Theoretical Study and Design of Functional Molecules: New Bonding, Structures, and Reactions

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In theoretical and computational chemistry, it is an important goal to develop functional molecules prior to or in cooperation with experiment. Thus, new bonds and structures provided by heavier atoms are investigated together with the reactivities. In addition, chemical modification and properties of nanocarbons are investigated to develop functional nanomolecular systems. Efficient computational methods are also developed to perform reliable quantum chemistry calculations for small and large molecular systems.

1. Quest for Stable Multiple Bonds between Lead Atoms

The heavier analogues of alkynes, REER (E = Si, Ge, Sn, Pb), have attracted special interest in main-group element chemistry. Accordingly, all the heavier analogues have been synthesized and isolated uo to now. The X-ray crystal structure of the heaviest analogue, Ar*PbPbAr* (Ar* = C_6H_3-2,6-(C_6H_2-2,4,6-^{i}$Pr_3$$)_2$), has shown that the Pb–Pb bond distance is much longer than Pb–Pb single bond distances. Theoretical calculations have revealed that Ar*PbPbAr* has no π bond between Pb atoms. Therefore, it has been widely accepted that the heaviest Pb analogues of alkynes take a singly bonded structure, unlike the Si, Ge, and Sn cases. However, we have pointed out that Ar*PbPbAr* has a triply bonded structure in solution and crystal structures are not very helpful for compounds with bulky groups.1)

The Pb–Pb bond distance of 3.071 Å calculated for the triply bonded structure of Ar*Pb–PbAr* is considerably longer than the Pb–Pb single bond distance of 2.844 Å in $Ph_3PbPbPh_3$. Since we have found that electropositive silyl groups decreases the Pb–Pb bond distance, several bulky silyl groups were tested using density functional calculations.2) The optimized structure of $R^{Si}PbPbR^{Si}$ (R^{Si} = $Si^iPr\{CH(SiMe_3)_2\}_2$) is depiched in Figure 1, the two Pb atoms being triply bonded. The Pb–Pb bond distance of 2.696 Å is remarkably shorter than the Pb–Pb single bond distance of 2.844 Å in $Ph_3PbPbPh_3$, and it is considerably shorter than the shortest Pb–Pb double bond distance of 2.903 Å known to date. However, the triply bonded structure is 4.3 kcal/mol less stable than the singly bonded structure. We are still searching for good substituent groups that stabilize a triply bonded structure with a sufficiently short Pb–Pb bond.

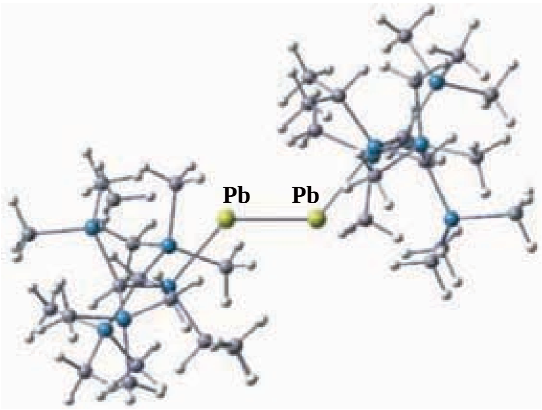


Figure 1. Triply bonded structure of $R^{Si}PbPbR^{Si}$.

As a new type of double bonds, diatomic molecules stabilized by the coordination of dative N-heterocyclic carbenes are of considerable interest currently. This stabilization has been performed for the synthesis and isolation of L:→Si=Si←:L and L:→Ge=Ge←:L (L = :C[N(2,6-^{i}Pr_2-C_6H_3)CH$]_2$). The Si–Si and Ge–Ge bond distances compare well with typical double bond distances of $R_2Si{=}SiR_2$ and $R_2Ge{=}GeR_2$. Because the heaviest Pb case remains unknown, we have investigated L:→Pb=Pb←:L.2) The optimized structure is shown in Figure 2. Molecular orbital analysis confirms that the two Pb atoms are doubly bonded. It is notable that the Pb–Pb double bond distance of 2.833 Å is considerably shorter than the shortest Pb–Pb double bond distance of 2.903 Å known to date and differs little from the Pb–Pb bond distance of Pb_2. It is expected that L:→Pb=Pb←:L is an interesting synthetic target.

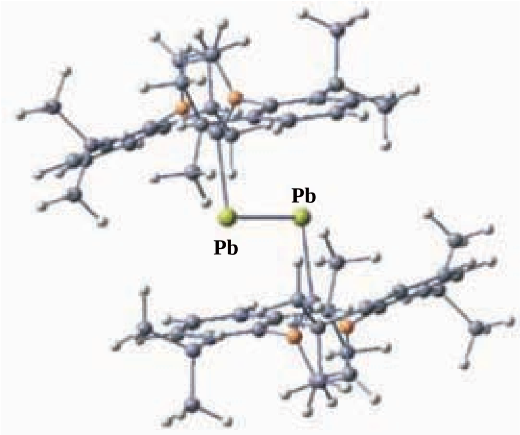
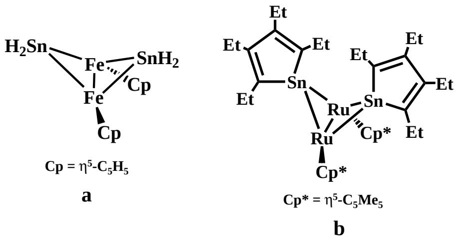


Figure 2. Optimized structure of L:→Pb=Pb←:L.

2. Short Bonds between Transition Metals

As a novel transition metal complex with an unsupported two-coordinate Fe atom, $R^*FeFe(\eta^5\text{-}C_5H_5)(CO)_2$ ($R^* = C_6H\text{-}2,6\text{-}Ar_2\text{-}3,5\text{-}{}^iPr_2$ where $Ar = C_6H_2\text{-}2,5,6\text{-}{}^iPr_3$) has recently been synthesized and investigated.3) X-ray crystal analysis shows that the Fe–Fe bond distances of 2.393 Å is much shorter than the known unsupported Fe–Fe bond distances (2.687–3.138 Å), suggesting that $R^*FeFe(\eta^5\text{-}C_5H_5)(CO)_2$ has the shortest unsupported Fe–Fe bond. Interestingly, calculations show that the Fe–Fe bond is greatly shortened in the bicyclic four-membered ring presented in Figure 3a.2)

Figure 3. Bicyclic four-membered ring complexes.



It is remarkable that the Fe–Fe bond distance of 2.045 Å is much shorter than the shortest Fe–Fe bond distance of 2.127 Å reported to date. This bond shortening assisted by two Sn atoms is very recently realized for the bicyclic four-membered Ru_2Sn_2 ring complex presented in Figure 3b.4) The Ru–Ru bond distance of 2.343 Å determined through X-ray crustal analysis agrees well with the calculated value of 2.363 Å. It is shorter than the Ru–Ru distance of 2.449–2.469 Å in the related bridge complexes, for which it is assumed that the two Ru atoms are triply bonded. Localized molecular orbital analysis reveals that one clear σ bond exists between the Ru atoms, while two three-centered σ orbitals are delocalized over each of the three-membered Ru_2Sn rings, which make an important contribution to Ru–Ru bonding. As a result, the Ru–Ru bond has a somewhat multiple-bond character.

It is also predicted theoretically that the Ru–Ru bond distance in the bicyclic four-membered Ru_2Sn_2 ring is shortened further in the bicyclic six-membered Ru_2Sn_4 ring. Experimental confirmation is in progress.

3. Nano-Carbon Systems

We have performed theoretical calculations for (a) polarized nonresonant Raman spectra of graphene nanoriboins5) and (b) transport properties of transition metal intercalated graphene.6) In collaboration with experiment, we have also performed calculations for (c) stable radical anions inside fullerene cages,7) (d) the core-shell interplay in carbide cluster metallofullerenes,8) (e) the cocrystal of La@C_{82} and nickel porphyrin with high electron mobility,9) and (f) chemical understanding of carbide cluster metallofullerenes.10)

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