In-Depth Investigation of a Donor–Acceptor Interaction on the Heavy-Group-14@Group-13-Diyls in Transition-Metal Tetrylone Complexes: Structure, Bonding, and Property

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ABSTRACT: Stabilization for tetrylone complexes, which carry ylidone(0) ligands \([\{\text{CO}\},\text{W-X}(\text{YPPh}_3)^*]_2\) (X = Ge, Sn, Pb; Y = B–Tl), has become an active theoretical research because of their promising application. Structure, bonding, and quantum properties of the transition-metal donor–acceptor complexes were theoretically investigated at the level of theory BP86 with several types of basis sets including SVP, TZVPP, and TZ2P+. The optimized structures reveal that all ligands X (YPPh3)* are strongly bonded in tilted modes to the metal fragment W(CO)5 and Cp* rings are mainly \(\eta_3\)-bonded to atom X. DFT-based bonding analysis results in an implication that the stability of W–X bond strength primarily stems from the donation \(\{\text{CO}\},\text{W} \leftarrow \text{X}(\text{YPPh}_3)^*\) formed by both \(\sigma\) and \(\pi\)-bondings and the electrostatic interaction \(\Delta E_{\text{elstat}}\). The W–X bond possesses a considerable polarizability toward atom X, and analysis on its hybridization is either \(sp^2\)-characteristic or mainly \(p\)-characteristic. EDA-NOCV-based results further imply that the ligands XY perform as significant \(\sigma\)-donors but minor \(\pi\)-donors. The visual simulations of NOCV pairs and the deformation densities assemble a comprehensive summary on different components of the chemical bond via \(\sigma\) and \(\pi\)-types in the complexes. This work contributes to the literature as an in-depth overview on predicted molecular structures and quantum parameters of the complexes \([\{\text{CO}\},\text{W-X}(\text{YPPh}_3)^*]_2\) (X = Ge, Sn, Pb; Y = B–Tl), conducive to either further theoretical reference or extending experimental research.

INTRODUCTION

In general, the Group-14 yldones XL2 with X = C–Pb, possessing two lone pairs at the X central atom, are called tetrylone ligands. They are composed of a central atom X(0) and two ligands L in a donor–acceptor coordination (L: \(\rightarrow X(0) \leftarrow \);L).

The latter was first reported as phosphines, i.e., PR3, including PPh3 and less bulky PH3. Regarding ligands L, there has been a variety of zero-valent Group-14 compounds XL2 that are of interest, such as L = N-heterocyclic carbenes (NHCs), YPh3* (Y = B–Tl), cAAC (cyclic alkyl amino carbene), etc. It is proposed that the divalent X(0) compounds isolated are stabilized by the \(\sigma\)-donating induced from two lone pairs of the ligand according to the octet rule. The mechanism of two strong \(\sigma\)-donating carbones supporting the heavier X(0) species (X = Si, Ge) was discovered by Roosky et al. and Driess et al. In addition, the extension of the XL2 group of yldones to other ligands was reported by Nikonov et al. and Flock et al. for germanium(0) compounds, Ge(0), and tin(0) compounds, Sn(0), respectively. Some theoretical studies projected the important role of tetrylone ligands for the stability of the X central atoms in the structures and electronic properties of the ylidone(0) ligands in complexes. Also, the marked dependence of X–L bond length on the donor–acceptor capability of ligand L was extensively demonstrated.

A recent study investigated the structures and chemical bonding of the main Group-14 elements in transition-metal (TM) complexes that carry bulky tetrylone ligands, i.e., \([\{\text{W(CO)}_4\},\{X(\text{PPh}_3)_2\}]\) (X = C–Pb). The work arrived at two main findings. First, the end-on bonding configuration was observable in carbone complexes and the heavier systems performed the side-on bonding manners. Second, the bond dissociation energy value has a positive correlation with molecular mass. Another research led to a conclusion that the tetrylones in the two systems \([\{\text{W(CO)}_4\},\{X(\text{PPh}_3)_2\}]\) and \([\{\text{W(CO)}_3\},\{X(\text{PPh}_3)_2\}]\) always utilize their two lone-pair orbitals available for donation ligand \(\rightarrow\) transition-metal complex.

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of chemical bonding for complexes. To the best of our
(NOCV) was used to obtain in-depth information on the nature
NOCV method combining energy decomposition analysis
using natural bond orbital (NBO) analysis. Finally, the EDA-
diyls ligands X(YCp

Klein and Frenking reported for the first time the structures and
bonding configuration of the new class of stable carbenes CL2,
in which L is a Group-13 diyl ligands YCp* (Y = B−Tl).
Many theoretical studies reported that the diyl ligand YCp*
appears as a stronger σ-donor and weaker π-acceptor, thus attracting much attention from scientists.30−22,23 This helps YCp*
ligands act as suitable candidates for stabilizing a divalent carbon(0) atom in the carbone ligand C(YCp*)2.27

It was demonstrated that the Group-13 diyl compounds Cp*Y
(Y = Al, Ga, In) play the role of Lewis bases thanks to the existence of the electron lone pair.29 In particular, monovalent
MR' metal ligands (M = Zn, Cd; R' = Me, Et, Cp*; and M = Au; R' = PMe3, PPh3) are considered as one-electron ligands of
chemistry.30−22,23 If Cp* groups with soft and flexible binding mode were associated, the intrinsic tension of aluminium and gallium
compounds would be reduced. The explanation relates to the unique steric and electronic features of the versatile ligand
YCp*, including the strong electron-donating, carbenoid character, the high flexibility of the Cp* binding modes. In particular, Nhung et al. also reported the new complexes between silylene SiL2 (L = Group-13 diyls; B−Tl)
with transition-metal compounds Mo(CO)5.31 The tetrylone ligands Si(YCp*)2 in complexes [(CO)5Mo-Si(YCp*)2] were theoretically predicted to perform as strong σ-donors and weak π-
donors. The results suggested that the Group-13 diyls could effectively stabilize the central Si atom.31

In this work, a detailed comprehensive theoretical research of
divalent ylidone(0) compounds on their geometric representation
of coordination modes is compiled. The complexes [(CO)5W-X(YCp*)2] contain heavy-Group-14@Group-13-
element ligands X(YCp*)2, in which X = Ge, Sn, Pb and Y = B−Tl, and W(CO)5. First, the equilibrium geometry, energy, and chemical bonding of tungsten complexes that carry Group-
diyls W(CO)5-X(YCp*)2 (W-XY) were calculated. The bond dissociation energies with and without dispersion corrections were then predicted with gradient corrected density functional theory (DFT). Bonding analysis was carried out by calculating the energetically low-lying occupied molecular orbitals for σ- and π-orbitals of the free ligands [X(YCp*)2] using natural bond orbital (NBO) analysis. Finally, the EDA-
NOCV method combining energy decomposition analysis (EDA) and charge of natural orbitals for chemical valence (NOCV) was used to obtain in-depth information on the nature of chemical bonding for complexes. To the best of our
knowledge, this is the first time that geometric structures, bonding properties, and complementary quantum parameters of
tungsten complexes that carry the heavy-Group-14@Group-13-
diyls ligands X(YCp*)2 are systematically summarized in an
overview-based research. Scheme 1 illustrates the Lewis structures of donor–acceptor compounds investigated in this
work, including the complete complexes (denoted as W-XY)
and the free ligands (denoted as XY).

Scheme 1. Overview of Donor−Acceptor Compounds
Investigated in This Work: (Left) Complexes: [W(CO)5-
X(YCp*)2] (W-XY) and (Right) Tetrylone Ligands:
[X(YCp*)2] (XY) with X = Ge, Sn, Pb; and Y = B−Tl

Geometrical Parameters of Optimized Structures and Energies. Figure 1 presents quantum parameters, including bond lengths and bond angles, of all optimized geometries of complexes W-XY. W−X bond length is negatively correlated with the mass of Y, from the lightest boron complexes W-XB to the heaviest thallium systems W-XTl. This reveals that the thallium-complexes have the shortest W−X bonds in their germylones, stannylones, and plumbylones, i.e., W-GeTl (W-Ge at 2.612 Å), W-SnTl (W-Tl at 2.807 Å), and W-PbTl (W-Pb at 2.880 Å), respectively. In contrast, X−Y bonds register the opposite tendency as their length increases when the mass of the adducts is heavier. The shortest length values are 2.078 and 2.088 Å (Ge-B) in germylones, 2.337 and 2.348 Å (Sn-B) in stannylones, and 2.472 and 2.487 Å (Pb-B) in plumbylones. The results are consistent with our previous study on silylone systems [(CO)5Mo-Si(YCp*)2], in which the bond length value of Mo−Si increases if the YCp* homologue is heavier while a negative correlation was observed between the Si−Y bond length and the mass of the Group-13 Y adducts (Y = B−Tl).31 The bonding mode of the Y-Cp* homologue is also acquired from the optimized structures of the complexes W-XY. The bond length values of Y and carbon atoms in the rings in all lighter complexes with atoms Y from B to In are nearly equal regarding each complex. The figures for germylones, stannylones, and plumbylones vary in the range of 1.811−2.649, 1.804−2.651, and 1.805−2.646 Å, respectively. This indicates that they perform quasi-η4 bonded manners, interacting through the center of the ring-planes. Meanwhile, the bond length of Tl and the carbon atoms of Cp* rings in tetrylone@thallium complexes W-XTl varies significantly, i.e., 2.643−2.864 Å for W-GeTl, 2.642−2.860 Å for W-SnTl, and 2.649−2.854 Å for W-PbTl. These suggest that Tl−Cp* bonding is between η2− and η1-configurations. The bonding modes are further illustrated and summarized in Table 1.

Table 1 and Figure 1 also provide information on bending angle α of the side-on bonding between ligands XY and metal
fragment W(CO)5. In general, the bending angle value of W-XY
bonds in the complexes follows the order germylones > stannylones > plumbylones in which bending angle α in W-
SnY and W-PbY becomes more acute in the heavier systems
(B−In). This resembles the tendency of other tetrylone ligands
bonded in a tilted orientation relative to the metal fragment
W(CO)5 (x = 4, 5) in their optimized structures.1,14 The studies have recently reported a decrease of the corresponding bending

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Figure 1. Selective parameters (bond lengths/Å and bond angles/°) of complex W-XY (X = Ge, Sn, Pb; Y = B−Tl) optimized structures at the BP86/def2-SVP level.
Table 1. Selective Parameters of Bond Length (Å), Bond Angle (°), Bending Angle (α/°), the Angle W−X−Z of Complexes W-XY Containing the Two Fragments [W(CO)$_5$] and [X(YCp)$_2$] where Z is the Midpoint of the Y−Y Distance, and Bonding Mode of YCp* with the Alternatives for the Cp* Ring for the Optimized Complexes W-XY (X = Ge, Sn, Pb; Y = B−Tl) Calculated at the BP86/def2-SVP Level

| complex   | bonding angle (α/°) | bonding mode of YCp* with the alternatives for the Cp* ring |
|-----------|---------------------|------------------------------------------------------------|
| W-GeB     | 125.1               | η$_5^*$                                                    |
| W-GeAl    | 98.8                | η$_3^*$                                                    |
| W-GeGa    | 104.4               |                                                            |
| W-GeIn    | 106.5               | η$_3^*$                                                    |
| W-GeTl    | 110.9               | η$_5^*$ to η$_3^*$                                         |
| W-SnB     | 112.9               | η$_5^*$                                                    |
| W-SnAl    | 94.4                | η$_3^*$                                                    |
| W-SnGa    | 98.6                | η$_3^*$                                                    |
| W-SnIn    | 99.8                | η$_3^*$                                                    |
| W-SnTl    | 105.3               | η$_5^*$ to η$_3^*$                                         |
| W-PbB     | 107.3               | η$_5^*$                                                    |
| W-PbAl    | 91.6                | η$_3^*$                                                    |
| W-PbGa    | 96.2                |                                                            |
| W-PbIn    | 97.4                | η$_3^*$                                                    |
| W-PbTl    | 102.7               | η$_3^*$ and η$_3^*$                                        |

angle from germylones to plumbylones, i.e., from $119.5^\circ$ in [(CO)$_5$W-Ge(PPh$_3$)$_2$] to $114.5^\circ$ in [(CO)$_5$W-Pb(PPh$_3$)$_2$] and from $105.5^\circ$ in [(CO)$_3$W-Ge(PPh$_3$)$_2$] to $99.3^\circ$ for [(CO)$_3$W-Pb(PPh$_3$)$_2$]. In each Group-14 homologue, boron systems exhibit the closest values to $180^\circ$, which are $125.1^\circ$ for W-GeB, $112.9^\circ$ for W-SnB, and $107.3^\circ$ for W-PbB. Meanwhile, the smallest corresponding figures are observed in aluminum complexes, which are $98.8^\circ$ for W-GeAl, $94.4^\circ$ for W-SnAl, and $91.6^\circ$ for W-PbAl. These reveal that the former is expected to be the most stable system as its main bonding is in highest alignment while the aluminum systems register the opposite property of stabilities as their W-XY bonds approach right-angled arrangements. From Al to Tl, the bonding angle $α$ is in a positive correlation with the complex mass and stands at $110.9^\circ$ for W-GeTl, $105.3^\circ$ for W-SnTl, and $102.7^\circ$ for W-PbTl.

The optimized geometries of free ligands XY were also investigated and are presented in Figure 2. B1−C and B2−C bonds of Cp* rings in complexes W-XY exhibit different bond length values when forming the two groups B1Cp* and B2Cp*. The ligand XB that embraces atom B1 is η$_3^*$-connected to the carbon atoms of Cp* rings whose bonding length varies narrowly from 1.812 to 1.847 Å for GeB, from 1.808 to 1.835 Å for SnB, and from 1.813 to 1.839 Å for PbB. However, the atom B2 η$_1^*$-bonds to the carbon atoms of Cp* rings whose bond lengths are in significantly wider ranges, i.e., 1.605−2.598 Å for GeB, 1.600−2.544 Å for SnB, and 1.597−2.549 Å for PbB. Also, Tl has a tendency of η$_3^*$ bonding in its link toward Cp*, with longest and shortest bonds being 2.458 and 3.208 Å for GeTl, 2.507 and 3.065 Å for SnTl, 2.513 and 3.064 Å for PbTl. Meanwhile, the calculated equilibrium structures of free ligands XY with Y = Al−In show that the YCp* is consistently η$_3^*$-linked to atoms Y with the bond length values Y−C of Cp* rings.

Table 2 shows the theoretically predicted BDEs, DFT-$D_0$ (kcal mol$^{-1}$), of the bond W−X for W-XY. Overall tendency sees an increase along with the rise of the complex mass (from B to Tl). However, there are noticeable inconsistencies occurring at W-XAI systems in stannylones and plumbylones. In detail, the value $D_0$ of the boron system in germylones W-GeB registers the smallest value of 44.4 kcal mol$^{-1}$ and the corresponding figure for other homologues in this tetrylone family increases for the heavier complexes. Regarding stannylone systems, the BDE values of W-SnB, W-SnAl, W-SnGa, W-SnIn, and W-SnTl are 49.0, 46.7, 49.5, 49.9, and 53.9 kcal mol$^{-1}$, respectively.

This is brief that BDE values of the complexes decrease when their mass increases accordingly from B to Al before the overall tendency is observed thereafter. A similar inconsistency is also recorded in the plumbylone family, in which W-PbAl reaches a low at 46.2 kcal mol$^{-1}$ between higher BDE values of W-PbB (50.5 kcal mol$^{-1}$) and W-PbGa (49.9 kcal mol$^{-1}$) and the thallium system that contains W-PbTl accounts for the highest BDE value (52.8 kcal mol$^{-1}$). In summary, the results suggest that the heavier complexes possess stronger bonds W−X than their lighter counterparts, except for stannylone and plumbylone boron-complexes. From this, it can be pointed out that the longer bonds length do not involve that the strength bonds are weaker.$^{32−34}$

In addition, dispersion forces might affect the theoretically calculated energy results, especially on the theoretical prediction for BDEs.$^{35−37}$ These are especially significant if the structures comprise bulky ligands, such as Cp* groups in this study. Therefore, the calculated BDEs with dispersion interactions on the main bonding W−X in complexes W-XY (DFT-D3) are also included in Table 2. Overall, the DFT-$D_0$ and DFT-D3 values of the (CO)$_3$W-X(YCp)$_2$ bond strength experience a similar varying pattern. Thallium complexes W-XTI still hold the highest figure for BDEs, which are 72.3, 75.7, and 75.0 kcal mol$^{-1}$ according to its germlynone, stannylone, and plumbylone homologues, respectively. The two latter complexes are followed by boron complexes, while the second highest value among germylones is observed in W-GeIn. In detail, with the inclusion of dispersion forces, the BDE results of complexes W-XY register elevated values whose average rising index is ca. 20 kcal mol$^{-1}$, from 5.0 kcal mol$^{-1}$ for other homologues in this tetrylone family increases. The BDE values for W-CO and W(CO)$_5$, which draws dispersive contribution from bulky Cp* groups, are$^{1,31,38}$ The contributions from dispersion interactions of germlylone complexes W-GeY, stannylone complexes W-SnY, and plumbylone complexes W-PbY are expressed in term of $D_0$, $D_-$, and W-XY. Overall tendency sees a similar changing tendency regarding WBI values.
of $W-X$ bonds, which are overall positively correlated with the complex mass in each family. The ranges are 0.58–0.98, 0.60–0.84, and 0.55–0.81 for germylone, stannylone, and plumbylone systems (from $W-XB$ to $WX-Tl$), respectively. However, WBI values of the $X-Y$ bond peak at 1.22, 1.13, and 1.10 for $W-GeAl$, $W-SnAl$, and $W-PbAl$, respectively. Meanwhile, the figures in their respective tetrylone family follow the order $W-XB > W-XGa > W-GeIn > W-GeTl$. In comparison to free ligands $XY$, the bond orders approximated by WBI indices of both $X-Y$ and $Y-Y$ bonds in their corresponding complexes are significantly lower. The calculated partial charges show that the metal fragment $W(CO)_5$ in $W-XY$ always carries a negative charge, which are between $-0.76e$ and $-0.86e$ in germylones, between $-0.90e$ and $-0.99e$ in stannylones, between $-0.91e$ and $-1.03e$ in plumbylones. This suggests that an inclination of charge donation $(YCp^*)_X W(CO)_5$ is expected in complexes. Therefore, the positive charges are likely to be localized at germylone, stannylone, and plumbylone ligands. In detail, tungsten atoms are calculated carrying significantly large negative charges, which are over $-1.80e$ in all the tetrylone complexes. In contrast, the Group-14 ($X$) and Group-13 ($Y$) atoms tend to be localized with a positive charge when in the systems $W-XY$. This excludes three aluminum atoms ($-0.50$ for $W-GeAl$, $-0.10$ for $W-SnAl$, $-0.01$ for $W-PbAl$). Without the contribution of tetrylone groups, the charge of the atoms (in the free ligands $XY$) both shifts toward more negative values.

Figure 2. Selective parameters (bond lengths/Å and bond angles/°) of free ligand $XY$ ($X = Ge, Sn, Pb; Y = B–Tl$) optimized geometries and bonding mode of $Y-Cp^*$ at the BP86/def2-SVP level.
Regarding plumblylone complexes W-PbY, a different arrangement of occupied molecular orbitals and orbital energy levels of σ- and π-type MOs is observed. In detail, the energy levels of the σ-type donor orbitals are lower-lying than those of the π-type donor orbitals except W-PbB.\cite{4,15} Besides, although the molecules investigated possess C1 symmetry, their frontier molecular orbitals of easy σ- and π-type MOs obtained by visual inspection do not always occur as symmetrical. Germylone complexes W-GeY have π-type symmetry in HOMO-2 and HOMO-7 and σ-type symmetry in HOMO-4 and HOMO-8. In terms of plumblylone complexes W-PbY, HOMO-2 to HOMO-4 and HOMO-6 are in π-type symmetry; meanwhile, HOMO, HOMO-3, and HOMO-4 are in σ-type symmetry. In addition, the shape of the MOs in complexes W-XY indicates that both σ- and π-contributions are (CO)\textsubscript{5}W→X(YCp\textsuperscript{*})\textsubscript{2}.31,38 Given the energy levels of the σ- and π-orbitals from the frontier orbital plotting, W–X bonds are formed by significantly strong σ- and π-bonding molecular orbitals. Because of the possible interaction between π-lone-pair orbitals of the ligands X(YCp\textsuperscript{*})\textsubscript{2} and the metal fragment W(CO)\textsubscript{5}, the strength of the π-orbitals is suggested with further examination.

The frontier orbitals with the plot of the energy levels of the highest energetically lying σ- and π-orbitals of the free ligands XY with X = Ge–Pb and Y = B–Tl are shown in Figure 4 for additional reference. Overall, W(CO)\textsubscript{5} adducts seem to stabilize the systems given the lower HOMO energy of the complex (CO)\textsubscript{5}W-X(YCp\textsuperscript{*})\textsubscript{2} than those of their corresponding free ligand X(YCp\textsuperscript{*})\textsubscript{2} counterparts. The inconsistent exceptions are addressed at π-type bonding orbitals of heavy tetrylones, including GeY (Y = In–Tl), SnY (Y = In–Tl), and PbY (Y = Al–Tl). This could be explained by the shape of the HOMO making it flawlessly suitable as π-donor orbitals.\cite{2,4}

The energy levels of the two highest-lying occupied MOs, which have σ- or π-symmetries for the free ligands X(YCp\textsuperscript{*})\textsubscript{2}, are briefed in Figure 5. It is clear that the energy level of the π- and the σ-orbitals of X–Y bonds decreases when its atom X becomes heavier. Also, the back-lobe of the tetrylone π-lone-pair can raise a certain bonding contribution toward atom Y. Therefore, the consequence could be a tilted configuration formed in the structure of tetrylone ligands XY bonded with the.
metal fragment W(CO)$_5$. This possibly explains the optimized structures of complexes W-XY, which are presented before in Figure 1 and Table 1.

Table 4 presents the polarization of the σ-bonds W–X between the transition-metal fragment and ylidone(0) ligands in W-XY and the hybridization of the W–X bonds at atom X (X = Ge, Sn, Pb) gained from NBO analysis. The polarization of atom
W in the bonds W−X rises with the rise of the tetrylone mass, which are from 35.4 to 46.9% for W-GeY, from 36.8 to 54.6% for W-SnY, and from 38.7 to 56.2% for W-PbY (Y = B−Tl). Regarding each tetrylone family, the value is positively correlated with the complex mass. This also means that the corresponding figure for X sees an opposite changing pattern. The hybridization of atom X with %s characteristics registers the largest values in complexes W-XB, i.e., 40.8, 43.3, and 37.8% for W-GeB, W-SnB, and W-PbB, respectively. The corresponding figures for heavier tetrylones in each family do not see noticeable differences, and all are under 20%. These indicate that the contribution of p-hybridization in borane systems is slightly more than their s-counterparts while the heavier complexes witness the marked dominance of p-hybridization whose contribution is within the range of 82.6−91.6%. The former explains the slightly tilted bonding of W−XY bonds in borane complexes W-GeB, W-SnB, and W-PbB given the approximate sp² hybridization; meanwhile, the W−XY bonds in heavier homologues exhibit mainly p-characteristics between σ-

Figure 4. Molecular orbitals and orbital energies (eV) of σ- and π-type MOs for the ligands XY (X = Ge, Sn, Pb; Y = B−Tl) at the BP86/def2-TZVPP level.

Figure 5. Energy levels (eV) of the σ- and π-type orbitals for the free ligands XY (X = Ge, Sn, Pb; Y = B−Tl) at the BP86/def2-TZVPP level.
Table 4. Polarization of σ-Bonds W–X and Hybridization at Atom X from the NBO Analysis of the Complexes W-XY (X = Ge, Sn, Pb; Y = B–Tl) at the BP86/def2-TZVPP // BP86/def2-SVP Level

| complex   | polarization W–X | hybridization | % (W) | % (X) | %s (X) | %p (X) |
|-----------|------------------|---------------|-------|-------|--------|--------|
| W-GeB     | 35.4             | 64.6          | 40.8  | 59.2  |        |        |
| W-GeAl    | 39.0             | 61.0          | 10.4  | 88.5  |        |        |
| W-GeGa    | 40.3             | 59.7          | 13.3  | 86.2  |        |        |
| W-GeIn    | 43.8             | 56.2          | 15.7  | 83.9  |        |        |
| W-GeTI    | 46.9             | 53.1          | 17.1  | 82.6  |        |        |
| W-SnB     | 36.8             | 63.2          | 43.3  | 56.3  |        |        |
| W-SnAl    | 44.7             | 55.3          | 9.4   | 89.5  |        |        |
| W-SnGa    | 46.1             | 53.9          | 11.4  | 88.3  |        |        |
| W-SnIn    | 48.7             | 51.3          | 11.7  | 88.0  |        |        |
| W-SnTI    | 54.6             | 45.4          | 12.3  | 87.7  |        |        |
| W-PbB     | 38.7             | 61.3          | 37.8  | 61.8  |        |        |
| W-PbAl    | 45.6             | 54.4          | 7.8   | 91.6  |        |        |
| W-PbGa    | 47.2             | 52.8          | 8.6   | 91.1  |        |        |
| W-PbIn    | 48.4             | 51.6          | 9.3   | 90.3  |        |        |
| W-PbTI    | 56.2             | 43.8          | 11.4  | 88.2  |        |        |

Donation of the metal fragment W(CO)₅ and π-lone-pair orbitals of the ligands, resulting in stronger side-on bonding configurations represented by smaller bending angles α. Overall, heavier tetrylones tend to be less polarized and more side-on bonded given their characteristics of W–X bonds whose explanation can be approached by the analysis of bonding polarization and hybridization.

Table 5 summarizes the quantum chemical parameters related to molecular electronic structures of the studied complexes of W-XY (X = Ge, Sn, Pb; Y = B–Tl). In principle, E_HOMO values represent the electron-accepting capability, and E_LUMO values provide information on the capability of electron donation. The reasoning refers to the modern explanation of electron transfer including electron tunneling and the electron hopping. The obtained E_HOMO values accord with the order W-XB > W-XAl > W-XGa > W-XIn > W-XTI regardless of tetrylone families. This is consistent with values of E_LUMO which are recorded with narrower differentials between systems. The HOMO energy varies from −3.35 to 4.83 eV, and the LUMO energy is within the range between −1.35 and −3.54 eV. These compile a rather inconsistent order of energy gap ΔE_GAP = E_LUMO − E_HOMO, W-X > W-XB > W-XGa > W-XIn > W-XTI, and a contrary order of electronegativity (χ), W-XB < W-XAl < W-XGa < W-XIn < W-XTI. Regarding each tetrylone group, W-GeAl, W-SnAl, and W-PbAl register the highest values of energy gap with over 2 eV; meanwhile, electronegativity values of W-GeTI, W-SnTI, and W-PbTI are 4.19, 4.17, and 4.16, respectively, accounting for the highest figures. The noticeable quantum chemical parameters, including energy gap (ΔE_GAP), ionization potential (I), electron affinity (A), and electronegativities (χ), imply that all the studied complexes can be considered as versatile ligands bondable with transition-metal fragments.

EDA-NOCV calculations are utilized for in-depth analysis of chemical bonding energy in the interactions between divalent ylidone(0) ligands X(YCp*)₂, and metal fragment W(CO)₅ in complexes W-XY. The obtained results are presented in Table 6. The values of BDEs, ΔDₑ (kcal mol⁻¹), calculated by EDA-NOCV at the BP86/TZ2P+/BP86/def-SVP level approximate DFT-Dₑ values (Table 2). Therefore, the energy is still positively correlated with the heaviness of the studied complexes. The observations include all gemylones W-GeY (44.6 to 54.7), stannylones W-SnY (49.3 to 54.2), and plumbylones W-PbY (50.9 to 54.3). Total instantaneous interaction energy ΔE_int is composed of contributions from Pauli repulsion (ΔEₚₚ), attractive electrostatic interaction (ΔEₑₑ), and orbital interactions (ΔEₗₗ). This represents the total interaction energy between substrates and functional groups in the complexes. EDA-NOCV data reveals that ΔE_int registers its highest level at −74.1, −67.1, and −66.9 kcal mol⁻¹ in each subgroup for W-GeTl, W-SnTl, and W-PbB, respectively. They were followed by W-GeB, W-SnB, and W-PbTl with the respective figures being −64.4, −66.5, and −66.2 kcal mol⁻¹. Meanwhile, there are marginal differentials recorded among the complex mass in each tetrylone family, according to the order W-XTI > W-XIn > W-XGa > W-XAI > W-XB. There is no

Table 5. Quantum Chemical Parameters for the Neutral Complexes of W-XY (X = Ge, Sn, Pb; Y = B–Tl) with the DFT at the BP86/def2-TZVPP Level

| complex   | E_HOMO (eV) | E_LUMO (eV) | ΔE (eV) | I = −E_HOMO | A = −E_LUMO | χ = (I + A)/2 |
|-----------|-------------|-------------|---------|-------------|-------------|--------------|
| W-GeB     | −3.35       | −1.43       | 1.92    | 3.35        | 1.43        | 2.39         |
| W-GeAl    | −4.57       | −2.29       | 2.28    | 4.57        | 2.29        | 3.43         |
| W-GeGa    | −4.60       | −2.45       | 2.15    | 4.60        | 2.45        | 3.53         |
| W-GeIn    | −4.83       | −3.02       | 1.81    | 4.83        | 3.02        | 3.92         |
| W-GeTI    | −4.83       | −3.54       | 1.29    | 4.83        | 3.54        | 4.19         |
| W-SnB     | −3.43       | −1.35       | 2.08    | 3.43        | 1.35        | 2.39         |
| W-SnAl    | −4.48       | −2.20       | 2.28    | 4.48        | 2.20        | 3.34         |
| W-SnGa    | −4.55       | −2.44       | 2.11    | 4.55        | 2.44        | 3.50         |
| W-SnIn    | −4.78       | −3.05       | 1.73    | 4.78        | 3.05        | 3.91         |
| W-SnTI    | −4.81       | −3.54       | 1.27    | 4.81        | 3.54        | 4.17         |
| W-PbB     | −3.53       | −1.38       | 2.15    | 3.53        | 1.38        | 2.45         |
| W-PbAl    | −4.45       | −2.14       | 2.31    | 4.45        | 2.14        | 3.29         |
| W-PbGa    | −4.54       | −2.47       | 2.07    | 4.54        | 2.47        | 3.49         |
| W-PbIn    | −4.76       | −3.05       | 1.71    | 4.76        | 3.05        | 3.90         |
| W-PbTI    | −4.81       | −3.52       | 1.29    | 4.81        | 3.52        | 4.16         |

ΔE (eV) was calculated from E_HOMO and E_LUMO values; electronegativities (χ) were obtained from ionization potential (I) and electron affinity (A).
significant difference observable in respective values between the tetrylone groups. Overall, their calculated values are in good agreement with those obtained from DFT analysis (Table 2). However, preparation energy values resemble differently. The highest figures are those of boron-complexes W-XB, i.e., 19.8 (W-GeB), 17.2 (W-SnB), and 17.0 kcal mol\(^{-1}\) (W-PbB). These were followed by W-XTI with energy values of 19.4, 12.9, and 11.9 kcal mol\(^{-1}\), respectively. The other tetrylones saw irregular arrangements. The total attractive interaction attaching any two fragments together is deemed to be a sum of attractive electrostatic interaction (\(\Delta E_{\text{elstat}}\)) and orbital interaction energy (\(\Delta E_{\text{orb}}\)). Since both the energy levels increase along with the mass of the complexes in each tetrylone homologue, the bond \(W-\bar{X}\) stability overall accords with the sequence \(W-\text{XTI} > W-\text{XAI} > W-\text{XGa} > W-\text{XSn} > W-\text{XB}\). In detail, attractive electrostatic interaction contributes more than orbital overlapping to the total capacity of bonding Group-13 diyl adducts with \(W\) atoms. Similarly, orbital interaction energy \(\Delta E_{\text{orb}}\) positively correlates with the increase of the molecular mass, thus resulting in more stable orbital overlapping by heavier Group-13 diyl adducts than their lighter counterparts. Furthermore, the \(\sigma\)-orbital contributions \(\Delta E_{\sigma}\) dominate the \(\pi\)-orbital contributions \(\Delta E_{\pi}\) and they increase for the \(X\)@heavier Group-13 tetrylone ligands.\(^{1,34}\) The reasoning relates to the existence of the \(\sigma\)-lone-pair orbital leading to the significantly strong \(\sigma\)-orbital interactions.\(^{1,31}\)

Schemes 2 and 3 are constructed in an attempt to illustrate the main interactions in the bondings \(X-Y\) and \(X-W\), respectively, in \(W-\bar{X}\) complexes. The former illustrates the effects of electron stabilizing donation of the p-atomic orbital at the \(W\) atom and \(\pi\) electron-sharing interactions as well as probable resonance of charge transfer between \(Y (= B-\bar{T})\) atoms of dimer (Y(Cp\(^*\))\(_2\)) and \(X (= Ge, Sn, Pb)\) atoms of tetrylone ligands X(Y(Cp\(^*\))\(_2\)). The latter shows the orbital interaction between heavier main-group atoms \(X (Ge, Sn, Pb)\) of tetrylone ligands X(Y(Cp\(^*\))\(_2\)) and metal fragment W(CO)\(_5\) via \(\sigma\)- and \(\pi\)-donations of donor–acceptor bonding. The interactive mechanism meets the implication on the roles of main elements in the complexes proposed as the outcome of NBO calculations (Table 3), suggesting atoms \(W\) as strong electron acceptors, atoms \(Y\) as strong electron donors, and atoms \(X\) as transitional channels.

We provide the charge transfer and energy levels to get insight into the chemical bonding in the variation of the donor–acceptor capacity in complexes between the substituted tetrylone@Group-13 ligands X(Y(Cp\(^*\))\(_2\)) and metal fragment W(CO)\(_5\). Furthermore, the orbital interaction energy \(\Delta E_{\text{orb}}\) of the EDA-NOCV results was additionally investigated in order to obtain more information on the nature of chemical bonding in complexes \(W-\bar{X}\). The pairs of orbitals \(\Psi_{\sigma}/\Psi_{\pi}\) for the most important \(\sigma\)- and \(\pi\)-orbital term contributions \(\Delta E_{\sigma}\) and \(\Delta E_{\pi}\) and associated deformation densities \(\Delta \rho\) characterized for bonding.
molecular orbitals in the representative complexes W-XY with X = Ge, Sn, Pb; Y = B, Al, T are depicted in Figures 6−9. Note that the complexes W-XGa and W-XIn demonstrate similar orbital shapes to the adducts W-XTl, so they are not shown in Figures 6−9. Bonding orbital pairs $\Psi_1/\Psi_\perp$ are represented by red/blue colors. The blue/orange colors in the deformation densities $\Delta\rho$ describe the charge flow, in which the blue spaces exhibit charge depletion and the orange spaces present charge accumulation; $\Delta E$ and $\Delta\rho$ are included under each simulation model.

Figure 6 displays the NOCV pairs $\Psi_1/\Psi_\perp$ and the deformation densities $\Delta\rho_1$ of the most significant pairs of $\sigma$-molecular orbitals for $\Delta E_\sigma$ in W-XY. Overall, the values of $\Delta\rho_1$ are approximately 80% of the total energy $\Delta E_\sigma$ (Table 6), which are from $-59.2$ to $-68.5$ kcal mol$^{-1}$ for W-XB, from $-49.8$ to $-57.6$ kcal mol$^{-1}$ for W-XAl, and from $-63.4$ to $-64.9$ kcal mol$^{-1}$ for W-XTl. These are significantly higher than those of $\pi$ molecular orbitals, which will be discussed later.

Therefore, the orbital pairs $\Psi_1/\Psi_\perp$ can be considered as the dominant sources contributing to $\sigma$-bonding for the tetrylone ligands X(YCp*)$_2$ in the three series W-XY. Also, the deformation density depicted reveals the charge flow in the molecular orbital from the donor atom X to the acceptor atom W. This confirms the direction of the $\sigma$-bond from the tetrylone ligand to the metal fragment (CO)$_5$W ← X(YCp*)$_2$ achieved by NBO analysis (Table 3).

Figure 6. Representative of NOCV pair, $\Psi_1/\Psi_\perp$, with the eigenvalue, $-\nu_1/\nu_\perp$, in parentheses, and density deformation contour channel blue $\rightarrow$ orange, $\Delta\rho_1$, and orbital stabilization energy, $\Delta E_\sigma$ (kcal mol$^{-1}$), describing the $\sigma$ interaction of W(CO)$_5$ ↔ X(YCp*)$_2$ (X = Ge, Sn, Pb; Y = B, Al and Tl) at the BP86/TZ2P+ level: (a1) W-GeB, (a2) W-GeAl, (a3) W-GeTl; (b1) W-SnB, (b2) W-SnAl, (b3) W-SnTl; (c1) W-PbB, (c2) W-PbAl, (c3) W-PbTl.
Despite the fact that the contributions of the $\pi$ stabilization $\Delta E_{\pi}$ is smaller than those of the $\sigma$-stabilization $\Delta E_{\sigma}$ in the three families $W-XY$, their values of energy level are restrictedly lower than 10 kcal mol$^{-1}$. The $\pi$ energy in tetrylone complexes exhibits

Figure 7. Contour plots of the representative $\pi$-types of NOCV interaction for boron complexes $W-XB$: (a$_1$) $W$-GeB, (a$_2$) $W$-GeB; (b$_1$) $W$-SnB, (b$_2$) $W$-SnB; (c$_1$) $W$-PbB, (c$_2$) $W$-PbB. The NOCV pairs, $\Psi_{-k}; \Psi_{k}$ ($k = 2, 3$), with the eigenvalues, $-\nu_k; \nu_k$ in parentheses, and deformation densities blue $\rightarrow$ orange, $\Delta \rho_{k}$, and orbital stabilization energies, $\Delta E_{k}^{orb}$ (kcal mol$^{-1}$), were selected to describe the $\pi$ interactions of $W(CO)_6 \leftrightarrow X(BCp^*)_2$ ($X = Ge, Sn, Pb$) at the BP86/TZ2P+ level.

Figure 8. Contours plots of the representative $\pi$-types of NOCV interaction for aluminum complexes $W-XAl$: (a$_1$) $W$-GeAl, (a$_2$) $W$-GeAl; (b$_1$) $W$-SnAl, (b$_2$) $W$-SnAl; (c$_1$) $W$-PbAl, (c$_2$) $W$-PbAl. The NOCV pairs, $\Psi_{-k}; \Psi_{k}$ ($k = 2, 3$), with the eigenvalues, $-\nu_k; \nu_k$ in parentheses, and deformation densities blue $\rightarrow$ orange, $\Delta \rho_{k}$, and orbital stabilization energies, $\Delta E_{k}^{orb}$ (kcal mol$^{-1}$), were selected to describe the $\pi$ interactions of $W(CO)_6 \leftrightarrow X(AlCp^*)_2$ ($X = Ge, Sn, Pb$) at the BP86/TZ2P+ level.
a significant contribution, which is shown by the shape of the molecular orbitals and charge transfer processes. Figures 7–9 illustrate the complementary NOCV pairs ($\Psi_{\pi}^{1}/\Psi_{\pi}^{2}$ or $\Psi_{\pi}^{3}/\Psi_{\pi}^{4}$) and the deformation densities ($\Delta\rho_{\pi}$; $k = 2, 3$) characterized for the most significant pairs of $\pi$ molecular orbitals for $\Delta E_{\pi}$ in W-XY. It clearly shows that the $\pi$-lone-pair donation from the tetrylone ligands to the metal fragment W(CO)$_5$ is very weak in terms of bonding energy. As those structural discussions mentioned above about the geometrically optimized structures terms of bonding energy. As those structural discussions mentioned above about the geometrically optimized structures of the complexes investigated W-XY (Figure 1 and Table 1), the tetrylone ligands XY bind to metal fragment W(CO)$_5$ in a side-on mode conducive to $\pi$-type hybridization from the $\pi$-lone-pair orbital of the tetrylones@Group-13 ligands X(YCp$^{*}$) into the second vacant coordination side of W(CO)$_5$ in complexes W-XY, so the shape of NOCV orbitals was visualized in order to answer a question that concerns the strength of the $\pi$ ligand–metal fragment donation. In detail, the figures for W-XB, W-XAl, and W-XTI vary between −1.6 and −2.8, −1.9 and −3.4, and −5.3 and −12.5 kcal mol$^{-1}$, respectively. This implies the geometrical structure of significance to the $\pi$ molecular orbitals. In addition, the complexes experienced irregular patterns of charge flow in the $\pi$-bonding orbitals. The weak $\pi$-style orbital interactions in W-XY stem from either $\pi$-donation (CO)$_3$W $\leftrightarrow$ X(YCp$^{*}$)$_2$, or $\pi$-backdonation (CO)$_3$W $\rightarrow$ X(YCp$^{*}$)$_2$ or partly each of the types. The contributing patterns depend on X and Y.

Figure 7 presents the corresponding deformation densities of W-XB with X = Ge, Sn, Pb in which the shape of the NOCV pairs $\Psi_{\pi}^{1}/\Psi_{\pi}^{2}$ and the deformation densities clearly reveal the charge flow $\Delta\rho_{\pi}$ ($k = 2, 3$). We found that the energy stabilizations are −2.8 and −2.3 kcal mol$^{-1}$ for germylone@boron W-GeB, −2.2, and −2.1 kcal mol$^{-1}$ for W-SnB, and −1.7 and −1.6 kcal mol$^{-1}$ for W-PbB, which mostly come from the relaxation of the metal fragment W(CO)$_5$. Thus, it clearly shows that the $\pi$-lone-pair donation from the tetrylone ligands to the metal fragment W(CO)$_5$ is very weak. Figure 8 lists the NOCV pairs for tetrylone@aluminum complexes W-XAl with X = Ge, Sn, Pb, and a comparison is made to get a detailed view of the NOCV shapes between tetrylone@aluminum and tetrylone@boron, which has the $\pi$-backdonation from atom W to X in a significant bonding. The deformation density $\Delta\rho_{\pi}$ exhibits that the weak $\pi$-style orbital interactions in W-XAl result not only from typical weak $\pi$-donation, (CO)$_3$W $\leftrightarrow$ X(AlCp$^{*}$)$_2$, but also from $\pi$-backdonation, (CO)$_3$W $\rightarrow$ X(AlCp$^{*}$)$_2$, where the charge flow $\Delta\rho_{\pi}$ shows energy stabilizations of −3.4 and −2.6 kcal mol$^{-1}$ for germylone@aluminum W-GeAl; −2.6 and −2.2 kcal mol$^{-1}$ for stannylone@aluminum W-SnAl, and −2.2 and −1.9 kcal mol$^{-1}$ for plumbylone@aluminum W-PbAl.

Interestingly, the $\pi$ interaction energy values $\Delta E_{\pi}$ of tetrylone@thallium complexes W-XTI given in Figure 9 are larger than those of tetrylone@boron W-XB and tetrylone@aluminum W-XAl. In detail, the germylone complex W-GeTI has the largest values ($\Delta E_{\pi} = −12.5$ kcal mol$^{-1}$; $\Delta E_{\pi}$ = −9.5 kcal mol$^{-1}$), while the plumbylone complex W-PbTI exhibits the smallest values ($\Delta E_{\pi} = −5.4$ kcal mol$^{-1}$; $\Delta E_{\pi}$ = −5.3 kcal mol$^{-1}$). Note that the shapes of the NOCV pairs $\Psi_{\pi}^{1}/\Psi_{\pi}^{2}$ and the deformation density $\Delta\rho_{\pi}$ ($k = 2, 3$) in Figure 9 also show the weak $\pi$-type orbital interactions in tetrylone@thallium complexes W-XTI with the charge flow mainly coming from typical $\pi$-backdonation (CO)$_3$W $\rightarrow$ X(TICp$^{*}$)$_2$. It can be realized that the tetrylone ligands XY have two $\pi$-lone-pair orbitals, but they can use their $\pi$-lone-pair electrons for donor–acceptor interactions in the side-on complexes. We found a rationale for the stronger bonding of the ligands XY provided by the calculated values for $\Delta E_{\pi}$ and electrostatic attraction $\Delta E_{\text{elstat}}$, which is shown in the increase of the donation (CO)$_3$W $\leftrightarrow$ X(YCp$^{*}$)$_2$ when Y becomes heavier.

**CONCLUSIONS**

This study provides a comprehensive overview of the structures, chemical bonding, and properties in transition-metal complexes...
of divalent ylidone(0) ligands \((\text{CO})_2W-X(Y\text{Cp}^\ast)\) in which \(X = \text{Ge, Sn, Pb}\) and \(Y = \text{B–Tl}\).

(a) Analysis on the geometrical structure reveals the main bonding configurations in the complexes, summarized as follows: (i) The ylidone(0) ligands \(XY\) in the complexes \(W-XY\) are bonded in a tilted orientation relative to the metal fragment \(W(\text{CO})_3\); (ii) \(Y\text{Cp}^\ast\) rings are mainly \(\pi\)-bonded to Group-14 atoms (B–Tl).

(b) Investigation using DFT yields information on quantum parameters of the tetrylones and speculation for the main bonding properties, including the following: (iii) BDEs of the complex in each tetrylone family vary differently regarding the change of relative molecular mass. The energy orders of germynes, stannylenes, and plumbynes are \(W-\text{GeTl} > W-\text{GeIn} > W-\text{GeGa} > W-\text{GeAl} > W-\text{GeB}, W-\text{SnTl} > W-\text{SnIn} > W-\text{XGa} > W-\text{SnB} > W-\text{SnAl}\), and \(W-PbTl > W-PbB > W-PbGa > W-PbAl\) respectively; (iv) dispersion interactions considered as the effect of bulky ligands play an important role in the calculation of the total BDEs, accounting for ca. 20–30% of DFT-D3 values; (v) the bond \(W-X\) is inclined to polarize toward atom \(X\), and the analysis on its hybridization suggests that borane systems \(W-\text{GeB}, W-\text{SnB},\) and \(W-PbB\) contain sp\(^2\)-characteristic \(W-X\) bonding while heavier homologues exhibit mainly p-characteristic configurations; (vi) bonding analysis speculates that the electron donation accords with the direction \((\text{CO})_2W \leftarrow X(Y\text{Cp}^\ast)_2\) formed by both \(\sigma\)- and \(\pi\)-types.

(c) EDA-NOCV calculations provide information on in-depth chemical bonding interactions and further confirm bonding suggestions speculated from DFT results, embracing the following: (vii) The values of \(D\) obtained from EDA-NOCV and DFT-D\(_3\) analyses are in good consistency; (viii) given attractive electrostatic interaction \(\Delta E_{\text{elstat}}\) and orbital interaction energy \(\Delta E_{\text{orbit}}\), the bond \(W-X\) stability overall accords with the sequence \(W-\text{XTI} > W-\text{XIn} > W-\text{XGa} > W-\text{XAl} > W-\text{XB}\); (ix) EDA-NOCV calculations imply that the tendency of \(W-X\) bond strength in complexes came from the change of \(W(\text{CO})_3 \leftarrow X(Y\text{Cp}^\ast)_2\) donation and electrostatic attraction. This also includes the additional weak \(\pi\)-style orbital interactions in \(W-XY\) stemming from either \(\pi\)-donation \((\text{CO})_2W \leftarrow X(Y\text{Cp}^\ast)\) or \(\pi\)-backdonation \((\text{CO})_2W \rightarrow X(Y\text{Cp}^\ast)\) or partly each of the types; (x) the depictions for NOCV pairs \(\Psi_i^\ast/\Psi_j\) and the deformation densities \(\Delta \rho_{ij}\) illustrate a comprehensive overview of different components of the chemical bond via \(\sigma\)- and \(\pi\)-types in complexes \(W-XY\).

### METHODS

#### Optimization of the Structure and Energy.

Geometrical structures of the molecules were optimized by a combination of Gaussian 09\(^\text{a0}\) and Turbomole 7.01\(^\text{a1}\) at the level of theory BP86/def2-SVP without using symmetric constraints. The stationary points of molecules corresponding to the structures in global energetic minima on the potential energy surfaces (PES) were determined by vibrational frequency calculations. Single-point energy calculations with the same functional but a larger basis set def2-TZVPP\(^\text{a5}\) were examined with the frozen-core approximation for non-valence-shell electrons. Small-core quasi-relativistic effective core potentials (ECPs) were applied for the heavier Group-14 atoms Sn and Pb and the heavier Group-13 atoms In and Tl. Resolution-of-identity (RI) approximation was used for all structure optimizations using the appropriate auxiliary basis sets.

#### Bonding Analysis.

The BP86 functional in DFT calculations in conjunction with the def2-TZVPP\(^\text{a5}\) basis set at BP86/def2-SVP level was used to calculate Wiberg bond indices (WBI), natural partial atomic (NPA) charges, and single-point energies (SPEs) using natural bond orbital methods.\(^\text{a6}\) These were carried out on the NBO program version 5.1. The bond dissociation energy (BDE), \(D\) (kcal mol\(^{-1}\)), was derived from the obtained SPE values. The effects of dispersion interactions on the calculated bond dissociation energies were estimated under the D3 dispersion corrections, suggested by Grimme’s DFT-D3 approximation.\(^\text{a5, a6}\) The influence of the ylidone(0) ligands \(X(Y\text{Cp}^\ast)\) with \(X = \text{Ge, Sn, Pb}\) and \(Y = \text{B–Tl}\) on the BDEs to the intrinsic bond strength under the consideration of interactions in complexes with and without dispersion corrections was determined at the level of theory BP86/def2-TZVPP/def2-SVP. Also, HOMO energy \(E_{\text{HOMO}}\) and LUMO energy \(E_{\text{LUMO}}\) were calculated, and their electron density distributions were illustrated. Energy gap \(\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}\) provides information on the reactivity tendency of inhibition efficacy of organic molecules toward the surface of metal elements. Ionization potential \((I)\) and electron affinity \((A)\) of inhibitory molecules were calculated by the application of Koopmans’ theorem\(^\text{a9}\) related to HOMO and LUMO energies as \(I = -E_{\text{HOMO}}\) and \(A = -E_{\text{LUMO}}\). The value of electronegativity \((\chi)\) was obtained by the following equation:

\[
\chi = (I + A)/2
\]

The nature of chemical bonding for complexes was verified by further investigation using energy decomposition analysis (EDA)\(^\text{a50–52}\) and charge of natural orbitals for chemical valence (NOCV)\(^\text{a53, 54}\) method. These were obtained via calculations with no restrictions at the relativistic DFT framework using the Amsterdam Density Functional (ADF)\(^\text{a55}\) program package 2018.01. The level BP86 in conjunction was applied with a triple-zeta-quality basis set TZ2P+ using uncontracted Slater-type orbitals (STOs) augmented by two sets of polarization functions, with a frozen-core approximation for the core electrons.\(^\text{a56}\) A standard triple-\(\xi\) basis set was employed for the heavier Group-14 elements Sn and Pb and the heavier Group-13 atoms In and Tl. An auxiliary set of s, p, d, \(\xi\), and \(\eta\) STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle.\(^\text{a57}\) Scalar relativistic effects were incorporated by applying the zeroth-order regular approximation (ZORA).\(^\text{a58}\) The BP86/TZ2P+ level using BP86/def2-SVP-optimized geometries was carried out to examine the nature of the \(W-XY\) bonds in complexes \(W-XY\) using the EDA-NOCV method under \(C_1\) symmetric geometries.

The EDA-NOCV scheme divides the total instantaneous interaction energy \(\Delta E_{\text{int}}\) into three main components: Pauli repulsion \(\Delta E_{\text{Pauli}}\), electrostatic interaction \(\Delta E_{\text{elstat}}\) and total orbital interaction \(\Delta E_{\text{orb}}\). This is expressed in eq. 1.

\[
\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}}
\]
\[ \Delta E( = -D_e) = \Delta E_{\text{int}} + \Delta E_{\text{prep}} \]  

(2) 

In the EDA-NOCV analysis, the orbital interaction energy \( \Delta E_{\text{orb}} \) of the interacting fragments orbitals, forming the deformation density, which is associated with the bond formation, \( \Delta \rho_{\text{orb}} \), into different components of the chemical bond is given by eq. \( 3 \). \( -F_{k,k}^{TS} \) and \( F_{k,k}^{TS} \) are diagonal Kohn–Sham matrix elements corresponding to natural orbitals for chemical valence with the eigenvectors, equalized with a sum of pairs of complementary orbitals \( (\Psi^-_{\text{orb}}, \Psi^+_{\text{orb}}) \) and eigenvalues equal in absolute value and eigenvector of the valence operator \( (\sigma) \). They provide an expression for orbital interaction and estimate its symmetry, direction of the charge flow, and energetic contribution to the total orbital interaction \( (\Delta E_{\text{orb}}) \). This information is assigned by visual inspection to simulate the shape of the deformation density, \( \Delta \rho_{\text{orb}} \). The function for the visualization is expressed in eq. \( 4 \).

\[ \Delta E_{\text{orb}} = \sum_{k=1}^{N/2} \Delta E_{k}^{\text{orb}} = \sum_{k=1}^{N/2} \rho_{k}[-F_{k,k}^{TS} + F_{k,k}^{TS}] \]  

(3) 

\[ \Delta \rho_{\text{orb}}(r) = \sum_{k=1}^{N/2} \rho_{k}[-\Psi_{\text{orb}}^{2}(r) + \Psi_{\text{orb}}^{2}(r)] = \sum_{k=1}^{N/2} \Delta \rho_{k}(r) \]  

(4) 

ASSOCIATED CONTENT

1. Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03237.

Cartesian coordinates and SCF energies from the systems at the BP86/def2-SVP level of theory (PDF)

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Notes

The authors declare no competing financial interest.

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