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John P. Graham
Arkansas Tech University, j.graham@uaeu.ac.ae

Robbie Davis
Arkansas Tech University

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Density Functional Studies of Structure and Bonding in Piano Stool Carbene Complexes

John P. Graham[1,2] and Robbie Davis[1]

[1]*Department of Physical Science, Arkansas Tech University, Russellville, AR 72801*

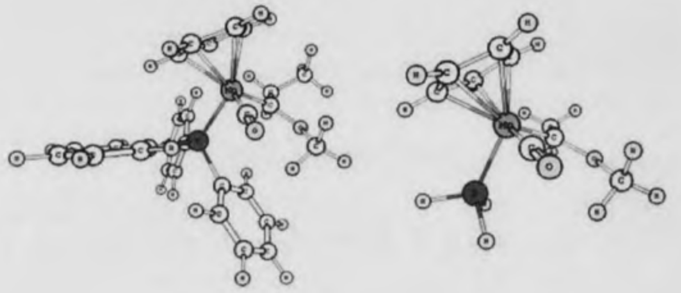
Correspondence: j.graham@uaeu.ac.ae

Recently we reported the results of approximate molecular orbital calculations used to explain the structural preferences and other properties of the chelating carbene complex $Cp'(CO)Mn\{C(OEt)CH_2PPh_2\}$ (**1**) and related complexes (Graham 2003). Since that time we have reexamined the electronic structure of the complex **1** using more quantitative density functional calculations. These calculations, unlike the previously published Fenske-Hall calculations, are well suited to determination of total energies and optimal geometries for molecular systems. The results of these new calculations are briefly described in this note.

Density functional calculations were used to optimize the geometries of the complexes $Cp'(CO)Mn\{C(OEt)CH_2PPh_2\}$ (**1**) and $Cp(CO)(PPh_3)Mn\{C(OMe)Et\}$ (**2**). Optimized geometries were also determined for the related model complexes $Cp(CO)Mn\{C(OMe)CH_2PH_2)$ (**1a**) and $Cp(CO)(PH_3)Mn(C(OMe)CH_2CH_3)$ (**2a**). All calculations were carried out using the Amsterdam Density Functional program, version ADF 2004.01 (ADF 2004, Velde et. al. 2001, Guerra et. al. 1998). The Local Density Approximation and a triple ζ basis set with polarization functions (LDA/TZP) were used. Ball and stick representations of the optimized structure of each complex are given in Fig. 1. It is observed that the optimized model complexes are very similar to the optimized structures for the full complexes in important structural features (such as metal ligand distances and angles). The optimized structures are also very close to the experimentally determined structures for the true complexes (Lugan, pers. comm.). These observations provide support for the earlier use of model complexes to describe the electronic structures of **1** and **2**.

Analysis of the molecular orbitals of complexes **1** and **2** shows picture of bonding similar to that previously derived from approximate molecular orbital calculations. In the chelating complex **1**, the largely metal-dπ based highest occupied molecular orbital (HOMO) receives little stabilization due to the lack of a π-acceptor orbital of suitable symmetry on either the carbene or carbonyl ligands. Consequently only two of the three dπ orbitals on the metal center are strongly stabilized resulting in an essentially non-bonding HOMO. The orbital energies of complex **2** indicate significant stabilization of all three dπ orbitals on the metal center, as the orientation of the ligands allows each of the dπ orbitals to back-donate to either the carbene or carbonyl ligands. The ADF calculated energies of the frontier dπ orbitals for complexes **1** and **2** are given in Table 1. The energies from Fenske-Hall calculations for model complexes **1a** and **2a** (Graham 2003) are also included for

Complex 1 Complex 1a



Complex 2 Complex 2a

Fig. 1. Optimized Geometries for Complexes **1**, **1a**, **2**, and **2a**.

Table 1. Calculated ADF and Fenske Hall (Graham 2003) Frontier Orbital Energies (SHOMO = Second Highest Occupied Molecular Orbital, THOMO = Third Highest Occupied Molecular Orbital).

	HOMO	SHOMO	THOMO
Complex 1 (ADF–LDA/TZP)	-3.47	-4.12	-4.74
Complex 2 (ADF-LDA/TZP)	-4.24	-4.59	-4.60
Model for Complex 1a (Fenske-Hall)	-4.26	-5.37	-6.69
Model for Complex 2a (Fenske-Hall)	-5.35	-5.85	-6.12

comparison. Although the energies of the orbitals obtained from ADF and Fenske-Hall calculations are quite different (as would be expected considering the very different levels of theory), the orbital energies for each complex/model complex follow similar patterns as described above.

For the non-chelating model complex **2a** two energy minima and two transition states were identified using DFT geometry optimizations. As would be expected, the energy minima occur at the two orientations of the carbene ligand that are parallel to the CO ligand. The transitions states occur at the two orientations where the carbene ligand is perpendicular to the CO. The variation in total energy (relative to atomic fragments) with angle is illustrated in Fig. 2. An estimate of 45 kJ/mole was calculated for the rotational barrier for the carbene ligand in the model complex.

The above analysis supports the proposal that the observed differences in properties of complexes **1** and **2** arise largely from the orientation of the carbene ligand relative to the carbonyl ligand. Further work incorporating exchange and correlation corrections is being carried out to calculate structures at higher levels of theory.

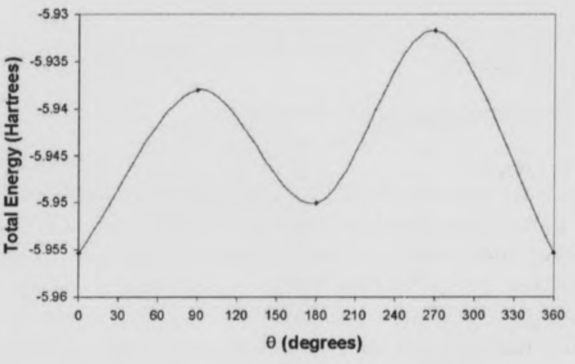


Fig. 2: Relative Total Energy Variation with Carbene – CO Angle for Complex **2a**.

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