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Property studies for the heterobimetallic phosphido-bridged W and Mo complexes through charge density analysis

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The chemical bonds and reactions of the (Cp)(CO)2W(m-PPh2)Mo(CO)5 (1) and (Cp)(CO)3W(m-PPh2)Mo(CO)5 (2) complexes were calculated by density functional theory (DFT) method to gain an insight into the property of heterobimetallic metal-metal bond. Based on quantum theory of atoms in molecules (QTAIM), all chemical bonds of optimized geometry will be characterized by bond critical point (BCP) and its associated topological properties, and these results are further compared with single crystal charge density experimental data. Using exchange functional PBE0-D3BJ can provide better calculation results whether it performed through the ZORA approximation of all-electron relativistic method or the pseudopotential method. In complex 1, the characters of the CO on Mo semibridges to W can be confirmed by the BCP between C and W (rc ~ 0.20 e/Å3). Based on fragment charge analysis of DFT calculations, Mo(CO)5 fragment of complex 1 (-0.092) is more positive than that of complex 2 (-0.184), and CpW(-CO)2 fragment of complex 1 (0.208) is more negative than CpW(CO)3 fragment of complex 2 (0.321). These results imply that a dative metal-metal bonding is formed by the electron donation from Mo to W. On the other hand, an intermediate without metal-metal bonding between Mo and W can be formed from complex 1 through semibridging CO transferring from Mo to W, and the transition state of this reaction can be located. This result explains the phenomenon of phosphine addition to Mo cis-site, which is observed in our previous publications.

Keywords: heterobimetallic, metal-metal bond, DFT