Structure, Bonding and Reactivity of Coinage Metal Complexes TML_2 and TML_2^+ (TM = Cu, Ag, Au) with Planar Tetracoordinate Carbon, A Theoretical Investigation

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Abstract

The structures and bonding of the complexes TML_2 and TML_2^+ with planar tetracoordinate carbons (TM = Cu, Ag and Au; L = $\text{C}_3\text{H}_2\text{BCH}_3$ and $\text{C}_3\text{Me}_2\text{BCMe}_3$) have been investigated using density functional theory M06 method, in which L are the derivatives of 2-borabicyclo[1.1.0]but-1(3)-ene. The lengths of Au-C and Ag-C bonds in AuL_2 and AgL_2 are longer than those of in TML_2^+ , whereas the lengths of Cu-C bonds in TML_2 are shorter than those of in TML_2^+ . The NBO analyses of TML_2 and TML_2^+ reveal that the Cu-C bonds in CuL_2 are conjugated π bonds, whereas Ag-C and Au-C in TML_2 (TM = Ag and Au) are σ bonds. The first electron transition energies of TML_2^+ result from the d- π transition, and the wavelengths are close to 260 nm. Theoretically, the variations of the Gibbs free energies of the reactions of $\text{Ag}(\text{C}_3\text{H}_2\text{BCH}_3)_2^+$ and $\text{Ag}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2^+$ with (tht)AuBr indicate that the two reactions are thermodynamically favorable. We also theoretically obtained the stable Au(III)

complexes $(\text{C}_3\text{H}_2\text{BCH}_3)_2\text{AuBr}_2^+$ and $(\text{C}_3\text{Me}_2\text{BCMe}_3)_2\text{AuBr}_2^+$ with planar tetracoordinate carbons from the reactions of $\text{Au}(\text{C}_3\text{H}_2\text{BCH}_3)_2^+$ and $\text{Au}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2^+$ with CsBr_3 .

Keywords

Coinage metal; Planar tetracoordinate carbon; Chemical bond; Density functional theory

1. Introduction

The complexes with the formula EL_2 , in which the center atom E can be either main group elements or transition metals and L are strong electron-donators, have been attracting increasing attention because of their special structures and catalytic activities [1-5]. The complex $\text{C}(\text{PPh}_3)_2$ was independently synthesized by Ramirez and Takagi in 1961, in which PPh_3 is an electron-donating ligand [6,7]. Besides the PPh_3 ligand, another two kinds of molecules of N-heterocyclic carbene (NHC) [8] and cyclic alkyl(amino) carbene (cAAC) [9-12] were also used to be ligands to form complexes EL_2 (L = NHC and cAAC). For instance, $\text{C}(\text{NHC})_2$ was successfully synthesized by Guy Bertrand and co-workers [13]. Subsequently, the structures, stability and bonding of the complexes EL_2 (E = Si, Ge and Sn; L is a five-membered cyclic ylidene or N-heterocyclic ylidene) have been investigated both theoretically and experimentally [14-16]. In 2009, $\text{Si}(\text{cAAC})_2$ [17] was predicted to be stable on the basis of theoretical calculations. In addition, $\text{Si}(\text{Cy-cAAC})_2$ and $\text{Si}(\text{Me}_2\text{-cAAC})_2$ [18] as well as $\text{Ge}(\text{Me}_2\text{-cAAC})_2$ and $\text{Ge}(\text{Cy}_2\text{-cAAC})_2$ [19] have been synthesized and further characterized by elemental and spectroscopy analyses. Specially, $\text{Si}(\text{cAAC})_2$ was found to have high reactivity towards hydrogen, ammonia, and carbon dioxide [20-22].

Besides the main group element complexes of EL_2 , many transition-metal complexes with TML_2 formula were obtained [23-25], in which TM are transition metals and L are PR_3 , NHC, cAAC and so on, for example, $Ni(NHC)_2$ [26], $Pd(PR_3)_2$ and $Pd(NHC)_2$ [27-29], $Mn(cAAC)_2$ [30], $Zn(cAAC)_2$ [31], $Fe(cAAC)_2$ and $Co(cAAC)_2$ [32] as well as $Co(Me_2-cAAC)_2$ [33] have been isolated successfully. Recently, Frenking and co-workers obtained the coinage metal complexes $TM(cAAC)_2$ and $TM(cAAC)_2^+$ (TM = Cu, Ag and Au) and confirmed by single-crystal X-ray diffraction, EPR spectra and theoretical calculations [34-36]. The interactions between metals and ligand in $TM(cAAC)_2$ are σ -donation and π back-donation [34]. Interestingly, both experimental and theoretical results show the lengths of TM-C bonds in $TM(cAAC)_2^+$ are longer than those of in $TM(cAAC)_2$ for TM = Cu, Ag and Au.

In 1970, Hoffmann firstly proposed novel molecule containing planar tetracoordinate carbon (ptC) can be stabilized on the basis of the theoretical predication [37]. Up to now, plenty of compounds with ptC were theoretically found to be stable and a few of compounds with ptC were observed experimentally. For example, Klas Sorger et al have obtained some molecules with ptC by density functional theory [38]. Walter Siebert and Anuradha Gunale reported some compounds with ptC, in which the ptC atom was stabilized by σ -donors and π -acceptors [39]. Also, a series of cyclic hydrocarbons analogs containing ptC were also predicted to be stable by theoretical calculation in 2006 [40]. Generally, the stable molecules containing ptC stabilized by σ -donors and π -acceptors have similar properties as π systems in aromatic molecules [41].

Our previous studies [42-44] provided the evidence that the derivatives of 2-borabicyclo[1.1.0]but-1(3)-ene ($C_3H_2BCH_3$) can also be electron-donators, similar to PPh_3 , NHC and cAAC. Moreover, C_3H_2BR (R = CH_3 , $CH_2C(CH_3)_3$, $CH_2C(CN)_3$, Cl, NO_2 and OH) can attach to AgCl and AuCl to form stable gold(I) and silver(I)

complexes with planar tetracoordinate carbon (ptC) [43,44]. In this contribution, we have theoretically obtained novel coinage metal complexes TML_2 (TM = Cu, Ag and Au; L are the derivatives of 2-borabicyclo[1.1.0]but-1(3)-ene). In addition, these complexes were found not only to contain two ptCs but also to have some similar properties to $TM(cAAC)_2$ and $TM(NHC)_2$ (TM = Cu, Ag and Au).

2. Computational methods

We have constructed the coinage metal complexes TML_2 and TML_2^+ (TM = Cu, Ag and Au; L = $C_3H_2BCH_3$ and $C_3Me_2BCMe_3$), in which L are the derivatives of 2-borabicyclo[1.1.0]but-1(3)-ene. The geometries of the six kinds of complexes have been optimized using density functional theory (DFT) meta-hybrid functional M06 [46] in combination with def2-SVP basis sets [47] and relativistic small-core pseudopotential for silver and gold, and 6-311+G** basis sets for other atoms. The vibrational frequencies of these complexes were calculated at the same level of theory to confirm the true minima on the potential energy surfaces. Wiberg bond indexes (WBIs), as well as population analysis of the lowest-energy complexes TML_2 and TML_2^+ were computed by the NBO methods [48]. All above calculations were performed by Gaussian 09 program [49].

3. Results and discussion

According to the orientations of two ligands L in the complexes TML_2 and TML_2^+ (TM = Cu, Ag and Au; L = $C_3H_2BCH_3$), each complex has *cis*-, *trans*- and *vertical*-configuration. Optimized geometries of $TM(C_3H_2BCH_3)_2$ and $TM(C_3H_2BCH_3)_2^+$ (TM = Cu, Ag and Au) with the lowest energy were displayed in Fig.

1. As seen from Fig. 1, the structures of $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ ($\text{TM} = \text{Cu, Ag and Au}$) are *cis*-configuration. The bond angles of C-TM-C in $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ ($\text{TM} = \text{Cu, Ag and Au}$) are 178.5° , 177.3° and 174.3° , respectively, which are close to a line. The bond distances of Cu-C bonds in complex $\text{Cu}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ are $1.863 \text{ \AA}$, which are well consistent with the experimental value of $1.8636(15) \text{ \AA}$ of $\text{Cu}(\text{Et}_2\text{-cAAC})_2$ [36]. The distances of C(Cu)-C, C(Cu)-C(H₂) and C(Cu)-B are 1.494 , 1.507 and $1.549 \text{ \AA}$, respectively, indicating the three bonds are all single bonds. The distances of Ag-C and Au-C bonds in $\text{Ag}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ and $\text{Au}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ are 2.144 and $2.083 \text{ \AA}$, respectively, which are slightly larger than the calculated value Ag-C($2.063 \text{ \AA}$) of $\text{Ag}(\text{cAAC})_2$ [34] and the experimental value Au-C($1.991 \text{ \AA}$) of $\text{Au}(\text{cAAC})_2$ [34,35]. The lengths of C(TM)-C, C(TM)-C(H₂) and C(TM)-B bonds in $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ ($\text{TM} = \text{Cu, Ag and Au}$) are close to 1.500 , 1.500 and $1.520 \text{ \AA}$, respectively, showing the C-C and C-B are single bonds. The sum of the bond angles of TM-C-B, TM-C-C(H₂), C(H₂)-C(TM)-C and B-C(TM)-B in $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ ($\text{TM} = \text{Cu, Ag and Au}$) are close to 360.0° , as a result, the C(TM) in $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ ($\text{TM} = \text{Cu, Ag and Au}$) is a ptC.

Fig. 1. Optimized geometries of the most stable complexes $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ ($\text{TM} = \text{Cu, Ag and Au}$) and their cations.

In contrast to the lowest energy structures of $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2$, the lowest energy isomers of $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2^+$ (TM = Cu, Ag and Au) are *vertical*-configuration as shown in Fig. 1. The distance of Cu-C bond in $\text{Cu}(\text{C}_3\text{H}_2\text{BCH}_3)_2^+$ is 1.920 Å and longer than that of in its neutral complex, which is consistent with the variation of Cu-C bond in $\text{Cu}(\text{cAAC})_2^+$ [34]. However, the lengths of Ag-C and Au-C bonds in $\text{Ag}(\text{C}_3\text{H}_2\text{BCH}_3)_2^+$ and $\text{Au}(\text{C}_3\text{H}_2\text{BCH}_3)_2^+$ are shorter than those of in $\text{Ag}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ and $\text{Au}(\text{C}_3\text{H}_2\text{BCH}_3)_2$, which are contrast with the vibration of TM-C bonds in $\text{TM}(\text{cAAC})_2^+$ (TM = Ag and Au). In order to better understand the variation of TM-C bonds in both $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2^+$ and $\text{TM}(\text{cAAC})_2^+$ compared with their neutral complexes, we have depicted the singly occupied molecular orbitals (SOMOs) of the complexes $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ (TM = Cu, Ag and Au) in Fig. 2. The SOMO of $\text{Cu}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ is a delocalized π bond covering the Cu atom and the two carbon atoms in ligands and consistent with that of $\text{TM}(\text{cAAC})_2$ [34], whereas the SOMOs of both $\text{Ag}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ and $\text{Au}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ are mainly the *d* orbitals of the Ag and Au atoms. Thus the lengths of Cu-C bonds in $\text{Cu}(\text{C}_3\text{H}_2\text{BCH}_3)_2^+$ are longer than those of in $\text{Cu}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ due to losing a bonding electron from the neutral complex. The lengths of TM-C bonds in $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2^+$ (TM = Ag and Au) are slightly shorter than those of in $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2$, which can attribute the decrease of the steric effect and the losing of an electron in the nonbonding SOMO. These results indicate the difference of bonding properties of cAAC and $\text{C}_3\text{H}_2\text{BCH}_3$ ligands.

Fig. 2. Plot of the SOMOs of the most stable complexes $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ and $\text{TM}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2$ (TM = Cu, Ag and Au).

We also carried out the natural bond orbital (NBO) analyses of $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ and $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2^+$ (TM = Cu, Ag and Au) and displayed the WBIs and total WBIs of ptCs in Fig. 3. The WBIs for the TM-C bonds in $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ (TM = Cu, Ag and Au) are 0.45, 0.34, 0.46, respectively. The WBIs of C(TM)-C, C(TM)-C(H₂) and C(TM)-B in $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ are close to 1.0, showing the C-C and C-B are single bonds. The total WBIs of ptCs in $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ (TM = Cu, Ag and Au) are 3.42, 3.50, 3.55 respectively, thus the ptCs obey the octal rule. The WBIs for the Cu-C bonds in $\text{Cu}(\text{C}_3\text{H}_2\text{BCH}_3)_2^+$ is smaller than that of in $\text{Cu}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ by 0.11, but that of Ag-C and Au-C in $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2^+$ (TM = Ag and Au) have a little variation compared with $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2$, as a result, the WBIs values are in agreement with the variation of the lengths of TM-C bonds. The WBIs of C(TM)-C bonds in $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2^+$ are around 1.34, indicating that C(TM)-C bonds are between single and double bonds.

Fig. 3. Selected WBIs (in plain) of bonds and total WBIs of carbon atoms (in bold) of the most stable complexes $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ (TM = Cu, Ag and Au) and their cations.

In order to investigate the steric effects of the ligands in $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ and $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2^+$ (TM = Cu, Ag and Au), $\text{TM}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2$ and $\text{TM}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2^+$ (TM = Cu, Ag and Au) were considered. Optimized geometries of the lowest energy structures of $\text{TM}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2$ and $\text{TM}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2^+$ were displayed in Fig. 4. The most stable structures of $\text{TM}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2$ are *trans*-configuration structures, different from the lowest energy structures of $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2$. Thus, the *trans*-configuration structures of $\text{TM}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2$ are favorable when the steric effect of the ligand increases. As can be seen from Fig. 4, the bond angles C-TM-C of the structures $\text{TM}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2$ are 179.8° , 176.2° and 175.9° , respectively, which are much closer to a line compared with $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2$. The lengths of Cu-C bonds in $\text{Cu}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2$ are approximate to those of in $\text{Cu}(\text{C}_3\text{H}_2\text{BCH}_3)_2$. The distances of C(Cu)-C, C(Cu)-C(Me₂) and C(Cu)-B bonds are 1.496, 1.515 and 1.540 Å, respectively. So the structure CuL_2 has no obvious difference with respect to different ligands of $\text{C}_3\text{H}_2\text{BCH}_3$ and $\text{C}_3\text{Me}_2\text{BCMe}_3$. In contrast, the structures of $\text{Ag}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2$ and $\text{Au}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2$ are significantly different from $\text{Ag}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ and $\text{Au}(\text{C}_3\text{H}_2\text{BCH}_3)_2$. For example, the distance of left TM-C bond in

TM(C₃Me₂BCMe₃)₂ (TM = Ag and Au) is shorter than those of right TM-C bond by 0.03 Å at least. Additionally, the lengths of C(Cu)-C, C(Cu)-C(Me₂) and C(Cu)-B bonds in Ag(C₃Me₂BCMe₃)₂ and Au(C₃Me₂BCMe₃)₂ are also different from those of in Ag(C₃H₂BCH₃)₂ and Au(C₃H₂BCH₃)₂. The sum of the bond angles of TM-C-B, TM-C-C(Me₂), C(Me₂)-C(TM)-C and B-C(TM)-B (TM = Cu, Ag and Au) are close to 360.0°, thus, the C(TM) is a ptC. In addition, the SOMOs of TM(C₃Me₂BCMe₃)₂ (TM = Cu, Ag and Au) are similar to the corresponding complexes of TM(C₃H₂BCH₃)₂ as displayed in Fig. 2.

Fig. 4. Optimized geometries of the most stable complexes TM(C₃Me₂BCMe₃)₂ (TM = Cu, Ag and Au) and their cations.

The most stable structures of TM(C₃Me₂BCMe₃)₂⁺ (TM = Cu, Ag and Au) are *vertical*-configuration, consistent with that of TM(C₃H₂BCH₃)₂⁺. The lengths of C(Cu)-C, C(Cu)-C(Me₂) and C(Cu)-B bonds in TM(C₃Me₂BCMe₃)₂⁺ are close to those of in TM(C₃H₂BCH₃)₂⁺, which the maximum difference is less than 0.005 Å. Therefore, the steric effects of ligands have little influence on the geometries of TML₂⁺ (TM = Cu,

Ag and Au).

Fig. 5 shows the WBIs of the C-C, C-B, TM-C bonds and the total WBIs of ptCs in $\text{TM}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2$ and $\text{TM}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2^+$. As seen from Fig. 5, the WBIs values of C-C, C-B, C-TM bonds and the total WBIs of ptCs in $\text{TM}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2$ and $\text{TM}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2^+$ have little variation compared with $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ and $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2^+$.

Fig. 5. Selected WBIs of bonds (in plain) and total bond indices of ptCs (in bold) of the most stable complexes $\text{TM}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2$ (TM = Cu, Ag and Au) and their cations.

Table 1 lists the electronic configurations of Cu, Ag and Au, as well as the binding energies of TML_2 (TM = Cu, Ag and Au; L = $\text{C}_3\text{H}_2\text{BCH}_3$ and $\text{TM}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2$) with respect to two ligands and TM. The electronic configurations of TM in $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ and $\text{TM}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2$ are around $4s^{0.50}3d^{9.70}$ (Cu), $5s^{0.70}4d^{9.80}$ (Ag) and $6s^{0.90}5d^{9.70}$ (Au), respectively, indicating the different ligands have little influence on the electronic configurations of TM. The orders of the binding energies of $\text{TM}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ and $\text{TM}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2$ (TM = Au, Ag and Au) are $\text{Cu} > \text{Au} > \text{Ag}$.

Table1

Electronic state, the smallest vibrational frequencies ($\nu_{\min}$, in cm^{-1}), electronic configuration (EC) of TM, bonding energies (E_b , in kcal/mol) with respect to (TM and two ligands) of the most stable structures TML_2 (TM = Cu, Ag and Au; L = $\text{C}_3\text{H}_2\text{BCH}_3$ and $\text{C}_3\text{Me}_2\text{BCMe}_3$).

Complexes	State	$\nu_{\min}$	EC	E_b
$\text{Cu}(\text{C}_3\text{H}_2\text{BCH}_3)_2$	^2A	30	$4s^{0.48}3d^{9.72}$	54.87
$\text{Ag}(\text{C}_3\text{H}_2\text{BCH}_3)_2$	^2A	20	$5s^{0.66}4d^{9.83}$	20.22
$\text{Au}(\text{C}_3\text{H}_2\text{BCH}_3)_2$	^2A	19	$6s^{0.91}5d^{9.67}$	33.11
$\text{Cu}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2$	^2A	18	$4s^{0.45}3d^{9.72}$	63.77
$\text{Ag}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2$	^2A	23	$5s^{0.62}4d^{9.83}$	26.07
$\text{Au}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2$	^2A	17	$6s^{0.87}5d^{9.68}$	38.88

As shown in Table 2, the NBO results of the silver complexes $\text{Ag}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ and $\text{Ag}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2$ indicate that a singly occupied Ag-C bonding orbital (occupation about 0.87) is strongly polarized to carbon (more than 70%). The NBO calculations of the gold complexes $\text{Au}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ and $\text{Au}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2$ reveal that there are two one-electron Au-C bonds (occupation about 0.90). Hence, the hybridization of both Ag-C and Au-C bonds may be identified as $\text{Ag} \leftarrow \text{L}$ and $\text{Au(s)} \leftarrow \text{L}$ σ donor bonds. In addition, the conjugate orbitals were not found in the molecular orbitals of $\text{Ag}(\text{C}_3\text{H}_2\text{BCH}_3)_2$, $\text{Ag}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2$, $\text{Ag}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ and $\text{Ag}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2$, thus, $\text{Ag(s)} \rightarrow \text{L}$ and $\text{Au(s)} \rightarrow \text{L}$ π back bonding do not exist. Interestingly, we did not find the localized molecular orbital between Cu and C but find a π orbital as illustrated in Fig. 2. Therefore, it further confirms that the TM-C bonds in $\text{Cu}(\text{C}_3\text{H}_2\text{BCH}_3)_2$ and $\text{Cu}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2$ origin from the conjugate effect.

Table 2

NBO results of the TM-C bonds in TML_2 (TM = Ag and Au; L = $C_3H_2BCH_3$ and $C_3Me_2BCMe_3$) at the M06/def2-SVP level of theory.

Species	occ.	polarization	hybridization(TM)	hybridization(C)
$Ag(C_3H_2BCH_3)_2$	0.87	Ag: 22.1%	s (87.7%), p (3.0%),	s (33.0%),
		C: 77.9%	d (9.4%)	p (67.0%)
$Au(C_3H_2BCH_3)_2$	0.89	Au: 27.5%	s (80.5%), p (1.75%),	s (30.0%),
		C: 72.5%	d (17.7%)	p (66.0%),
$Au(C_3H_2BCH_3)_2$	0.89	Au: 20.1%	s (82.4%), p (2.4%),	s (38.4%),
		C: 79.9%	d (15.1%)	p (61.5%),
$Ag(C_3Me_2BCMe_3)_2$	0.85	Ag: 28.7%	s (87.5%), p (3.8%),	s (10.7%),
		C: 71.3%	d (8.7%)	p (89.2%),
$Au(C_3Me_2BCMe_3)_2$	0.92	Au: 32.4%	s (81.5%), p (2.4%),	s (19.7%),
		C: 67.6%	d (16.1%)	p (80.3%),
$Au(C_3Me_2BCMe_3)_2$	0.89	Au: 21.8%	s (82.5%), p (3.5%),	s (37.6%),
		C: 78.2%	d (14.0%)	p (62.4%),

The vertical electron transition energies and the associated transition orbitals of the most stable $TM(C_3H_2BCH_3)_2^+$ and $TM(C_3Me_2BCMe_3)_2^+$ (TM = Cu, Ag and Au) calculated at M06 level were listed in Table 3. The first vertical transition energies of $TM(C_3H_2BCH_3)_2^+$ are 274.64, 243.34 and 246.24 associated with the $d-\pi$ transition as seen from Fig. 1S (in Supporting Information). The first vertical transition energies of $TM(C_3Me_2BCMe_3)_2^+$ are light blue shift compared with the $TM(C_3H_2BCH_3)_2^+$. Moreover, the first vertical transition energies are consistent with those of $TM(NHC)_2$ [45].

Table 3

The smallest vibrational frequencies ($\nu_{\min}$, in cm^{-1}), the first vertical transition energies (λ , in nm), oscillator strengths (f) and the associated transition orbitals of the most stable TML_2^+ complexes (TM = Cu, Ag and Au; L = $\text{C}_3\text{H}_2\text{BCH}_3$ and $\text{C}_3\text{Me}_2\text{BCMe}_3$).

Species	$\nu_{\min}$	λ	f	Transition orbitals
$\text{Cu}(\text{C}_3\text{H}_2\text{BCH}_3)_2^+$	25	274.64	0.0131	HOMO→LUMO
$\text{Ag}(\text{C}_3\text{H}_2\text{BCH}_3)_2^+$	17	243.34	0.0082	HOMO→LUMO
$\text{Au}(\text{C}_3\text{H}_2\text{BCH}_3)_2^+$	16	246.24	0.0098	HOMO→LUMO
$\text{Cu}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2^+$	16	290.83	0.0046	HOMO→LUMO
$\text{Ag}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2^+$	16	253.69	0.0094	HOMO→LUMO
$\text{Au}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2^+$	16	261.25	0.0122	HOMO-1→LUMO

We have further designed the reactions of $\text{Ag}(\text{C}_3\text{H}_2\text{BCH}_3)_2^+$ and $\text{Ag}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2^+$ with (tht)AuBr to yield Au(I) complexes of $(\text{C}_3\text{H}_2\text{BCH}_3)\text{AuBr}$ (**A1**), ionic $\text{Au}(\text{C}_3\text{H}_2\text{BCH}_3)_2^+$ (**B1**), $(\text{C}_3\text{Me}_2\text{BCMe}_3)\text{AuBr}$ (**C1**), and $\text{Au}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2^+$ (**D1**). Optimized geometries of **A1**, **B1**, **C1** and **D1** were showed in Fig. 6. The variations of the energies including zero point energies and the Gibbs free energies of the four reactions are all negative, showing these reactions are thermodynamically favorable. Moreover, the reactions of $(\text{C}_3\text{H}_2\text{BCH}_3)\text{AuBr}$ (**A1**), ionic $\text{Au}(\text{C}_3\text{H}_2\text{BCH}_3)_2^+$ (**B1**), $(\text{C}_3\text{Me}_2\text{BCMe}_3)\text{AuBr}$ (**C1**), and $\text{Au}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2^+$ (**D1**) with CsBr_3 to produce Au(III) complexes of $(\text{C}_3\text{H}_2\text{BCH}_3)\text{AuBr}_3$ (**A3**), $(\text{C}_3\text{H}_2\text{BCH}_3)_2\text{AuBr}_2^+$ (**B3**), $(\text{C}_3\text{Me}_2\text{BCMe}_3)\text{AuBr}_3$ (**C3**) and $(\text{C}_3\text{Me}_2\text{BCMe}_3)_2\text{AuBr}_2^+$ (**D3**) were also theoretically carried out.

Fig. 6. The processes of the reactions of $\text{Ag}(\text{C}_3\text{H}_2\text{BCH}_3)_2^+$ and $\text{Ag}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2^+$ with $(\text{tht})\text{AuBr}$ and optimized geometries and the smallest vibrational frequencies in the parentheses (in cm^{-1}) of **A1**, **B1**, **C1**, **D1**, **A2**, **B2**, **C2** and **D2**.

Optimized geometries, WBIs and the smallest vibrational frequencies of Au(III) complexes **A3**, **B3**, **C3** and **D3** were displayed in Fig. 7. The calculated vibrational frequencies of the lowest structures **A3**, **B3**, **C3** and **D3** are positive, indicating they are the true minima on the potential energy surfaces. The distances of the horizontal C-C and Au-C bonds in **A3**, **B3**, **C3** and **D3** are in the range of 1.420-1.431 and 2.060-2.090 Å, respectively, indicating that the horizontal C-C and Au-C bonds in **A3**, **B3**, **C3** and **D3** were not influenced by the groups bound to C and B atoms. However, the lengths of C-C and C-B bonds in **A3**, **B3**, **C3** and **D3** have a significant relationship with the groups bound to C and B atoms. The lengths of C(Au)-C(H₂) or C(Au)-C(Me₂) bonds in **A3**, **B3**, **C3** and **D3** are 1.503, 1.518, 1.540 and 1.567(1.564), respectively, which shows C(Au)-C(H₂) or C(Au)-C(Me₂) are single bonds. The C(Au)-B bonds in **A3**, **B3**, **C3** and **D3** are also single bonds, whose lengths are 1.547, 1.568, 1.528 and 1.538(1.537),

respectively. The variations of lengths of C(Au)-C(H₂) or C(Au)-C(Me₂) and C(Au)-B bonds in **A3**, **B3**, **C3** and **D3** are **A3**<**B3**<**C3**<**D3** and **C3**<**D3**<**A3**<**B3**. Therefore, when the H atoms bound to C and B atoms in ligands 2-borabicyclo[1.1.0]but-1(3)-ene are replaced with –Me groups, the lengths of C(Au)-C(H₂) bonds increase, while the distances of C(Au)-B bonds decrease. The sum of the bond angles of Au-C(Au)-B, Au-C(Au)-C(H₂), C(H₂)-C(Au)-C and C-C(Au)-B in **A3**, **B3**, **C3** and **D3** are close to 360.0°, thus, the C(Au) in **A3**, **B3**, **C3** and **D3** are ptCs.

Fig. 7. Optimized geometries (in plain), WBIs (in bold) and the smallest vibrational frequencies in the parentheses (in cm⁻¹) of Au(III) complexes **A3**, **B3**, **C3** and **D3** obtained from the reactions of **A1**, **B1**, **C1** and **D1** with CsBr₃.

4. Conclusions

We theoretically designed the complexes TML₂ and TML₂⁺ with ptCs (TM = Cu, Ag and Au; L are the derivatives of 2-borabicyclo[1.1.0]but-1(3)-ene, C₃H₂BCH₃ and C₃Me₂BCMe₃) and investigated their stabilities as well as bonding using density

functional theory M06 method. The main conclusions are, (1) the lengths of Au-C and Ag-C bonds in TML_2 (TM = Ag and Au) are longer than those of in their cations, while the lengths of Cu-C in CuL_2 are smaller than those of in CuL_2^+ ; (2) the NBO analyses of TML_2 and TML_2^+ (TM = Cu, Ag and Au) reveal that the Cu-C bonds in CuL_2 are conjugated π bonds, whereas Ag-C and Au-C in TML_2 (TM = Ag and Au) are σ bonds; (3) the first electron transition energies of TML_2^+ (TM = Cu, Ag and Au) results from the d - π transition, and the wavelengths are close to 260 nm; (4) the reactions of $\text{Ag}(\text{C}_3\text{H}_2\text{BCH}_3)_2^+$ and $\text{Ag}(\text{C}_3\text{Me}_2\text{BCMe}_3)_2^+$ with (tht)AuBr were theoretdynamicaly favorable; (5) the Au(III) complexes $(\text{C}_3\text{H}_2\text{BCH}_3)_2\text{AuBr}_2^+$ and $(\text{C}_3\text{Me}_2\text{BCMe}_3)_2\text{AuBr}_2^+$ with ptCs were theoretically found to be stable.

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