(4 days, 25 °C), followed by filtration and recrystallization, gave 68% of $(Mes_2AsGaMe_2)_n$ as a white solid, mp 200 °C dec. Lack of suitable crystals and the limited solubility of the mono- and bis(arsino)gallanes (eq 2–4) prohibited determination of their degree of association.

The structure of **1**, determinined by a single-crystal X-ray analysis,[5] is illustrated in Figure 1, with selected bond lengths and bond angles listed in Table I. The gallium atom is bonded to the three arsenic atoms in a trigonal-planar configuration and is positioned 0.149 Å out of the plane formed by the three arsenic atoms. The Ga–As bond lengths at 2.498 (1), 2.508 (1), and 2.470 (1) Å are all shorter than the mean Ga–As single bond length of 2.524 Å found in the four-coordinate dimer $(R_2AsGaPh_2)_2$ (R = CH_2SiMe_3).[2c] The mean As–C bond length and C–As–C bond angle at 1.977 Å and 105.1°, respectively, are similar to the values of 1.976 Å and 108° observed in Mes_3As.[6] However, the geometry at the arsenic atoms is considerably distorted from tetrahedral with Ga–As–C angles ranging from 93.1 (1) to 112.1 (1)°. The dimesitylarsino groups are oriented as staggered propeller blades when viewed down the Ga–As bonds. The dihedral angles between the normal to the plane through the arsenic atoms and those through the arsenic lone pair–As–Ga vector, which reflect the extent of As lone pair–Ga 4p orbital overlap, are 58, 86, and 52°, respectively, for As(1), As(2), and As(3).

The gallium and arsenic atoms are efficiently shielded from intermolecular associations by the bulky mesityl substituents. In addition to the outward extension of the mesityl groups from the Ga–As core, planes through C(17), C(27), and C(39′) and through C(19′), C(29′), and C(37) lie approximately parallel to but on opposite sides of the As atom plane. The shortest Ga···H distances, at 2.58 and 2.47 Å, involve respectively C(17) and C(37) methyl group hydrogens and, accordingly, there is no evidence for any Ga–H bonding interaction.

The electronic spectrum of **1** exhibits bands at 224 nm (ϵ 34 400 M^{-1} cm^{-1}) and 276 nm (ϵ 17 900 M^{-1} cm^{-1}). The long-wavelength band can be assigned to an As → π^* CT transition, on the basis of studies of mesitylarsines and the same assignment to the 276-nm band of Mes_3As.[7] However, unlike the latter compound and four-coordinate arsinogallanes, **1** is bright orange due to tailing of the 276-nm band into the visible region. This tailing is tentatively attributed to a partly obscured lower intensity As → Ga CT transition, although perturbation of the As → π^* transition resulting from reduction of the ionization potential of the As lone-pair electrons by steric strain cannot be ruled out.

In summary, the coupling reaction of a lithium arsenide with gallium halides provides a useful method for the preparation of Ga–As compounds. Arsinogallanes containing large substituents, including bis(arsino)- and tris(arsino)gallanes, can be prepared. Permesitylation serves to suppress intermolecular As → Ga association, although the bond lengths and angles of **1** suggest steric effects minimize the ground-state interaction of the As lone-pair electrons and the vacant Ga 4p orbital.

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Registry No. **1**, 102651-38-7; **2**, 101860-09-7; $(Mes_2AsGaCl_2)_n$, 101836-85-5; $((Mes_2As)_2GaCl)_n$, 101836-87-7; $(Mes_2AsGaMe_2)_n$, 102634-11-7.

Supplementary Material Available: Tables of positional and thermal parameters, hydrogen atom coordinates, bond lengths and angles, and displacements of atoms from least-squares planes for **1** (11 pages). Ordering information is given on any current masthead page.

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(5) Crystal data for tris(dimesitylarsino)gallane at 25 °C: $C_{54}H_{66}As_3Ga$, M_R 1009.61, triclinic, space group $P\bar{1}$ (from Laue symmetry and structure refinement), a = 12.702 (1) Å, b = 17.500 (2) Å, c = 11.810 (2) Å, α = 103.44 (1)°, β = 102.79 (1)°, γ = 77.79 (1)°, V_{obsd} = 2454.2 $Å^3$, Z = 2, D_{calcd} = 1.366 g cm^{-3}, μ (Cu Kα radiation, λ = 1.5418 Å) = 32.6 cm^{-1}. Sample dimensions: 0.20 × 0.40 × 0.70 mm. Intensity data ($h,\pm k,\pm l$, θ_{max} = 67°) for 8720 nonequivalent forms were recorded on an Enraf-Nonius CAD-4 diffractometer (Cu Kα radiation, incident-beam graphite monochromator; ω–2θ scans). Those 7083 reflections with $I > 3.0\sigma(I)$ were retained and corrected for Lorentz and polarization effects. An empirical absorption correction (relative range of transmission factors 0.63–1.0), based on a series of ϕ scans at χ ca. 90°, was also applied to these data. The structure was solved by direct methods (MULTAN11/82). All hydrogen atoms were located by difference Fourier synthesis. Full-matrix least-squares refinement of atomic parameters (anisotropic carbon, arsenic, and gallium; isotropic hydrogen) converged to R = 0.040 (R_w = 0.056). The function minimized in the least-squares calculations was $\sum w(||F_o| - |F_c||)^2$, where $w = 1/\sigma^2(|F_o|)$. All calculations were performed on a PDP11/44 computer by use of the Enraf-Nonius SDP suite of programs. Tables of atomic parameters and bond lengths and angles are included as supplementary material.

(6) Sobolev, A. N.; Romm, I. P.; Chernikova, N. Y.; Belsky, V. K.; Guryanova, F. N. *J. Organomet. Chem.* **1981**, *219*, 35–42.

(7) Cullen, W. R.; Green, B. R.; Hochstrasser, R. M. *J. Inorg. Nucl. Chem.* **1965**, *27*, 641–651.

A Cu–(μ-H) Bond Can Be Stronger Than an Intramolecular P→Cu Bond. Synthesis and Structure of $Cu_2(\mu\text{-}H)_2[\eta^2\text{-}CH_3C(CH_2PPh_2)_3]_2$[1a]

Sir:

We have reported earlier[1b] the dramatic influence of the identity of the phosphine on the aggregation and structure of phosphine adducts of CuH. We describe here the outcome of attempts to use a threefold symmetric tridentate phosphine in order to generate a four-coordinate complex containing a terminal hydride on Cu(I).

Hydrogenolysis (1 atm. 23 °C, 5 h) of the Cu–O bond of $(CuO\text{-}t\text{-}Bu)_4$ proceeds under mild conditions in THF in the presence of a stoichiometric amount (1 mol/mol of Cu) of $MeC(CH_2PPh_2)_3$ ("tripod") to produce t-BuOH and, as the only metal-containing product, a compound of empirical formula HCu(tripod) (isolated yield 75%). This compound is thermally unstable toward deposition of copper metal in toluene solution above 40 °C. The infrared spectrum of the compound shows an absorption assigned as ν(CuH) at 950 cm^{-1}, which shifts to 680 cm^{-1} when H_2 is replaced by D_2 in the synthesis ($\nu(H)/\nu(D)$ = 1.40). This frequency is too low to be the stretching mode of a terminal hydride.[2] Reinforcing this conclusion is the fact that the 220-MHz ^1H NMR spectrum shows an excessive number of aliphatic and of aromatic resonances for a threefold symmetric HCu(tripod) monomer.[3] The ^2H NMR of DCu(tripod) shows a broad yet unstructured resonance at a *positive* δ value (1.83 ppm), in the chemical shift region of the hydride ligands of $(HCuPPh_3)_6$ and $H_8Cu_8[Ph_2P(CH_2)_3PPh_2]_4$.[1b] The $^{31}P\{^1H\}$NMR spectrum at −40 °C provides further understanding of these data, exhibiting one broad (full width at half-height = 10 Hz) resonance at −21.0 ppm (intensity 2) and *two* sharp resonances (−28.9 and −29.7 ppm, total intensity 1). The latter values lie sufficiently close to the signal of free $CH_3C(CH_2PPh_2)_3$ in toluene at −40 °C (−27.3 ppm) to suggest a dangling (uncoordinated) phosphine arm. The two resonances of the dangling arms coalesce to a singlet at 20 °C, but these do not merge with the resonance of coordinated phosphine up to the sample decomposition temperature.

As anticipated by the spectroscopic data, an X-ray diffraction study shows the unit cell of HCu(tripod) to be composed of centrosymmetric dimers (Figure 1).[4] Two bridging hydrides link

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(1) (a) Taken from: Goeden, G. V. Ph.D. Thesis, Indiana University, 1982. (b) Lemmen, T. H.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1985**, *107*, 7774.

(2) Muetterties, E. L. *Transition Metal Hydrides*; M. Dekker: New York, 1971.

(3) Chemical shifts in C_6D_6 at 19 °C: 0.91, 1.83, 2.20, 2.43, 2.66, 6.86, 7.02, 7.43, 8.02, 8.36 ppm. Free THF is also seen at 1.43 and 3.59 ppm. While the THF signals are sharp and well resolved, those of the tripod ligand are all broad.

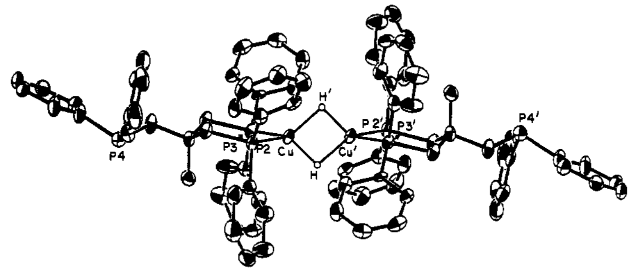

Figure 1. ORTEP drawing of $H_2Cu_2[CH_3C(CH_2PPh_2)_3]_2$, with thermal ellipsoids drawn at 50% probability. Carbon-bound hydrogens have been omitted for clarity. Metal-bound hydrides are shown in their refined locations. Unlabeled atoms are carbons. Primed atoms are related to unprimed atoms by a center of symmetry. Selected structural parameters: Cu–P2 = 2.229 (2) Å, Cu–P3 = 2.229 (2) Å, Cu–H = 1.66 (8) Å, Cu–H′ = 1.81 (8) Å; P2–Cu–P3 = 101.3 (1)°, P2–Cu–H = 113 (3)°, P3–Cu–H = 116 (3)°, H–Cu–H′ = 9 4 (3)°, Cu–H–Cu′ = 86 (3)°.

the copper centers, each of which is additionally coordinated by only two arms of the potentially tridentate phosphine. The Cu–(μ-H) distances are identical to within 1.4σ (difference), and the Cu/Cu separation, 2.371 (2) Å, is among the shortest yet observed, being surpassed only by the 2.348 (2) Å value established[5] in $Cu_3(TolylN_5Tolyl)_3$. The noncoordinated phosphorus atom is over 6.6 Å from the copper center to which the ligand is attached and is also well separated from neighboring molecules. The P_2CuH_2 unit approximates tetrahedral geometry, and the $P_4Cu_2H_2$ unit as a whole resembles the structure of B_2H_6.[6,7]

Given the large P2–Cu–P3 angle in $H_2Cu_2(tripod)_2$, the question arises as to whether this compound is dimeric because of the steric inability of tripod to be tridentate on a tetrahedral metal or whether it reflects greater bond strength in the $Cu(\mu\text{-}H)_2Cu$ unit than in two Cu–P bonds. The reactivity of $H_2Cu_2(tripod)_2$ permits an answer to this question. This hydride dimer reacts immediately in toluene at 25 °C with 1 atm of CO_2 to deposit $(tripod)CuO_2CH$ (89% yield), which was shown by ^{31}P NMR (singlet at −85 °C at −29.1 ppm), IR (1614 and 1315 cm^{-1}) and ^1H NMR to have $(\eta^3\text{-tripod})Cu(\eta^1\text{-}O_2CH)$ linkage.[8,9] The fact that the $(\eta^2\text{-tripod})Cu(\eta^2\text{-}O_2CH)$ structural option is not observed argues persuasively that $H_2Cu_2(tripod)_2$ does not owe its dimeric character to prohibitive strain in a $(\eta^3\text{-tripod})CuH$ form. Thus, while $MeC(CH_2PPh_2)_3$ is capable of redirecting the phenyl group from its common μ-bridging function to a terminal position in (tripod)CuPh,[10] the hydride ligand displays an even greater preference for bridging under the same circumstances. Note also, for comparison, that in $(tripod)CuBH_4$ the phosphine is trihapto while BH_4 is monohapto.[11] However, $H_2Cu_2(tripod)_2$ exhibits the lowest degree of aggregation yet characterized in a molecular copper hydride, as well as the first example of μ-hydride bridging between two copper centers. Since one donor arm of the tripod ligand is not coordinated in $H_2Cu_2(tripod)_2$, it is particularly curious that the seemingly equivalent ligand $Ph_2P(CH_2)_3PPh_2$ (dppp) does not give an analogous dimeric copper hydride (i.e., $H_2Cu_2(dppp)_2$), but rather $H_8Cu_8(dppp)_4$.[1b] This point warrants careful investigation if the aggregation of copper hydrides is to be understood.

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Supplementary Material Available: Tables of atomic positional and thermal parameters for $H_2Cu_2[MeC(CH_2PPh_2)_3]_2$ and an alternate view of the structure (4 pages). Ordering information is given on any current masthead page.

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(4) Yellow cubic crystals grown from THF have the stoichiometry HCu(tripod)·THF and adopt space group $P2_1/n$ with (−160 °C) a = 15.130 (3) Å, b = 19.869 (5) Å, c = 14.368 (3) Å, β = 116.89 (1)°, Z = 4, $R(F)$ = 0.0888, and $R_w(F)$ = 0.0825 for 3792 reflections (Mo K_α) with $F > 2.33\sigma(F)$, refining non-hydrogen atoms anisotropically; all hydrogen positional parameters were varied, each being assigned a B value equal to 1 unit greater than the isotropic equivalent of the atom to which they are attached.

(5) Beck, J.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 409.

(6) With the structure established, the isomers detected in solution by ^{31}P NMR might be attributed to cis in addition to trans disposition of methyl substituents in the chelate rings; alternatively, there may be restricted rotation of dangling phosphine arms.

(7) Any equilibrium of the dimer with monomeric HCu(tripod) would simultaneously cause time-averaged equivalence of the three arms of the phosphine. The ^1H and ^3P NMR data permit the conclusion that such an equilibrium is not operative.

(8) ^1H NMR (220 MHz, $CDCl_3$, ppm); 1.51 (s, 3 H), 2.36 (s, 6 H), 7.04 (m, 18 H), 7.50 (m, 12 H), 9.34 (s, 1 H). $^{31}P\{^1H\}$NMR (40.5 MHz, CH_2Cl_2, −85 °C, ppm): −29.1 (s). IR (Nujol, cm^{-1}): $\nu(CO_{asym})$ = 1614; $\nu(CO_{sym})$ = 1315. Compare ref 9.

(9) Bianchini, C.; Ghilardi, C. A.; Meli, A.; Midollini, S.; Orlandini, A. *J. Organomet. Chem.* **1983**, *248*, C13.

(10) Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1984**, *3*, 1444.

(11) Ghilardi, C. A.; Midollini, C. A.; Orlandini, A. *Inorg. Chem.* **1982**, *21*, 4096.