M_5H_5X (M = Ag, Au, Pd, Pt; X = Si, Ge, P, S): Hydrometal Pentagons with D_{5h} Planar Pentacoordinate Nonmetal Centers

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Received: June 6, 2005; In Final Form: July 3, 2005

A density functional theory investigation has been presented in this work on M_5H_5X hydrometal pentagons (M = Ag, Au, Pd, P) with D_{5h} planar pentacoordinate nonmetal centers (X = Si, Ge, P, S). The introduction of the nonmetal centers X introduces p aromaticity to M_5H_5X complexes. These novel planar complexes are favored in thermodynamics and confirmed to be aromatic in nature. They may be expanded to one, two, or even three dimensions with multiple planar pentacoordinate silicon and other nonmetal centers.

1. Introduction

The structures and properties of planar tetra-,[1−7] penta-,[8,9] and hexacoordinate[10−12] carbons have aroused great interest among chemists in the past thirty years, while much less attention has been paid to their silicon analogues beyond the traditional tetrahedron concept. Planar tetracoordinate (PT) silicon was first studied about twenty years ago[13] and recently observed in C_{2v} MAl_4 and MAl_4^- (M = Si, Ge).[14] Utilizing the frameworks of the polygonal hydrocoppers (Cu_nH_n) proposed by Tsipis et al.,[15] our group recently presented the possibility of hosting PT carbon in squared M_4H_4C (M = Cu, Ni),[5] planar pentacoordinate (PP) carbon in pentagonal Cu_5H_5X (X = B, C, N, O),[9] and planar hexacoordinate (PH) silicon in hexagonal Cu_6H_6Si [16] at the density functional theory (DFT) level. Inspired by the novel design of planar pentacoordinate carbons,[8] we have also proposed a universal structural pattern at DFT to incorporate planar hypercoordinate silicons in the C_{2v} B_nE_2Si series ($n = 2-5$; E = Si, CH, BH) with Si as periphery atoms in these molecular fans.[17] In this report, we continue the research by exploring the possibility at DFT of hosting D_{5h} PP silicon and other nonmetals at the centers of pentagonal hydrometals M_5H_5 [15,18] to form M_5H_5X complexes with M = Ag, Au, Pd, Pt and X = Si, Ge, P, S. As heavy transition metal elements in group 11 and group 10 in the periodic table, Ag and Au and Pd and Pt are isolobal in valence electron configurations with Cu and Ni, respectively, but they are systematically bigger in atomic size. $Pt_5H_5^-$ and $Pd_5H_5^-$ pentagons are found to provide the right cavities to match D_{5h} PP Si and Ge centers both geometrically and electronically. To the best of our knowledge, there has been no investigation reported to date on PP Si or Ge at the center of a perfect pentagon with the high symmetry of D_{5h}. The present work and our previous investigations combined provide strong DFT evidence that polygonal hydro-transition-metals M_nH_n (M = group 10 and 11 transition metals; $n = 4-6$) may serve as effective ligands to host planar coordinate carbon, silicon, and other nonmetal atoms at their geometry centers with the high symmetry of D_{nh}.

2. Computational Procedure

Initial structures were optimized using the Gaussian 03 program[19] at the hybrid DFT functional level of B3LYP with the bases of Lanl2dz for transition metals (which contains a Los Alamos effective core potential) and 6-311+G(d) for nonmetal atoms. Imaginary vibrational frequencies were checked at the same theoretical level. To assess the aromaticity of the systems, the nucleus independent chemical shifts (NICS)[20,21] were calculated by using the gauge-independent atomic orbital (GIAO) procedure at B3LYP with the same basis. The vertical one-electron detachment energies of anions were calculated employing the outer valence Green's function (OVGF)[22] to facilitate future photoelectron spectroscopic measurements. Figure 1 depicts the optimized structures (upper) of the Ag_5H_5X series (X = Si, P, S) and their highest occupied molecular orbital (HOMO) pictures (lower) and Figure 2 shows the optimum geometries of $Au_5H_5P^+$, $Pt_5H_5Ge^-$, and $M_5H_5Si^-$ (M = Pd, Pt) and their lithium salts LiM_5H_5Si. Four typical delocalized out-of-plane molecular orbitals (MOs) of D_{5h} $Pt_5H_5Si^-$ are shown in Figure 3. The important DFT bond lengths, lowest vibrational frequencies, Wiberg bond indices of the X centers, NICS(1) values calculated with ghost atoms located 1.0 Å above the M_5 planes (the structural centers have been occupied by X atoms), and the low-lying one-electron vertical detachment energies of anions are summarized in Table 1. The reversed values of the HOMO energies listed in Table 1 approximately represent the ionization potentials (IPs) of corresponding complexes in Koopmans' theorem. Their HOMO-LUMO energy gaps are also tabulated in Table 1.

3. Results and Discusions

As shown in Figure 1, Figure 2, and Table 1, D_{5h} $Ag_5H_5P^+$, $Au_5H_5P^+$, $Ag_5H_5S^{2+}$, and $Au_5H_5S^{2+}$ are all true minima on their

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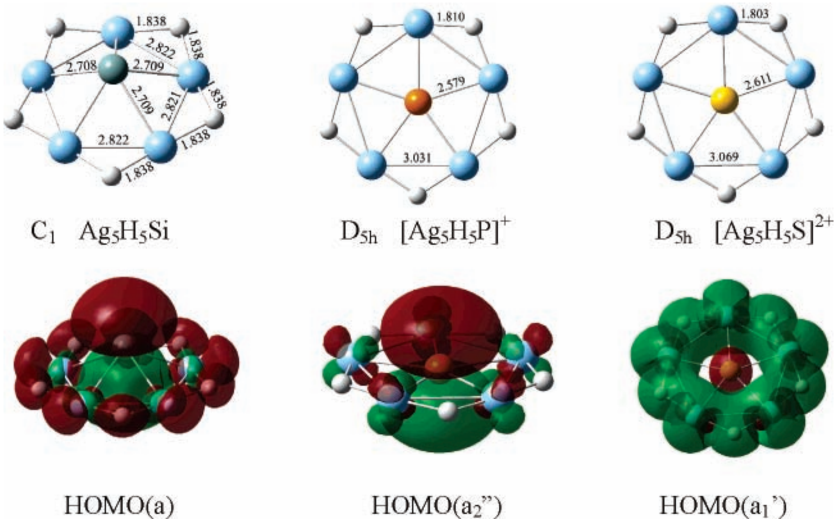
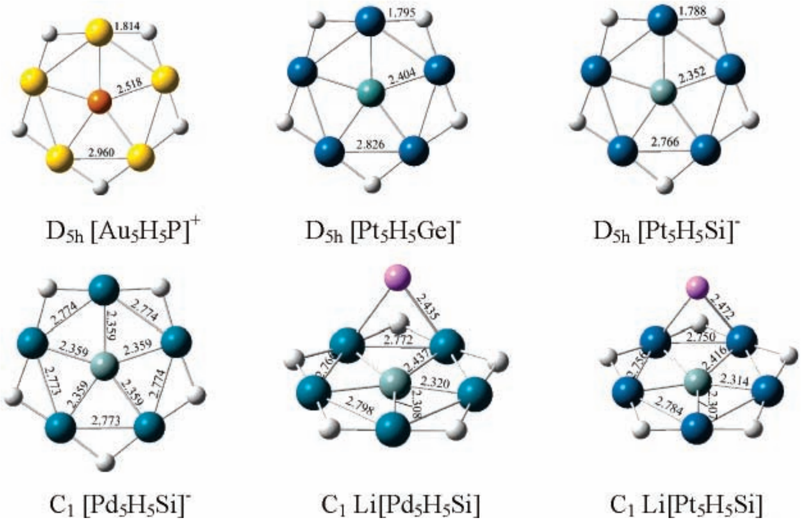


C_1 Ag_5H_5Si D_{5h} $[Ag_5H_5P]^+$ D_{5h} $[Ag_5H_5S]^{2+}$

HOMO(a) HOMO(a_2'') HOMO(a_1')

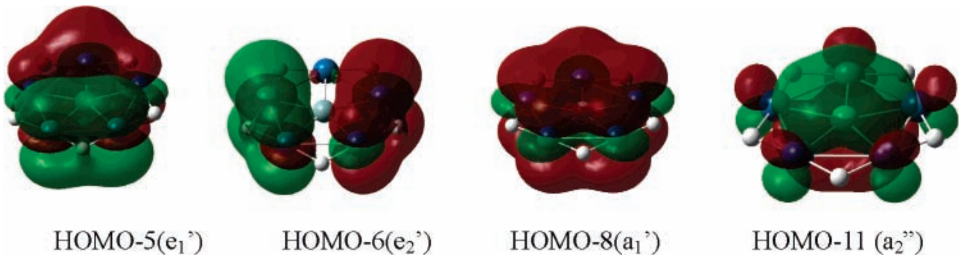
Figure 1. Optimized structures (upper) and corresponding HOMO pictures (lower) of Ag_5H_5X neutral and cations (X = Si, P, S).



D_{5h} $[Au_5H_5P]^+$ D_{5h} $[Pt_5H_5Ge]^-$ D_{5h} $[Pt_5H_5Si]^-$

C_1 $[Pd_5H_5Si]^-$ C_1 $Li[Pd_5H_5Si]$ C_1 $Li[Pt_5H_5Si]$

Figure 2. Optimum geometries of $[Au_5H_5P]^+$, $[Pt_5H_5Ge]^-$, and $[M_5H_5Si]^-$ anions (M = Pd, Pt) and their lithium complexes $Li[M_5H_5Si]$.



HOMO-5(e_1') HOMO-6(e_2') HOMO-8(a_1') HOMO-11 (a_2'')

Figure 3. Four typical delocalized out-of-plane MOs of D_{5h} $Pt_5H_5Si^-$.

potential energy surfaces without imaginary vibrational frequencies. But a D_{5h} Ag_5H_5Si turned out to be a transition state with one imaginary frequency at 95i cm^{-1} (an a_2'' vibrational mode with the Si center vibriating up and down along the 5-fold molecular axis perpendicular to the Ag_5 plane) and a D_{5h} Au_5H_5Si is a third-order stationary point with three imaginary frequencies at 341i, 320i, and 116i cm^{-1}. However, the optimizations of both C_{5v} Ag_5H_5Si and C_{5v} Au_5H_5Si had convergence problems at the DFT level used in this work. Totally removing the symmetry constrains during structural optimization, we obtained two C_1 pentagonal pyramid structures for Ag_5H_5Si and Au_5H_5Si, which possess the approximate symmetry of C_{5v} (see Figure 1) with Si atoms located about 1.2 Å above the transition metal planes. Orbital analyses indicate that a D_{5h} $Ag_5H_5P^+$ possesses 2 π electrons in its HOMO (a_2'') and therefore conforms with the $(4n + 2)\pi$ electron counting rule, while the approximate C_{5v} Ag_5H_5Si has a distorted π HOMO in its ground-sate structure (see Figure 1). Although the HOMO of D_{5h} $Ag_5H_5S^{2+}$ is an in-plane delocalized bond (a_1') composed mainly of the Ag 4d atomic orbitals (AOs) and H 1s AOs, its HOMO-1 (a_2'') turns out to be a delocalized π MO. The π MOs of these complexes are mainly composed of the contributions from the $3p_z$ AOs of the nonmetal centers Si, P, and S, respectively. A similar situation happens to Au_5H_5Si, $Au_5H_5P^+$, and $Au_5H_5S^{2+}$. Obviously, both hydrosilver Ag_5H_5 and hydrogold Au_5H_5 are unsuitable to host the much concerned D_{5h} PP Si at their geometrical centers. This situation is similar to that of the Cu_4H_4X series (X = B, C, N, O),[5] in which

TABLE 1: Optimized Important Bond Lengths, r_{X-M} and r_{M-M}, the Lowest Vibrational Frequencies, V_{min}, Total Wiberg Bond Indices of the X Centers (WBI_X), Calculated NICS(1) Values, HOMO Energies, and HOMO-LUMO Energy Gaps (Gap) of the Complexes Studied in This Work and the Low-Lying One-eLectron Vertical Detachment Energies (VDEs) of $M_5H_5X^-$ Anions with Pole Strengths Greater than 0.90 at DFT

	symmetry	r_{X-M} (Å)	r_{M-M} (Å)	V_{min} (cm^{-1})	WBI_X	NICS(1) (ppm)	HOMO (eV)	gap (eV)	VDEs (eV)
Ag_5H_5	$\sim D_{5h}$		2.87	30		−0.6	−7.56	5.76	
Ag_5H_5Si	$\sim C_{5v}$	2.71	2.82	40	2.1	−11.0	−4.63	1.33	
$Ag_5H_5P^+$	D_{5h}	2.58	3.03	45	2.2	−6.9	−9.99	2.09	
$Ag_5H_5S^{2+}$	D_{5h}	2.61	3.07	48	1.77	−15.6	−15.7	2.43	
Au_5H_5	$\sim D_{5h}$		2.77	38		−1.4	−8.05	5.48	
Au_5H_5Si	$\sim C_{5v}$	2.68	2.75	11	2.3	−6.8	−4.68	1.41	
$Au_5H_5P^+$	D_{5h}	2.52	2.96	38	2.31	−11.1	−9.89	2.27	
$Au_5H_5S^{2+}$	D_{5h}	2.54	2.98	46	2.0	−15.5	−16.2	3.12	
$Pd_5H_5Si^-$	$\sim D_{5h}$	2.36	2.77	10	3.46	−0.3	−2.14	2.46	4.88(e_2'), 5.49(e_1')
$Pd_5H_5Ge^-$	$\sim D_{5h}$	2.42	2.84	21	3.34	−2.3	−2.13	2.33	4.80(e_2'), 5.47(e_1')
$Pt_5H_5^-$	D_{5h}		2.62	17		+107	−2.32	1.16	
$Pt_5H_5Si^-$	D_{5h}	2.35	2.77	38	3.69	−6.2	−2.36	2.34	5.16(e_2'), 5.61(a_2'), 5.93(e_1')
$Pt_5H_5Ge^-$	D_{5h}	2.40	2.83	40	3.58	−8.2	−2.45	2.26	5.10(e_2'), 5.95(e_1')
Pt_5H_5P	C_s	2.33	2.74	9	3.75	−11.6	−6.80	2.03	
Li[Pd_5H_5Si]	$\sim C_s$	2.32	2.77	11	3.48	+1.4	−5.96	2.58	
		2.44	2.80						
Li[Pt_5H_5Si]	$\sim C_s$	2.31	2.75	36	3.75	−8.8	−6.13	2.45	
		2.42	2.78						

$Cu_4H_4B^-$ and Cu_4H_4C prefer C_{4v} pyramids to D_{4h} squares, while $Cu_4H_4N^+$ and $Cu_4H_4O^{2+}$ take planar squared structures with the high symmetry of D_{4h}.

Extensive searches at DFT indicate that the long-sought D_{5h} planar pentacoordinate silicon can be stabilized at the centers of both D_{5h} $Pt_5H_5Si^-$ and C_1 $Pd_5H_5Si^-$ (which has the actual symmetry of D_{5h} at DFT) as shown in Figure 2, with the bond lengths of $r_{Si-M} \approx 2.35$ and $r_{M-M} \approx 2.77$ Å. These pentagonal complexes contain D_{5h} Si centers with five transition-metal ligands evenly distributed around them. Similarly, D_{5h} Ge centers can be stabilized in perfect pentagons $Pt_5H_5Ge^-$ and $Pd_5H_5Ge^-$ with the Ge−M bond lengths close to 2.40 Å. Introducing an alkaline counterion Li^+ into $M_5H_5Si^-$ (M = Pd and Pt), we obtained two C_1 structures with the approximate symmetry of C_s for Li[Pd_5H_5Si] and Li[Pt_5H_5Si] (see Figure 2), in which the planar $M_5H_5Si^-$ structural units and PP Si centers are well maintained. The calculated natural charges of Li atoms in these complexes are found to be close to +0.90|e| and these alkaline cations form ionic bonds with the planar $M_5H_5X^-$ structural cores. As indicated by the total Wiberg bond indices ranging from $WBI_X = 3.34$ to 3.75 (see Table 1), the D_{5h} Si, Ge, and P centers in these planar M_5H_5X complexes (M = Pd, Pt) follow the octet rule in interacting with the transition metal ligands.

Concerning the stability of D_{5h} $Pt_5H_5X^-$ (X = Si, Ge) complexes, the following reaction

$$Pt_5H_5^-(D_{5h}) + X = Pt_5H_5X^-(D_{5h})$$

has the calculated DFT energy changes of $\Delta E = -810.8$, −935.9, enthalpy changes of $\Delta H = -814.0$, −940.6, and free Gibbs energy changes of $\Delta G = -767.6$, −894.1 kJ/mol for X = Ge and Si, respectively. Obviously, pentagonal $Pt_5H_5X^-$ complexes with D_{5h} Si and Ge centers are strongly favored in thermodynamics with respect to a $Pt_5H_5^-$ anion and a free X atom.

The negative NICS(1) values tabulated in Table 1 indicate that the M_5H_5X complexes studied in this work are aromatic in nature, except for Li[Pd_5H_5Si], which has a slightly positive NICS value (+1.4 ppm), partially explaining the stability of these nonmetal-atom-centered planar molecules. These NICS(1) values are comparable with the corresponding values of benzene (−10.1 ppm at the same theoretical level). It is interesting to notice that M_5H_5X complexes have higher negative NICS values than the corresponding hydrometals M_5H_5 in all cases for the reason that the introduction of X centers introduces p aromaticity to the M_nH_nX complexes. For instance, as clearly indicated in Figure 1, Ag_5H_5X complexes (X = Si, P, S) possess 2 π electrons in their HOMO or HOMO-1 which are mainly composed of the contribution of the $3p_z$ orbitals of the nonmetal centers. In the case of $Pt_5H_5Si^-$, the π-type HOMO-11(a_2'') (see Figure 3) mainly reflects the contribution of Si $3p_z$ AO. It should be pointed out that the d aromaticity existing in M_4H_4 and Li_2M_4 [21] should exist in the M_5H_5X complexes (X = Ag, Au, Pd, Pt) studied in this work. In the four typical delocalized out-of-plane MOs of $Pt_5H_5Si^-$ shown in Figure 3, HOMO-5 and HOMO-6 consist purely of Pt $5d_{z^2}$ contributions, while HOMO-8, which is dominated by the in-phase overlap of Pt $5d_{z^2}$ AOs, also includes the contribution of the Si 3s AO. Two other degenerate antibonding MOs (HOMO-1(e_2'), which are not shown in Figure 3) represent the out-of-phase interactions of the five Pt $5d_{z^2}$ AOs.

4. Summary

In conclusion, we have presented DFT evidence in this work that planar pentacoordinate silicon and other nonmetal centers can be stabilized in perfect pentagonal hydro-transition-metals to form M_5H_5X complexes (M = Ag, Au, Pd, Pt; X = Si, Ge, P, S). These planar complex units are favored in thermodynamics and confirmed to be aromatic in nature. Our M_nH_nX complex series[5,9,16] containing D_{nh} C, Si and other D_{nh} nonmetal centers coordinated to n transition metal ligands (n = 4, 5 ,6; M = Cu, Ag, Au, Ni, Pd, Pt) may be expanded to one, two, or even three dimensions with multiple nonmetal centers.

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