

Hexacoordinate Planar Main Group Atoms Centered in Hexagonal Hydrocopper Complexes  $\text{Cu}_6\text{H}_6\text{X}$  ( $\text{X} = \text{Si}, \text{P}, \text{As}$ )

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Ab initio theoretical evidence of hexacoordinate planar main group atoms centered in hexagonal hydrocopper complexes  $\text{Cu}_6\text{H}_6\text{X}$  ( $\text{X} = \text{Si}, \text{P}, \text{As}$ ) is presented at the density functional theory level in this work. The results obtained extend the bonding capacity of silicon, phosphorus, and arsenic to planar hexacoordination in hydrocopper complexes which are important in fundamental research and may shed new insight into catalyst chemistry.

Considerable progress has been achieved in the past 30 years on planar coordinate carbons, including tetra-,<sup>1–5</sup> penta-,<sup>6</sup> and hexacoordinate planar carbons,<sup>7,8</sup> while much less attention has been paid to their silicon and germanium analogues. Contrary to traditional tetrahedral structures which dominate the chemistry of Si and Ge, tetracoordinate planar Si and Ge were recently observed in  $\text{MAL}_4$  and  $\text{MAL}_4^-$  ( $\text{M} = \text{Si}, \text{Ge}$ ).<sup>9</sup> Penta- and hexacoordinate silicons are well-known in the literature,<sup>10</sup> but there have been no investigations reported on hexacoordinate planar silicon or germanium to date. In searching for novel planar coordinate carbon-containing systems, our group proposed recently the possibility of tetracoordinate planar main group atoms centered in  $D_{4h}$   $\text{M}_4\text{H}_4\text{X}$  ( $\text{M} = \text{Cu}, \text{Ni}; \text{X} = \text{B}, \text{C}, \text{N}, \text{O}$ )<sup>11</sup> and the corresponding pentacoordinate nonmetal centers in  $D_{5h}$   $\text{Cu}_5\text{H}_5\text{X}$ .<sup>12</sup> In this work, we continue to present ab initio

theoretical evidence of hexacoordinate planar (HP) main group atoms centered in hexagonal hydrocopper complexes  $\text{Cu}_6\text{H}_6\text{X}$  ( $\text{X} = \text{Si}, \text{P}, \text{As}$ ). The results obtained extend the bonding capacity of silicon, phosphorus, and arsenic to planar hexacoordination in hydrometal complexes which are important in fundamental research and may shed new insight into catalyst chemistry.

## Computational Methodology

Keeping both geometrical and electronic considerations in mind, we choose the hexagonal hydrocopper  $\text{Cu}_6\text{H}_6$  proposed by Tsipis et al.<sup>13</sup> to host Si, P, Ge, and As. Initial structures obtained at density functional theory (DFT) B3LYP/LanL2dz were further optimized at DFT B3LYP/6-311+G(d,p) and imaginary frequencies checked at the same theoretical level. When refined at MP2/6-311+G(d,p) with the frozen-core approximation, the DFT bond lengths are systematically shortened by about 2–5%. The stability of the  $\text{Cu}_6\text{H}_6$ -Si complex with respect to dissociation to hydrocopper  $\text{Cu}_6\text{H}_6$  and free Si atom is demonstrated by the binding energies of  $\Delta E = 183.6$  kJ/mol for the reaction of  $\text{Cu}_6\text{H}_6\text{Si} = \text{Cu}_6\text{H}_6 + \text{Si}$  (which also involves obvious structural relaxations of the  $\text{Cu}_6\text{H}_6$  hexagon as indicated in Table 1). The NMR shielding tensors of hydrogen atoms were calculated by employing the gauge-independent atomic orbital (GIAO) procedure.<sup>14</sup> The optimized structures and corresponding highest occupied molecular orbital (HOMO) pictures are depicted and compared with  $D_{6h}$   $\text{Cu}_6\text{H}_6$  at B3LYP/6-311+G(d,p) in Figure 1. Table 1 summarizes the optimized DFT bond parameters, lowest vibrational frequencies, and calculated NMR chemical shifts  $\delta_{\text{H}}$  of H atoms relative to the shielding tensor of H in  $T_d$   $\text{Si}(\text{CH}_3)_4$  (32.0 ppm). All the calculations were performed using the Gaussian 03 program.<sup>15</sup>

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**Table 1.** Optimized Bond Lengths  $R$  (Å), Lowest Vibrational Frequencies  $\nu_{\min}$  ( $\text{cm}^{-1}$ ), and NMR Chemical Shifts  $\delta_{\text{H}}$  (ppm) of  $\text{Cu}_6\text{H}_6\text{X}$  Complexes (X = Si, P, Ge, As) Compared with the Corresponding Values of  $D_{6h}$   $\text{Cu}_6\text{H}_6$  at B3LYP/6-311+G(d,p)

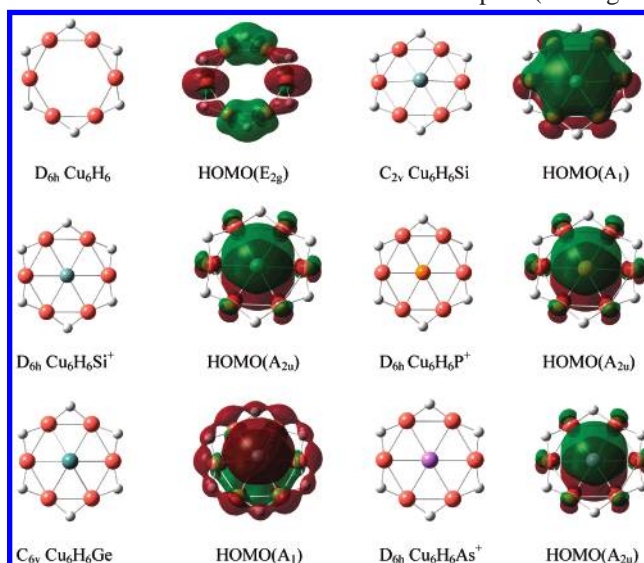
	$\text{Cu}_6\text{H}_6\text{X}$							
	$\text{Cu}_6\text{H}_6$ ( $D_{6h}$ )	$\text{Cu}_6\text{H}_6\text{Si}$			$\text{Cu}_6\text{H}_6\text{Si}^+$ ( $D_{6h}$ )	$\text{Cu}_6\text{H}_6\text{P}^+$ ( $D_{6h}$ )	$\text{Cu}_6\text{H}_6\text{Ge}$ ( $C_{6v}$ )	$\text{Cu}_6\text{H}_6\text{As}^+$ ( $D_{6h}$ )
$R_{\text{Cu}-\text{Cu}}$	2.554	2.452	2.461	2.461	2.525	2.483	2.462	2.541
$R_{\text{Cu}-\text{H}}$	1.591	1.601	1.599	1.601	1.594	1.584	1.605	1.587
$R_{\text{Cu}-\text{X}}$		2.475	2.461	2.463	2.525	2.483	2.571	2.541
$\nu_{\min}$	13	42	-29	-27	33	19	43	35
$\delta_{\text{H}}$	+0.8	+7.4	+8.2	+8.2	+2.2	+5.4	+5.8	+5.4

## Results and Discussions

Both the perfect planar  $D_{6h}$   $\text{Cu}_6\text{H}_6\text{Si}$  and pyramidal  $C_{6v}$   $\text{Cu}_6\text{H}_6\text{Si}$  with Si lying 0.12 Å above the  $\text{Cu}_6$  plane were confirmed to be transition states with one imaginary frequency. When symmetry constraint was removed during structural optimization, the slightly distorted  $C_{2v}$  minimum was reached from either the  $C_{6v}$  pyramid or  $D_{6h}$  hexagon with Si atom located 0.33 Å above the  $\text{Cu}_6$  plane. *However, the energy differences among the  $C_{2v}$  pyramid,  $C_{6v}$  pyramid, and  $D_{6h}$  hexagon are smaller than their differences in zero-point energies. Therefore, the vibrationally averaged structure of  $\text{Cu}_6\text{H}_6\text{Si}$  is actually planar and has the approximate symmetry of  $D_{6h}$ , similar to the situation observed in the vibrationally averaged  $D_{4h}$   $[\text{Al}_4\text{C}]^-$ .*<sup>2</sup> The aim to form a perfect  $D_{6h}$  Si center is achieved by removing one electron from  $\text{Cu}_6\text{H}_6\text{Si}$  to form a  $D_{6h}$   $\text{Cu}_6\text{H}_6\text{Si}^+$  cation, in which the Cu–Cu separations are increased by 0.07 Å to create a slightly bigger  $\text{Cu}_6$  hexagon to host the HP Si center. Both  $D_{6h}$   $\text{Cu}_6\text{H}_6\text{P}^+$  and  $\text{Cu}_6\text{H}_6\text{As}^+$  cations containing perfect HP nonmetal centers are confirmed to be true minima. However, the Ge atom is too big in size to be hosted in  $\text{Cu}_6\text{H}_6$ , and the lowest energy structure of  $\text{Cu}_6\text{H}_6\text{Ge}$  is a  $C_{6v}$  pyramid with Ge atom located 0.73 Å above the  $\text{Cu}_6$  plane. The Cu–Cu bond lengths listed in Table 1 show that all  $\text{Cu}_6\text{H}_6\text{X}$  complexes are inward contracted compared to the original  $D_{6h}$   $\text{Cu}_6\text{H}_6$ . This implies that the introduction of X centers helps to stabilize the complexes, as substantiated by the considerable binding energy of  $\text{Cu}_6\text{H}_6\text{Si}$  mentioned above and the observation that all  $\text{Cu}_6\text{H}_6\text{X}$  complexes have higher lowest vibrational frequencies  $\nu_{\min}$  than  $D_{6h}$   $\text{Cu}_6\text{H}_6$ <sup>13</sup> (see Table 1).

Different from the degenerate  $\sigma$  HOMO of  $D_{6h}$   $\text{Cu}_6\text{H}_6$ , the HOMOs of  $\text{Cu}_6\text{H}_6\text{X}$  complexes feature delocalized  $\pi$  orbitals as shown in Figure 1. Orbital analyses indicate that the  $np_z$  valence orbitals of the central atoms dominate the

HOMOs of the systems, while the nearly fully filled Cu 3d orbitals are only slightly involved. Natural charge calculations indicate that the X atom in  $\text{Cu}_6\text{H}_6\text{X}$  serves as the negative charge center, Cu ligands form a positively charged ring, and the bridging H atoms carry negative charges to keep the overall charge balance. In the case of  $C_{2v}$   $\text{Cu}_6\text{H}_6\text{Si}$ , the calculated atomic charges are Si  $-1.31$ , H  $-0.41$ , and Cu  $+0.63$  |e|, and the corresponding values of  $D_{6h}$   $\text{Cu}_6\text{H}_6\text{Si}$  are Si  $-1.38$ , H  $-0.41$ , and Cu  $+0.64$  |e|. Even in the positively charged  $D_{6h}$   $\text{Cu}_6\text{H}_6\text{X}^+$  series, the HP nonmetal centers still carry the negative charges of Si  $-0.60$  |e|, P  $-1.02$  |e|, and As  $-0.93$  |e|, with Cu atoms possessing the positive charges of  $+0.66$ ,  $+0.71$ , and  $+0.71$  |e| correspondingly. This “sandwich” charge distribution of  $\text{Cu}_6\text{H}_6\text{X}$  complexes reflects the consequences of electron transfers within the systems inferable from configuration analyses. For instance, the electron configurations of  $C_{2v}$   $\text{Cu}_6\text{H}_6\text{Si}$  are Cu  $[\text{Ar}]4s^{0.47}-3d_{xy}^{1.96}3d_{xz}^{1.99}3d_{yz}^{1.99}3d_{x^2-y^2}^{2.18}3d_z^{2.99}$ , Si  $[\text{Ne}]3s^{1.83}3p_x^{0.79}-3p_y^{0.79}3p_z^{1.86}$ , and H  $1s^{1.41}$ . Here, the occupancy of the Cu 4s valence orbital is decreased from  $4s^1$  in free Cu atom to  $4s^{0.47}$  in the complex, while Cu 3d orbitals are all practically fully filled. Obviously, the 4s electrons of the Cu ligands are partially transferred to the more electronegative Si and H atoms (about 3 electrons transferred in total in this case). More importantly, this configuration pattern shows that Si center uses its three  $sp^2$  hybrids to form six nearly equivalent bonds with surrounding Cu ligands, while its nearly doubly occupied  $3p_z$  orbital is widely delocalized over the whole molecule to form the  $\pi$  HOMO of the complex (see Figure

**Figure 1.** Optimized structures and corresponding HOMO pictures of  $\text{Cu}_6\text{H}_6\text{X}$  complexes (X = Si, P, Ge, As) compared with  $D_{6h}$   $\text{Cu}_6\text{H}_6$  at the B3LYP/6-311+G(d,p) level.

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1).  $D_{6h}$   $\text{Cu}_6\text{H}_6\text{Si}$  has practically the same electron configurations (Cu [Ar]4s<sup>0.46</sup>3d<sub>xy</sub><sup>1.96</sup>3d<sub>xz</sub><sup>1.99</sup>3d<sub>yz</sub><sup>1.99</sup>3d<sub>x<sup>2</sup>-y<sup>2</sup></sub><sup>1.89</sup>3d<sub>z<sup>2</sup></sub><sup>1.99</sup>, Si [Ne]3s<sup>1.82</sup>3p<sub>x</sub><sup>0.82</sup>3p<sub>y</sub><sup>0.82</sup>3p<sub>z</sub><sup>1.88</sup>, and H 1s<sup>1.40</sup>) as  $C_{2v}$   $\text{Cu}_6\text{H}_6\text{Si}$ , and similar configuration patterns exist in the isoelectronic  $C_{6v}$   $\text{Cu}_6\text{H}_6\text{Ge}$ ,  $D_{6h}$   $\text{Cu}_6\text{H}_6\text{P}^+$ , and  $D_{6h}$   $\text{Cu}_6\text{H}_6\text{As}^+$ . In these high-symmetry complexes, the six X–Cu bonds are exactly equivalent.

The special electron configuration of Si [Ne]3s<sup>1.86</sup>3p<sub>x</sub><sup>0.85</sup>3p<sub>y</sub><sup>0.85</sup>3p<sub>z</sub><sup>1.00</sup> in  $D_{6h}$   $\text{Cu}_6\text{H}_6\text{Si}^+$  cation is especially interesting. The Si 3p<sub>z</sub> orbital is singly occupied here, and the removed electron mainly comes from the originally nearly doubly occupied Si 3p<sub>z</sub> in the neutral complex. The much lowered occupancy of the Si 3p<sub>z</sub> orbital makes the  $\pi$  HOMO of the cation less widely delocalized and less effective than the neutral, as substantiated by the 6.31 eV difference in energies between the neutral and cation. Contrary to planar coordinate carbon, which usually possess doubly occupied HOMOs,<sup>7,12</sup>  $D_{6h}$   $\text{Cu}_6\text{H}_6\text{Si}^+$  provides the first hypercoordinate planar nonmetal (HPN) center which has a singly occupied MO (SOMO) at the highest energy level.

As the geometrical centers of the  $\text{M}_6\text{H}_6\text{X}$  hexagons are occupied by nonmetal atoms, the widely used NICS index<sup>6,7</sup> cannot be utilized to assess the aromaticity of the complexes. We choose to observe the variation of the NMR chemical shifts  $\delta_{\text{H}}$  calculated for H atoms outside the  $\text{Cu}_6$  ring. The upfield NMR chemical shifts ( $\delta_{\text{H}} > 0$ ) tabulated in Table 1 clearly indicate that the aromaticity of hydrocopper  $\text{Cu}_6\text{H}_6$ <sup>13</sup> vanishes with the introduction of a nonmetal center which has one nearly lone pair of  $np_z$  valence electrons. The isoelectronic  $\text{Cu}_6\text{H}_6\text{Si}$ ,  $\text{Cu}_6\text{H}_6\text{P}^+$ ,  $\text{Cu}_6\text{H}_6\text{Ge}$ , and  $\text{Cu}_6\text{H}_6\text{As}^+$ , which all have the nearly doubly occupied X  $np_z$  orbitals, possess the upfield chemical shifts narrowly ranging from  $\delta_{\text{H}} = +5.4$  to  $\delta_{\text{H}} = +7.4$  ppm, while  $\text{Cu}_6\text{H}_6\text{Si}^+$ , the only case with a singly occupied Si 3p<sub>z</sub>, has a much smaller chemical shift of  $\delta_{\text{H}} = +2.2$  ppm. The big difference in  $\delta_{\text{H}}$  values between  $\text{Cu}_6\text{H}_6\text{Si}$  and  $\text{Cu}_6\text{H}_6\text{Si}^+$  with different 3p<sub>z</sub> occupancies clearly demonstrates the antiaromatic effect of the occupied  $np_z$  orbitals of the nonmetal centers. This finding is in line with the results obtained for the  $\text{M}_4\text{H}_4\text{X}$  and  $\text{Cu}_5\text{H}_5\text{X}$  series.<sup>11,12</sup>

## Summary

We summarize here the bonding features of the hydrometal complexes  $D_{nh}$   $\text{M}_n\text{H}_n\text{X}$  ( $n = 4-6$ ) centered with HPNs, on the basis of our investigations on  $D_{4h}$   $\text{M}_4\text{H}_4\text{X}$ ,<sup>11</sup>  $D_{5h}$   $\text{Cu}_5\text{H}_5\text{X}$  ( $\text{M} = \text{Cu}, \text{Ni}; \text{X} = \text{B}, \text{C}, \text{N}, \text{O}$ ),<sup>12</sup> and  $D_{6h}$   $\text{Cu}_6\text{H}_6\text{X}$  ( $\text{X} = \text{Si}, \text{P}, \text{As}$ ). First, the HPN center provides three sp<sup>2</sup> hybrids to form  $n$  equivalent X–M bonds with surrounding metal ligands and its nearly doubly occupied (or singly occupied

in  $\text{Cu}_6\text{H}_6\text{Si}^+$ ) X  $np_z$  valence orbital dominates the delocalized  $\pi$  HOMO perpendicular to the molecular plane. Second, the  $n$  metal ligands partially transfer their 4s valence electrons to the more electronegative HPN center and  $n$  bridging H atoms, providing electrons to form the delocalized multi-centered bonds to stabilize the complexes. Third, the bridging H atoms, which may be substituted by other radical groups, play important roles in maintaining the planarity of the complexes by forming two-electron three-center bridging bonds with neighboring transition metal atoms. Finally, the HPN center follows the octet rule by forming  $n$  equivalent X–M partial bonds. For instance, in terms of the Wiberg bond indices (WBIs),  $D_{6h}$   $\text{B}_6\text{C}^{2-}$  has the bond order of  $\text{WBI}_{\text{C-B}} = 0.63$ <sup>7</sup> and  $C_{2v}$   $\text{Cu}_6\text{H}_6\text{Si}$  has the bond order of  $\text{WBI}_{\text{Si-Cu}} = 0.30$  and  $\text{WBI}_{\text{Si-H}} = 0.12$  and the total bond order of  $\text{WBI}_{\text{Si}} = 2.52$ . The corresponding atom–atom overlap-weighted bond orders are Si–Cu 0.41 and Si–H 0.10, and the total bond order of Si approaches 3.06. In  $C_{4v}$   $\text{Cu}_4\text{H}_4\text{C}$  pyramid and  $D_{5h}$   $\text{Cu}_5\text{H}_5\text{C}$  pentagon,  $\text{WBI}_{\text{C-Cu}} = 0.37$  and 0.34 and  $\text{WBI}_{\text{C-H}} = 0.24$  and 0.15, respectively. Similar situations happen in other  $\text{Cu}_6\text{H}_6\text{X}$  complexes. Obviously, these X–Cu bonds have lower bond orders than the C–B bonds in  $\text{B}_6\text{C}^{2-}$ . However, the nonnegligible X–H interactions in  $\text{Cu}_n\text{H}_n\text{X}$  complexes also help to stabilize the nonmetal centers and the WBIs, which do not include the multicenter bondings existing in  $\text{Cu}_n\text{H}_n\text{X}$  complexes, can only be treated as semiquantitative measures in estimating the relative bond strengths. In the view of geometrical requirement, the first-row elements B, C, N, and O can be hosted at the centers of squared  $\text{M}_4\text{H}_4$  ( $\text{M} = \text{Cu}, \text{Ni}$ ) and pentagonal  $\text{Cu}_5\text{H}_5$ ,<sup>11,12</sup> but they are too small to form effective X–Cu bonds at the center of  $\text{Cu}_6\text{H}_6$  hexagon, while the second-row Si and P and third-row As have approximately the right sizes to form  $D_{6h}$  HP centers in  $\text{Cu}_6\text{H}_6\text{X}$  neutral or cations. These high-symmetry hydro–transition-metal complexes centered with HPNs can be modified to form various derivatives and may expand in one, two, or even three dimensions.

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**Supporting Information Available:** Cartesian coordinates for the optimized complexes discussed in this work and the corresponding harmonic frequencies at the B3LYP/6-311+G(d,p) level. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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