	0.2338	0.5270	0.4664

<sup>a</sup>  $B_{\text{iso}} = 6.0 \text{ \AA}^2$  for all hydrogen atoms.

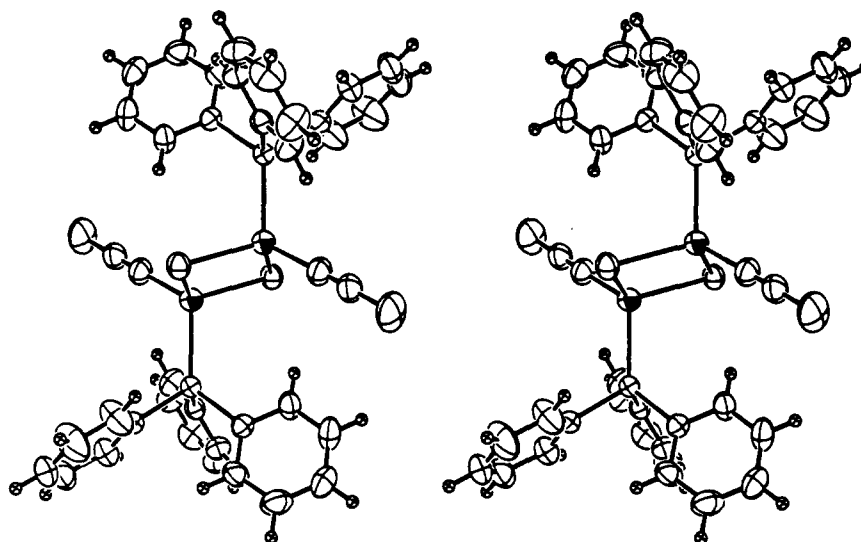
**Synthesis of  $[(AsPh_3)(MeCN)CuI]_2$ .** A solution of copper(I) iodide (0.494 g, 0.0026 mol) and triphenylarsine (0.804 g, 0.0026 mol) in acetonitrile (75 mL) was refluxed under argon for 12 h. The hot solution was filtered. Slow evaporation of solvent from this solution yielded small colorless crystals of  $[(AsPh_3)(MeCN)CuI]_2$ . Crystals

- (1) Part 11: Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 1133–1138.  
 (2) Teo, B.-K.; Calabrese, J. C. *Inorg. Chem.* **1976**, *15*, 2474–2486.  
 (3) Teo, B.-K.; Barnes, D. M. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 681–687.

Table III. Anisotropic Thermal Parameters (in Å<sup>2</sup>)<sup>a</sup> with Esd's

atom	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Cu	3.329 (19)	3.906 (20)	3.416 (19)	0.879 (15)	0.652 (15)	0.766 (15)
I	3.916 (12)	3.965 (12)	3.432 (11)	1.140 (8)	1.343 (8)	1.525 (8)
As	2.796 (14)	2.822 (15)	2.670 (14)	0.643 (11)	0.740 (11)	0.689 (11)
N	3.82 (14)	4.51 (15)	4.42 (15)	1.52 (12)	1.30 (12)	1.46 (12)
C(1)	4.49 (18)	5.06 (20)	3.85 (17)	1.92 (16)	1.20 (14)	1.17 (15)
C(2)	7.16 (29)	9.14 (35)	7.27 (29)	5.73 (27)	2.37 (23)	3.19 (26)
C(11)	3.35 (14)	3.09 (14)	2.81 (13)	0.86 (11)	0.93 (11)	1.05 (11)
C(12)	3.36 (15)	3.64 (16)	3.80 (16)	0.68 (12)	0.52 (12)	1.36 (13)
C(13)	4.19 (18)	4.20 (18)	4.76 (19)	-0.33 (15)	0.58 (15)	1.66 (15)
C(14)	6.63 (25)	3.44 (18)	5.81 (23)	0.40 (17)	1.64 (19)	1.89 (16)
C(15)	5.24 (22)	4.64 (21)	7.44 (27)	1.92 (17)	1.71 (19)	3.34 (19)
C(16)	3.57 (16)	4.40 (18)	5.59 (21)	1.21 (14)	1.26 (15)	2.23 (16)
C(21)	2.90 (13)	2.51 (13)	3.54 (15)	0.80 (10)	0.80 (11)	0.98 (11)
C(22)	4.61 (18)	4.47 (18)	3.36 (16)	2.01 (15)	0.29 (14)	0.24 (14)
C(23)	4.44 (20)	5.15 (22)	5.22 (22)	1.78 (17)	-0.56 (17)	0.72 (17)
C(24)	3.61 (17)	4.76 (20)	6.51 (24)	1.75 (15)	1.63 (17)	1.92 (18)
C(25)	4.86 (20)	5.56 (22)	5.35 (21)	2.68 (17)	2.71 (17)	2.21 (17)
C(26)	4.27 (17)	4.63 (18)	3.63 (16)	1.76 (14)	1.71 (13)	1.66 (14)
C(31)	2.94 (14)	3.59 (15)	2.75 (13)	0.50 (11)	0.71 (11)	0.87 (11)
C(32)	8.85 (31)	4.41 (20)	4.60 (21)	-1.50 (20)	2.88 (20)	0.63 (16)
C(33)	10.00 (36)	7.05 (29)	5.02 (24)	-2.12 (26)	3.64 (24)	1.74 (22)
C(34)	5.18 (22)	8.22 (30)	3.50 (18)	1.12 (20)	2.15 (16)	1.48 (19)
C(35)	5.95 (22)	5.72 (22)	3.70 (18)	2.39 (18)	1.65 (16)	0.75 (16)
C(36)	5.12 (19)	3.97 (17)	3.65 (16)	1.36 (15)	1.57 (14)	1.04 (14)

<sup>a</sup> The anisotropic thermal parameters enter the expression for the calculated structure factor in the form  $\exp[-1/4(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$ .

Figure 1. Stereoscopic view of the [(AsPh<sub>3</sub>)(MeCN)CuI]<sub>2</sub> molecule (ORTEP-II diagram).

are best obtained from the initial reaction mixture; recrystallization from acetonitrile is not so satisfactory for yielding crystals suitable for crystallographic work. [This problem is common throughout phosphine-copper-halide chemistry, where many different stoichiometries of product are possible.<sup>4,5</sup>

**Collection and Processing of the X-ray Diffraction Data.** The crystal selected for the analysis showed no diffraction symmetry other than the Friedel condition; it was assumed to be triclinic. The crystal was mounted on a Syntex P2<sub>1</sub> automated diffractometer. Crystal alignment and determination of the orientation matrix and accurate unit cell parameters were carried out as described previously.<sup>6</sup> All relevant details appear in Table I. Data were corrected from absorption, redundant data were averaged [ $R(I) = 1.72\%$  for 316 pairs of reflections], and the resulting reduced data set was converted to unscattered  $|F_o|$  values following correction for Lorentz and polarization effects.

**Solution and Refinement of the Structure.** All computations were performed with use of the Syntex XTL system as implemented and modified by our research group at SUNYAB. Analytical scattering factors for neutral atoms were used;<sup>7a</sup>  $\Delta f'$  and  $\Delta f''$  terms were included for all nonhydrogen atoms.<sup>7b</sup> The function minimized during least-squares refinement was  $\sum w(|F_o| - |F_c|)^2$ , where the weights are derived from the stochastic  $\sigma(|F_o|)$  modified by an "ignorance factor" of 0.015.

Data were placed on an approximate absolute scale by means of a Wilson plot ( $B = 3.3 \text{ \AA}^2$ ). Intensity statistics (distribution of  $|E|$  values, etc.) favored the centric space group  $P\bar{1}$  over the acentric space group  $P1$ .

The heavy atoms (I, As, Cu) were all located from a Patterson map, and the remaining nonhydrogen atoms were located from a difference-Fourier map. Full-matrix least-squares refinement of positional and anisotropic thermal parameters for all nonhydrogen atoms (with phenyl hydrogens in calculated<sup>8</sup> positions and with a correction for

(4) Part 10: Churchill, M. R.; Rotella, F. J. *Inorg. Chem.* 1979, 18, 166-171.

(5) Gill, J. T.; Mayerle, J. J.; Welcker, P. S.; Lewis, D. F.; Ucko, D. A.; Barton, D. J.; Stowens, D.; Lippard, S. J. *Inorg. Chem.* 1976, 15, 1155-1168.

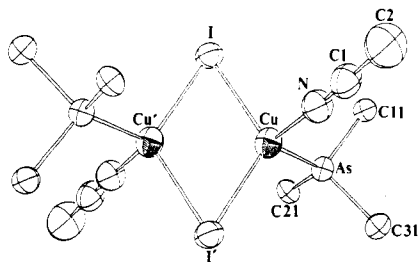
(6) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* 1977, 16, 265-271.

(7) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) pp 99-101; (b) pp 149-150.

(8)  $d(\text{C-H}) = 0.95 \text{ \AA}$ . See: Churchill, M. R. *Inorg. Chem.* 1973, 12, 1213-1214.

**Table IV.** Interatomic Distances (in Å) with Esd's for [(AsPh<sub>3</sub>)<sub>2</sub>(MeCN)CuI]<sub>2</sub>

A. Atoms-Symmetry Related Atoms Distances			
Cu...Cu'	2.779 (1)	I...I'	4.545 (1)
B. Bonding Distances from Copper			
Cu-I	2.690 (1)	Cu-As	2.381 (1)
Cu-I'	2.637 (1)	Cu-N	2.022 (3)
C. Arsenic-Carbon Distances			
As-C(11)	1.942 (4)	As-C(31)	1.947 (3)
As-C(21)	1.947 (3)		
D. Distances within the Acetonitrile Group			
N-C(1)	1.125 (6)	C(1)-C(2)	1.479 (7)
E. Carbon-Carbon Distances			
C(11)-C(12)	1.384 (5)	C(21)-C(22)	1.377 (5)
C(12)-C(13)	1.375 (6)	C(22)-C(23)	1.388 (6)
C(13)-C(14)	1.391 (6)	C(23)-C(24)	1.374 (6)
C(14)-C(15)	1.363 (7)	C(24)-C(25)	1.357 (6)
C(15)-C(16)	1.383 (7)	C(25)-C(26)	1.381 (6)
C(16)-C(11)	1.387 (5)	C(26)-C(21)	1.386 (5)
C(31)-C(32)	1.376 (6)	C(34)-C(35)	1.351 (7)
C(32)-C(33)	1.385 (7)	C(35)-C(36)	1.389 (6)
C(33)-C(34)	1.369 (8)	C(36)-C(31)	1.382 (5)

**Figure 2.** Labeling of atoms in the core of the molecule. Carbon atoms of the phenyl groups are labeled cyclicly, starting with C(11), C(21), and C(31), respectively.

secondary extinction<sup>9</sup>) led to convergence [ $(\Delta/\sigma)_{\max} < 0.1$ ] with  $R_F = 3.2\%$ ,  $R_{wF} = 3.1\%$ , and GOF = 1.34 for all 3553 reflections (none rejected). Discrepancy indices for those 3187 reflections with  $|F_o| > 3\sigma(|F_o|)$  are  $R_F = 2.5\%$ ,  $R_{wF} = 3.0\%$ , and GOF = 1.37.

The largest peak on a final difference-Fourier map was  $0.4 \text{ e } \text{Å}^{-3}$  in height, and there were no unambiguous indications as to the locations of the methyl hydrogens. The analysis is thus complete.

Final positional and thermal parameters are presented in Tables II and III.

### Discussion

The reaction of [(AsPh<sub>3</sub>)<sub>2</sub>CuI]<sub>4</sub> in acetonitrile, or the reaction of equimolar quantities of AsPh<sub>3</sub> and CuI in acetonitrile, leads to the formation of the dimeric species [(AsPh<sub>3</sub>)<sub>2</sub>(MeCN)CuI]<sub>2</sub>, which has precise (crystallographically-imposed) *Ci* symmetry.

Interatomic distances and angles are collected in Tables IV and V; least-squares planes are given in Table VI. A stereoscopic view of the molecule appears as Figure 1, while Figure 2 gives the atomic labeling scheme for the molecular core.

The copper(I) centers are in tetrahedral environments and are connected via two asymmetrically bridging iodide ligands (Cu-I = 2.690 (1) Å, Cu-I' = 2.637 (1) Å); they are, in addition, each bonded to a triphenylarsine (Cu-As = 2.381 (1) Å) and an acetonitrile ligand (Cu-N = 2.022 (3) Å). Bond angles around the copper(I) centers are rather irregular, a particular point of interest being the inequivalence of the angles As-Cu-I = 102.99 (2)° and As-Cu-I' = 111.42 (2)°.

The Cu<sub>2</sub>(μ-I)<sub>2</sub> core planar, with a Cu...Cu' distance of 2.779 (1) Å and an I...I' distance of 4.545 (1) Å. The acute Cu-I-Cu' angle of 62.88 (2)° is not symptomatic of direct copper-copper bonding; rather, it results from repulsion between

**Table V.** Bond Angles (in Deg) for [(AsPh<sub>3</sub>)<sub>2</sub>(MeCN)CuI]<sub>2</sub>

A. Angles about Copper			
I-Cu-I'	117.12 (2)	As-Cu-N	112.51 (10)
As-Cu-I	102.99 (2)	I-Cu-N	104.07 (10)
As-Cu-I'	111.42 (2)	I'-Cu-N	108.56 (10)
As-Cu...Cu'	124.34 (2)	Cu'...Cu-N	122.50 (10)
B. Angle about Iodine			
Cu-I-Cu'	62.88 (2)		
C. Angles about Arsenic			
Cu-As-C(11)	112.62 (10)	C(11)-As-C(21)	100.84 (14)
Cu-As-C(21)	120.55 (10)	C(11)-As-C(31)	100.60 (14)
Cu-As-C(31)	117.63 (10)	C(21)-As-C(31)	101.56 (14)
D. Angles within Acetonitrile Group			
Cu-N-C(1)	176.0 (3)	N-C(1)-C(2)	179.6 (5)
E. Internal Angles of the Phenyl Rings			
C(16)-C(11)-C(12)	118.4 (3)	C(26)-C(21)-C(22)	119.2 (3)
C(11)-C(12)-C(13)	121.0 (4)	C(21)-C(22)-C(23)	119.8 (4)
C(12)-C(13)-C(14)	119.6 (4)	C(22)-C(23)-C(24)	120.7 (4)
C(13)-C(14)-C(15)	119.9 (4)	C(23)-C(24)-C(25)	119.3 (4)
C(14)-C(15)-C(16)	120.3 (4)	C(24)-C(25)-C(26)	121.1 (4)
C(15)-C(16)-C(11)	120.6 (4)	C(25)-C(26)-C(21)	120.0 (4)
C(36)-C(31)-C(32)	118.6 (4)	C(33)-C(34)-C(35)	119.6 (5)
C(31)-C(32)-C(33)	120.3 (5)	C(34)-C(35)-C(36)	120.7 (4)
C(32)-C(33)-C(34)	120.6 (5)	C(35)-C(36)-C(31)	120.2 (4)

**Table VI.** Least-Squares Planes<sup>a</sup> within the [(AsPh<sub>3</sub>)<sub>2</sub>(MeCN)CuI]<sub>2</sub> Molecule

atom	dev, Å	atom	dev, Å
Plane I: $0.3734X - 0.0300Y - 0.9272Z = -2.2296$			
C(11)	-0.011 (3)	C(14)	-0.011 (5)
C(12)	-0.002 (4)	C(15)	-0.002 (5)
C(13)	-0.013 (4)	C(16)	0.013 (4)
Plane II: $-0.3491X - 0.9370Y - 0.0154Z = -1.6628$			
C(21)	-0.008 (3)	C(24)	-0.004 (5)
C(22)	0.004 (4)	C(25)	-0.001 (5)
C(23)	0.002 (5)	C(26)	0.007 (4)
Plane III: $-0.8983X + 0.1768Y - 0.4022Z = -1.8000$			
C(31)	0.003 (3)	C(34)	0.001 (5)
C(32)	0.004 (6)	C(35)	0.006 (5)
C(33)	-0.007 (6)	C(36)	-0.008 (4)

<sup>a</sup> Planes are given in the orthonormalized coordinate system X, Y, Z.

the two iodide ligands. (The van der Waals radius for iodine is ca. 2.15 Å.)<sup>10</sup> The associated I-Cu-I angle is 117.12 (2)°.

The Cu-As-C(ipsos) angles are all increased from the regular tetrahedral angle of 109.47°, with values ranging from 112.62 (10) to 120.55 (10)°. The C-As-C bond angles are thus compressed, ranging from 100.60 (14) to 101.56 (14)°.

The acetonitrile ligand is linear (Cu-N-C(1) = 176.0 (3)° and N-C(1)-C(2) = 179.6 (5)°) with N-C(1) = 1.125 (6) Å and C(1)-C(2) = 1.479 (7) Å.

An intriguing feature of the molecule synthesized is that it provides a potential route into simple chiral tetrahedral copper(I) complexes via the bridge-splitting reaction (1). The [(AsPh<sub>3</sub>)<sub>2</sub>(MeCN)CuI]<sub>2</sub> + 2L → 2(AsPh<sub>3</sub>)(MeCN)(L)CuI (1)

utility of this synthetic route is currently being investigated.

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**Registry No.** [(AsPh<sub>3</sub>)<sub>2</sub>(MeCN)CuI]<sub>2</sub>, 75812-50-9.

**Supplementary Material Available:** Table of observed and calculated structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

(9)  $k = 0.116 \times 10^{-6}$  where  $|F_{o,cor}| = (1.0 + k|F_o|)F_{o,uncor}$ .

(10) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, N.Y., 1960; p 260.