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Monomeric (Trimesitylphosphine)copper(I) Bromide. X-ray Crystallographic Evidence for the First Two-Coordinate Copper(I) Phosphine Halide Complex

Sir:

The stereochemistry and bonding of metal cluster compounds attracts much attention due to their importance in many organometallic and bioinorganic catalytic systems. Extensive structural studies over several years have attempted to elucidate the steric and electronic characteristics of one class of cubane-like metal cluster compounds, namely the tetrameric 1:1 complexes formed by copper(I) and silver(I) halides with phosphines.[1-3] The X-ray structural results of Churchill and co-workers[2] and Teo and Calabrese[3] have demonstrated the dominant role of large halogen atoms and bulky phosphine ligands in $L_4M_4X_4$ tetramers in destabilizing the normal "cubane structure" relative to the "chair" (or "step") structure. In one instance it was shown that the bulk of the phosphine prevented tetramer formation; i.e., the 1:1 complex of CuCl with tricyclohexylphosphine (PCy_3, $\theta = 170°$)[4] was dimeric, with trigonal-planar copper(I) geometry.[5] These earlier studies[1-5] suggested that even bulkier phosphines should lead to the observation in the 1:1 series of other three-coordinate dimers or even two-coordinate monomers. The recent report by Goel and Beauchamp[6] that the 1:1 complex of CuBr and tri-*tert*-butylphosphine ($P(t\text{-}Bu)_3$, $\theta = 180°$) is a tetramer with nearly ideal T_d symmetry for the Cu_4Br_4 core is thus very surprising. This sharp contrast to the previous trend, developed from many structural determinations with small phosphines (e.g. PPh_3, $\theta = 145°$; PEt_3, $\theta = 132°$),[4] led us to examine the geometry of copper(I) in the 1:1 adduct of CuBr and trimesitylphosphine ($P(C_6H_2Me_3)_3 = P(mes)_3$, $\theta = 212°$).[4] We have previously reported[7] the large steric effects of $P(mes)_3$ in Mo, Ag, Hg, Pd, and Pt compounds.

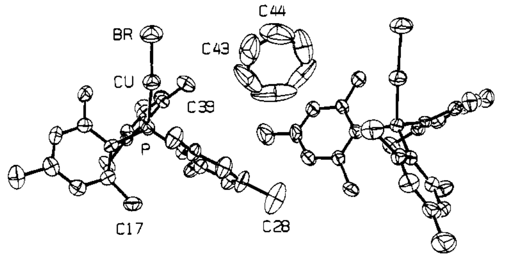

Figure 1. Molecular structure of $CuBrP(mes)_3$. Two monomeric molecules are shown with the benzene of solvation lying on a crystallographic twofold axis between them. Some intermolecular distances are as follows (Å): Cu···Cu = 10.308 (1); Br···Br = 10.267 (1); P···P = 10.685; Cu···C(42)(benzene) = 4.01 (6); Br···C(43)(benzene) = 4.09 (6).

Copper(I) bromide was reacted with $P(mes)_3$ in a 1:1 molar ratio in refluxing benzene. After filtration to remove some insoluble material, the product was isolated by evaporation of the solvent and dried under vacuum. The white product (yield 64%) gave a sharp melting point (175–178 °C). Fine white crystals suitable for X-ray diffraction analysis were afforded from a benzene/petroleum ether solvent mixture placed in a refrigerator. Decomposition of these crystals to a black color with time was attributed to solvent loss as one benzene molecule per two $CuBrP(mes)_3$ molecules was present in the unit cell (vide infra). The three-dimensional X-ray structural analysis[8] was thus determined for a single crystal coated with epoxy to prevent loss of the solvent of crystallization.

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(4) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. The bulk of phosphines is commonly judged by their cone angles as estimated from CPK molecular models. The cone angle θ is the angle needed to encompass rotation of the ligand about the metal at the apex. More quantitative θ values and "ligand profiles" are available for some bulky phosphines from their X-ray coordinates: Ferguson, G.; Roberts, P. J.; Alyea, E. C.; Khan, M. *Inorg. Chem.* **1978**, *17*, 2965.

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(8) Crystal data for $[CuBrP(mes)_3]\cdot{}^1/_2C_6H_6$, $C_{27}H_{33}CuPBr\cdot 0.5C_6H_6$: monoclinic, space group *C*2/*c*, $a = 37.788$ (5) Å, $b = 10.090$ (1) Å, $c = 15.136$ (5) Å, $\beta = 106.19$ (2)°, $V = 5542.5$ Å^3, $Z = 8$, $D_{calcd} = 1.37$ g cm^{-3}. Accurate cell parameters were obtained by least-squares refinement of the setting angles of 25 reflections ($10 \le \theta \le 15°$) measured on an Enraf-Nonius CAD4 diffractometer. Intensity data were collected at 21 °C by the $\omega/2\theta$ method for a small plate crystal (0.20 × 0.23 × 0.40 mm) to a maximum θ of 20° with use of graphite-monochromatized Mo Kα radiation. Of the 2589 unique data obtained, 1687 with $I > 3\sigma(I)$ were labeled observed. All calculations were carried out on a Digital PDP-8 computer using the NRC crystal structure package (Gabe et al., 1981). The structure was solved by conventional heavy-atom Patterson and Fourier methods with refinement by block-diagonal least-squares calculations with anisotropic thermal parameters. Geometrically idealized positions for the hydrogen atoms were included in the final rounds of calculations, only an overall isotropic thermal parameter was refined for the H atoms. Refinement converged with $R = 0.0356$ and $R' = [\sum w\Delta^2/\sum wF_o^2]^{1/2} = 0.0302$. A final difference map was featureless.

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The molecular structure and numbering scheme for the title compound are shown in Figure 1. The molecular geometry involves two-coordinate[1,9] Cu atoms in discrete CuBrP(mes)$_3$ molecules. Complexes of the general formula $L_m(CuX)_n$ between tertiary phosphines (and arsines and other monodentate ligands) have been extensively studied and display a variety of stoichiometries and structures.[1,2,9] As mentioned, with the exception of dimeric [CuClPCy$_3$]$_2$,[5] the 1:1 complexes have tetrameric "cubane" or "chair" Cu$_4$X$_4$ cores. All monomeric species previously characterized by X-ray analyses involve three- and four-coordinated Cu(I) centers;[1,9] these include CuCl(PPh$_3$)$_3$, CuCl(AsMe$_2$Ph)$_2$, and several species not containing phosphine and arsine ligands.[10] The related compound (Ph$_3$P)Cu(η^5-C$_5$H$_5$)[11] is not strictly comparable as it does not contain a halide ion. Other species presented as monomeric, such as CuX(SPPh$_3$),[12] are more likely ligand- or halide-bridged polymers.[1,9,10] There is evidence that various phosphine–copper(I) halide complexes dissociate in solution to products that include monomeric species, but no firm structural data are available.[13-15] The structure of CuBrP(mes)$_3$ is therefore noteworthy for several reasons: (i) it is the first[1,9] two-coordinate phosphine copper(I) halide complex: (ii) it confirms the expectation[1-3,5] that tetrameric M$_4$X$_4$ clusters will fragment into MX units if the associated ligand is sufficiently large; (iii) it demonstrates dramatically the steric effect for the largest known phosphine ligand, P(mes)$_3$.[7]

Each copper(I) atom is diagonally coordinated by a P(mes)$_3$ ligand (Cu–P = 2.193 (2) Å) and a terminal Br atom Cu–Br = 2.225 (1) Å). The Cu–P bond length is comparable to that reported in [CuClPCy$_3$]$_2$ (2.183 (2) Å)[5] and several 1:1 tetrameric complexes[16-18] while the Cu–Br bond distance appears to be very significantly shortened by comparison,[16-18] a result that is in keeping with the lower coordination number. The angles at the Cu and P atoms are Br–Cu–P = 173.7 (1)°, Cu–P–C(11) = 103.8 (2)°, Cu–P–C(21) = 108.0 (2)°, and Cu–P–C(31) = 111.7 (2)°. The Cu–P–C angles are markedly irregular as compared to M–P–C angles in other P(mes)$_3$ complexes,[7] indicative of steric interactions not observed in the earlier structures. We attribute the nonlinearity of the Br–Cu–P angle, and the irregularity of the Cu–P–C angles, to the repulsive interaction between mesityl rings of adjacent molecules. The benzene of solvation lies in a cavity between two almost parallel Cu–Br bonds related by a twofold axis with only van der Waals contacts between benzene carbons and Cu or Br (see the legend of Figure 1 for details).

Other bond distances in the CuBrP(mes)$_3$ molecule are in close agreement with those reported for other P(mes)$_3$ complexes[7] and in free P(mes)$_3$.[19] The P–C bond lengths are approximately equivalent, averaging 1.847 (6) Å. The C–C distances within the mesitylene rings average 1.395 (9) Å while the ring to methyl C–C distances are 1.512 (9) Å on average. The large C–P–C angles, averaging to 111.3 (3)°, reflect the much greater bulkiness of P(mes)$_3$ as compared to that of other phosphines (e.g. average C–P–C angles are 103° in PPh$_3$ complexes).[6] Detailed analyses of intramolecular and intermolecular interactions and calculation of θ and a "ligand profile"[4] of the P(mes)$_3$ ligand are under way.

Our preliminary attempts to characterize the title complex in solution have focused on NMR studies. The ^{1}H NMR spectrum shows the expected downfield shifts for methyl resonances and an increased $^4J(^{31}P-^1H)$ coupling constant (4 Hz) for the meta protons of the mesitylene rings. The main feature of the $^{13}C\{^1H\}$ NMR spectrum of CuBrP(mes)$_3$ is the lack of observable $^{31}P-^{13}C$ coupling and the 9 ppm downfield shift of the *ipso* carbon atoms (C(11), C(21), and C(31)) as compared to the position in free phosphine. The single resonance at −28.6 ppm (with respect to 85% H$_3$PO$_4$) in the $^{31}P\{^1H\}$ NMR spectrum of a CDCl$_3$ solution of CuBrP(mes)$_3$ at ambient temperature corresponds to a coordination chemical shift[20] of +7.2 ppm for P(mes)$_3$. In contrast, a coordination chemical shift of −15.9 ppm[21] was found for P-*t*-Bu$_3$ in the 1:1 CuBrP-*t*-Bu$_3$ complex (reported as dimeric in dichloroethane solution).[6] The $^{31}P\{^1H\}$ NMR spectrum of the green decomposition product obtained by exposure of CuBrP(mes)$_3$ to air for an extended period shows resonances due to uncomplexed P(mes)$_3$ and OP(mes)$_3$ only; an oxide cluster as proved[22] for the analogous PEt$_3$ tetramer is apparently not formed. Other NMR results and solution characterization measurements will be reported together with our continuing studies on analogous CuXP(mes)$_3$ complexes.

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Registry No. [CuBrP(mes)$_3$]·$^1/_2$C$_6$H$_6$, 97920-99-5.

Supplementary Material Available: Listings of atom coordinates, temperature factors, bond distances and angles, and structure factors for the title compound (23 pages). Ordering information is given on any current masthead page.

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(RC$_5$H$_4$)MoFe(Te$_2$X)(CO)$_5$: Carbonyl Clusters Containing Hypervalent Main-Group Centers

Sir:

The associative binding of a Lewis base to a polynuclear metal carbonyl generally induces a change in the net metal–metal bond order of the cluster.[1] This pattern has been codified in various valence electron counting schemes.[2] In this report we describe

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