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## Homoleptic Carbonyls of the Second-Row Transition Metals: Evaluation of Hartree−Fock and Density Functional Theory Methods[†]

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**Abstract:** The homoleptic mono- and multinuclear carbonyls for Mo, Tc, Ru, and Rh, namely, $Mo(CO)_6$, $Ru(CO)_5$, $Tc_2(CO)_{10}$, $Ru_3(CO)_{12}$, $Rh_4(CO)_{12}$, and $Rh_6(CO)_{16}$, are investigated theoretically by the Hartree−Fock method and three density functional theory (DFT) methods, i.e., BP86, B3LYP, and MPW1PW91, along with the SDD ECP basis sets. The results predicted by all the methods are basically in agreement with each other. The MPW1PW91 and BP86 methods predict geometric parameters and vibrational spectra, respectively, closest to the experimental values. For $Ru_3(CO)_{12}$ the relative energies of the $D_{3h}$ isomer with only terminal CO groups and the $C_{2v}$ isomer with two bridging CO groups are within 3 kcal/mol of each other with the lower energy isomer depending upon the computational method used. For $Rh_4(CO)_{12}$ the global minimum is predicted to have $C_{3v}$ symmetry, with three bridging and nine terminal carbonyls, in accord with experiment. The $Rh_6(CO)_{16}$ structure has $T_d$ symmetry and satisfies the Wade-Mingos rules for an octahedral cluster. Using the MPW1PW91 method the Rh−Rh distances in $Rh_4(CO)_{12}$ are found to be 2.692 Å and 2.750 Å and those in $Rh_6(CO)_{16}$ to be 2.785 Å.

## 1. Introduction

Well characterized isolable homoleptic carbonyl derivatives of the second-row transition metals include $Mo(CO)_6$,[1−3] $Tc_2(CO)_{10}$,[4,5] $Ru(CO)_5$,[6] and $Ru_3(CO)_{12}$.[7,8] In addition, multinuclear homoleptic rhodium carbonyls were observed as early as 1943.[9] Subsequent X-ray diffraction studies[10−12] have shown these rhodium carbonyls to be tetranuclear $Rh_4(CO)_{12}$ and hexanuclear $Rh_6(CO)_{16}$. The geometric parameters for $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ have then been determined by subsequent experimental work.[13−20] Comparison of the structures of second-row transition-metal carbonyls with those of the corresponding first-row transition-metal carbonyls is of interest since in some cases the structures are different. For example, the structure of $Ru_3(CO)_{12}$ has all terminal CO groups with an equilateral $Ru_3$ triangle,[7,8] whereas the structure of the corresponding isoelectronic $Fe_3(CO)_{12}$ has ten terminal CO groups and two bridging CO groups with an isosceles $Fe_3$ triangle.[21]

Density functional theory (DFT) certainly appears to be a powerful and effective computational tool to study organotransition-metal chemistry.[22−39] In this connection we have used the B3LYP and BP86 methods along with the all-electron DZP basis sets to study a series of first-row transition-metal carbonyl derivatives.[40−47] Our results also show that the BP86 method may be somewhat more reliable than the B3LYP method for those organometallic systems.

There are fewer theoretical studies on compounds containing the second-row transition metals. All electron computations on second-row transition-metal derivatives are expected

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to be much more expensive in terms of computing resources than those on corresponding first-row transition-metal derivatives. Effective core potential (ECP) and related basis sets[48−51] provide a simple but efficient approach for reducing the computational effort while considering relativistic effects, especially for the second- (and third-) row transition metals. ECP methods have been tested on the second-row metal carbonyls $Mo(CO)_6$ and $Ru(CO)_5$ in 1996[52] and were subsequently used to study the molecular structures of $Ru_3$-$(CO)_{12}$ isomers[53] and most recently[54] the infrared spectra of rhodium carbonyl clusters. In the present paper we use ECP basis sets to explore the performance of different DFT methods, including a new generation DFT method as well as a Hartree−Fock method on the experimentally known second-row transition-metal carbonyls. We anticipate this work to provide a basis for more extensive future DFT studies on second-row transition-metal carbonyls and related organometallic compounds.

## 2. Theoretical Methods

A Hartree−Fock method and three different density functional theory (DFT) methods were used in the present study. The Hartree−Fock self-consistent-field (SCF) method was chosen by us here despite its lack of treatment for the electron correlation effect because it was found by Cotton and co-workers[55] to give satisfactorily optimized geometry and other properties for compounds containing the second- and third-row transition-metal atoms, such as the palladium(III) derivative $Pd_2(hpp)_4Cl_2$.

The density functional theory (DFT) methods used here include the B3LYP method, which is the hybrid DFT/Hartree−Fock method using Becke's three-parameter functional (B3) with the Lee−Yang−Parr (LYP) correlation functional.[56,57] The second DFT method is the BP86 method, which uses Becke's 1988 exchange functional (B) with Perdew's 1986 gradient corrected correlation functional method (P86).[58] The third DFT method is a new generation functional MPW1PW91, which is a combination of the modified Perdew−Wang exchange functional with Perdew−Wang's 91 gradient-correlation functional.[59] This MPW1PW91 functional has been shown to be better than the first generation functional for the heavy transition-metal compounds.[60]

The Stuttgart/Dresden double-$\zeta$ (SDD) ECP basis sets[61,62] were used for the Mo, Tc, Ru, and Rh heavy atoms. In these basis sets the 28 core electrons in the transition-metal atoms are replaced by an effective core potential (ECP), and the valence basis sets are contracted from (8s7p6d) primitive sets to (6s5p3d). The effective core approximation includes relativistic contributions which become significant for the heavy transition-metal atoms. For the C and O atoms, the all electron DZP basis sets are used. They are Huzinaga−Dunning's contracted double-$\zeta$ contraction sets[63,64] plus a set of spherical harmonic d polarization functions with the orbital exponents $\alpha_d(C) = 0.75$ and $\alpha_d(O) = 0.85$. The DZP basis sets for C and O atoms may be designated as (9s5p1d/4s2p1d). For $Rh_6(CO)_{16}$, there are 696 contracted Gaussian functions. All of the computations were carried out with the Gaussian 03 program[65] in which the fine grid (99 590) is
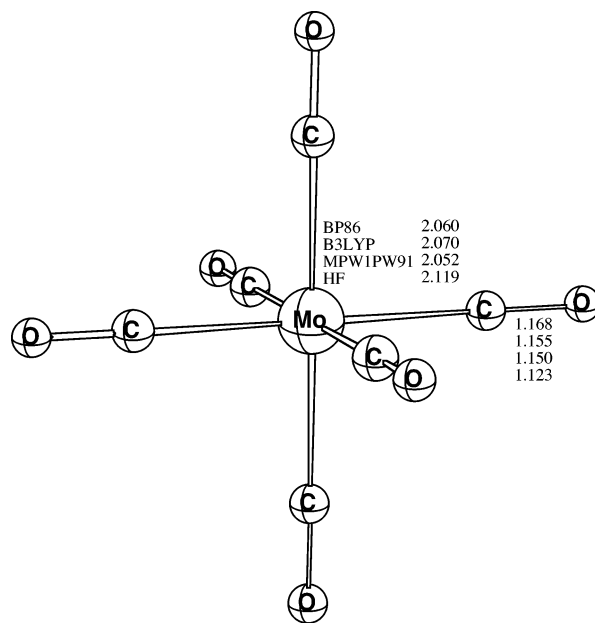


**Figure 1.** The optimized structure of $Mo(CO)_6$ ($O_h$ symmetry). The distances are given in Å.

**Table 1.** Comparison of Experimental and Theoretical Geometrical Parameters of $Mo(CO)_6$ ($O_h$)

|  | BP86 | B3LYP | MPW1PW91 | HF | exp.[5] | exp.[3] |
|---|---|---|---|---|---|---|
| Mo−C | 2.060 | 2.070 | 2.052 | 2.119 | 2.063(3) | 2.059(3) |
| C−O | 1.168 | 1.155 | 1.150 | 1.123 | 1.145(2) | 1.125(5) |
| mean absolute errors | 0.017 | 0.014 | 0.012 | 0.035 |  |  |

chosen for evaluating integrals numerically. In order to assess the performance of the f functions for the transition-metal atoms, we have also run the Hartree−Fock method with the SDD basis sets plus a set of polarization f functions, and the results are compared with the Hartree−Fock results without the f functions.

The geometries of all structures were fully optimized using the HF method and the three DFT methods independently. The harmonic vibrational frequencies were also obtained at the same levels. The corresponding infrared intensities were evaluated analytically as well.

## 3. Results and Discussion

**3.1. $Mo(CO)_6$.** The infrared vibrational spectrum for molybdenum hexacarbonyl $Mo(CO)_6$ was first reported in 1955 and in 1962.[1] Its geometric parameters have been measured by electron diffraction[2] and X-ray diffraction.[3]

The optimized structure of $Mo(CO)_6$ is the expected octahedron (Figure 1). The related geometric parameters as well as the available experimental bond distances are listed in Table 1. There are only two independent bond distances, namely the equivalent Mo−C bonds and the equivalent C−O bond. The theoretical bond distances with different methods are in reasonable agreement with each other. However, the MPW1PW91 results are the closest to the experimental values.

**3.2. $Tc_2(CO)_{10}$.** Although the element technetium does not exist in nature, its carbonyl derivative ditechnetium deca-

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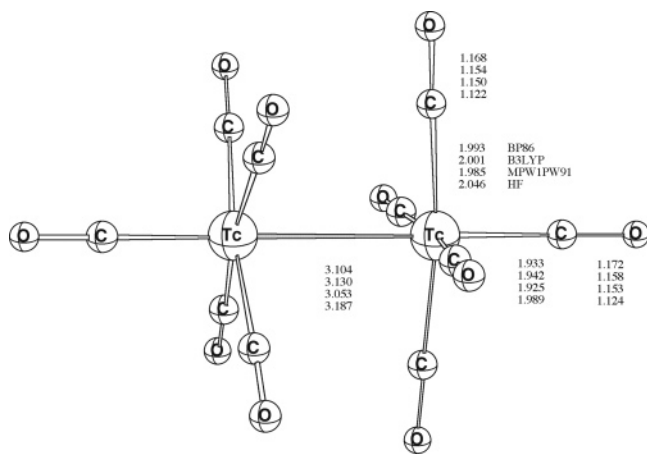
**Figure 2.** The optimized structure of Tc$_2$(CO)$_{10}$ ($D_{4d}$ symmetry). The distances are given in Å.

**Table 2.** Comparison of Experimental and Theoretical Geometrical Parameters of Tc$_2$(CO)$_{10}$ ($D_{4d}$)

|  | BP86 | B3LYP | MPW1PW91 | HF | exp.[5] |
|---|---|---|---|---|---|
| Tc−Tc | 3.104 | 3.130 | 3.053 | 3.187 | 3.036(6) |
| Tc-C (eq) | 1.993 | 2.001 | 1.985 | 2.046 | 2.000(13) |
| C−O (eq) | 1.168 | 1.154 | 1.150 | 1.122 | 1.122(12) |
| Tc−C (api) | 1.933 | 1.942 | 1.925 | 1.989 | 1.899(11) |
| C−O (api) | 1.172 | 1.158 | 1.153 | 1.124 | 1.205(13) |
| mean absolute errors | 0.038 | 0.043 | 0.028 | 0.074 |  |

carbonyl Tc$_2$(CO)$_{10}$ was first prepared as early as in 1961, and its crystal unit was reported in 1962.[4] Subsequently the geometrical parameters of Tc$_2$(CO)$_{10}$ were measured.[5]

The optimized structure of Tc$_2$(CO)$_{10}$ has $D_{4d}$ symmetry (Figure 2). The theoretical geometrical parameters as well as the experimental bond distances are listed in Table 2. The theoretical axial Tc−Tc distances fall in the range from 3.05 to 3.19 Å, among which the HF method predicts it too long (3.187 Å) and the MPW1PW91 method predicts it to be the shortest (3.053 Å) and closest to the experimental value (3.036 Å).[5] The MPW1PW91 method gives Tc−C and C−O bond distances closest to the experimental values.

**3.3. Ru(CO)$_5$ and Ru$_3$(CO)$_{12}$.** Ruthenium is in the same group as iron, and the carbonyls of ruthenium are expected to be similar to those of iron. Indeed, ruthenium pentacarbonyl Ru(CO)$_5$ and triruthenium dodecacarbonyl Ru$_3$(CO)$_{12}$ have been found to be stable species.[6,7] However, the structure of Ru$_3$(CO)$_{12}$ is different from that of Fe$_3$(CO)$_{12}$.

The optimized structure of Ru(CO)$_5$, like that of Fe(CO)$_5$, has $D_{3h}$ symmetry (Figure 3). The theoretical geometrical parameters as well as the experimental bond distances are listed in Table 3. The theoretical Ru−C distances, whether axial or equatorial, fall in the range from 1.94 to 2.02 Å. For most bond distances the HF method predicts the longest and the MPW1PW91 method predicts the shortest with the MPW1PW91 method giving values closes to the experimental values.

Possible triangular structures for Ru$_3$(CO)$_{12}$ include the experimentally known[7,8] $D_{3h}$ structure with all terminal CO groups (Figure 4) or a $C_{2v}$ structure (Figure 5) similar to the known structure[21] of Fe$_3$(CO)$_{12}$ with two CO groups bridging
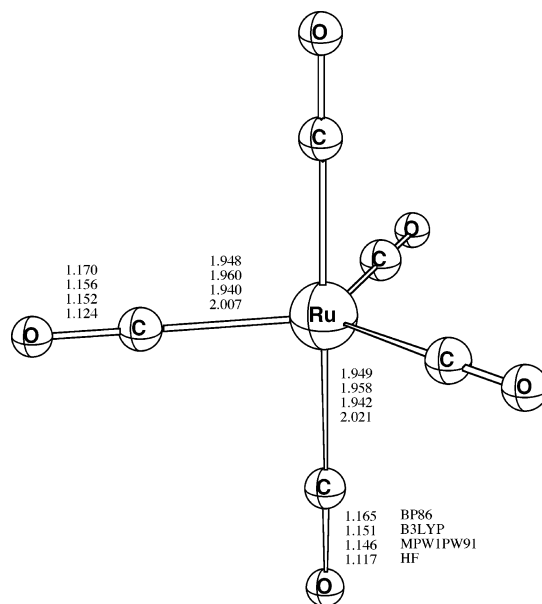


**Figure 3.** The optimized structure of Ru(CO)$_5$ ($D_{3h}$ symmetry). The distances are given in Å.
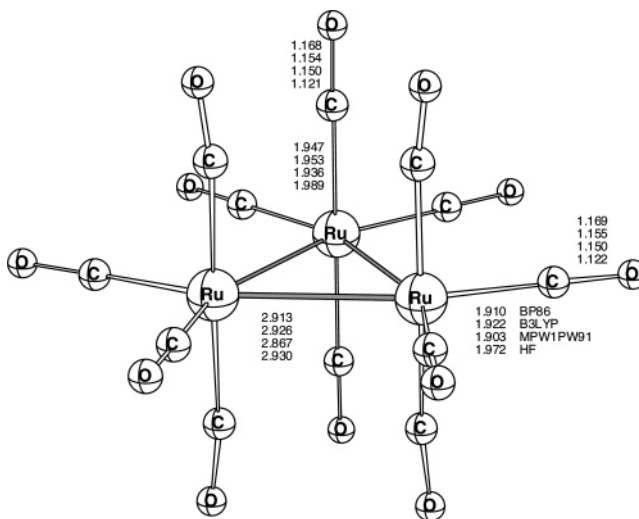


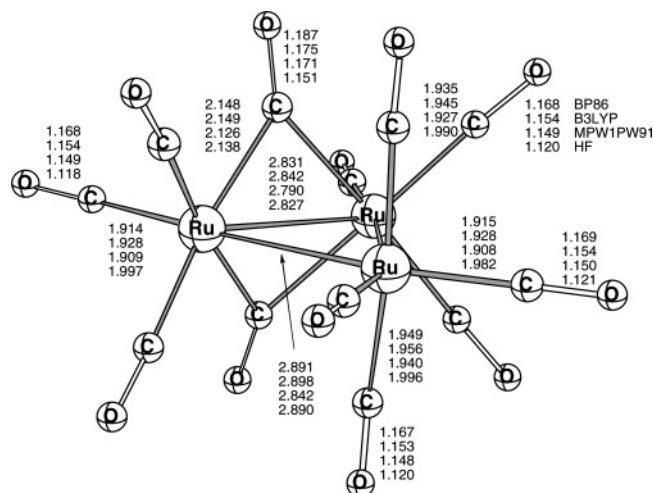**Figure 4.** The optimized unbridged structure of Ru$_3$(CO)$_{12}$ ($D_{3h}$ symmetry). The distances are given in Å.

**Table 3.** Comparison of Experimental and Theoretical Geometrical Parameters of Ru(CO)$_5$ ($D_{3h}$)

|  | BP86 | B3LYP | MPW1PW91 | HF | exp.[6] |
|---|---|---|---|---|---|
| Ru−C(ax) | 1.949 | 1.958 | 1.942 | 2.021 | 1.941(13) |
| C−O (ax) | 1.165 | 1.151 | 1.146 | 1.117 | 1.126(2) |
| Ru-C(eq) | 1.948 | 1.960 | 1.940 | 2.007 | 1.961(9) |
| C−O (eq) | 1.170 | 1.156 | 1.152 | 1.124 | 1.127(2) |
| mean absolute errors | 0.026 | 0.018 | 0.017 | 0.034 |  |

one of the edges of the triangle. The relative energetics of the two types of structures (Table 4) depends on the computational method used. Only the Hartree−Fock method indicates the known $D_{3h}$ isomer of Ru$_3$(CO)$_{12}$ to be much lower in energy (18.3 kcal/mol) than the $C_{2v}$ isomer. The DFT methods show the two isomers of Ru$_3$(CO)$_{12}$ to have energies within ≤3 kcal/mol of each other. The BP86 and

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**Figure 5.** The optimized dibridged structure of $Ru_3(CO)_{12}$ ($C_{2v}$ symmetry). The distances are given in Å.

**Table 4.** Total Energies (hartrees) and Relative Energies (kcal/mol) for the Two $Ru_3(CO)_{12}$ Isomers

| | BP86 | B3LYP | MPW1PW91 | HF |
|---|---|---|---|---|
| $Ru_3(CO)_{12}$ ($D_{3h}$) | −1645.72062 (0.0) | −1645.33769 (0.0) | −1645.02067 (0.0) | −1635.54622 (0.0) |
| $Ru_3(CO)_{12}$ ($C_{2v}$) | −1645.72394 (−2.1) | −1645.33334 (2.7) | −1645.02122 (−0.3) | −1635.51702 (18.3) |

**Table 5.** Comparison of Experimental and Theoretical Geometrical Parameters of the Unbridged Isomer of $Ru_3(CO)_{12}$ ($D_{3h}$)

| | BP86[a] | BP86[b] | B3LYP | MPW1PW91 | HF | exp.[7] |
|---|---|---|---|---|---|---|
| Ru−Ru | 2.913 | 2.912 | 2.926 | 2.867 | 2.930 | 2.854(4) |
| Ru−C(eq) | 1.910 | 1.916 | 1.922 | 1.903 | 1.972 | 1.921(5) |
| C−O (eq) | 1.169 | | 1.155 | 1.150 | 1.122 | 1.127(2) |
| Ru−C(ax) | 1.947 | 1.957 | 1.953 | 1.936 | 1.989 | 1.942(4) |
| C−O (ax) | 1.168 | | 1.154 | 1.150 | 1.121 | 1.133(2) |
| mean absolute errors | 0.030 | | 0.027 | 0.016 | 0.038 | |

[a] This work. [b] Calculations in ref 53.

MPW1PW91 methods predict lower energies for the $C_{2v}$ isomer by 2.1 and 0.3 kcal/mol, respectively, whereas the B3LYP method predicts a lower energy for the $D_{3h}$ isomer by 2.7 kcal/mol. These calculations taken together suggest that the energies of both isomers of $Ru_3(CO)_{12}$ are so similar that one isomer is readily converted to the other isomer. These similar energies of the $D_{3h}$ and $C_{2v}$ isomers of $Ru_3(CO)_{12}$ are consistent with previous calculations[66] as well as the fluxional properties[67] found experimentally by NMR methods for $Ru_3(CO)_{12}$.

For the experimentally known $D_{3h}$ isomer of $Ru_3(CO)_{12}$ (Figure 4) the HF method predicts too long Ru−Ru (2.93 Å) and Ru−C (1.972 Å and 1.989 Å) distances (Table 5). The three DFT methods predict similar results, among which again the MPW1PW91 method predicts the shortest bond distances (e.g., 2.867 Å for the Ru−Ru distances) but closest to the experimental results.[7]

Table 6 provides information on the geometrical parameters computed by various methods for the doubly bridged isomer of $Ru_3(CO)_{12}$ (Figure 5). The single Ru−Ru edge of
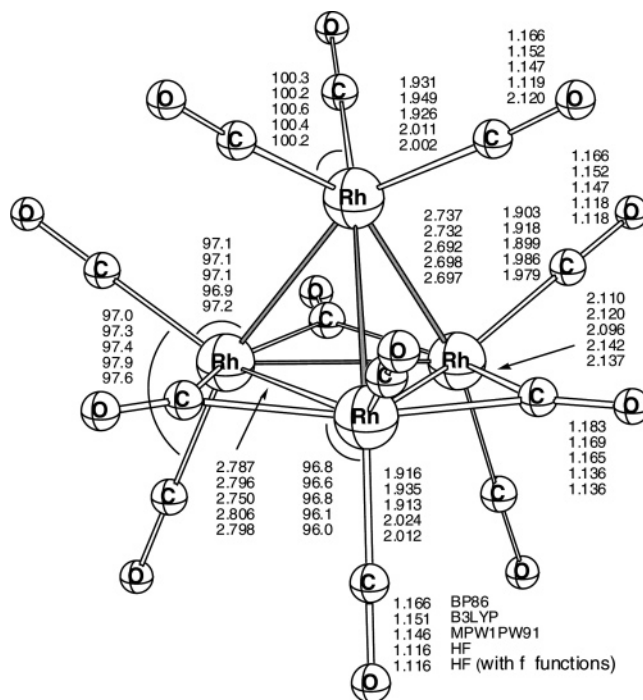


**Figure 6.** The optimized geometry of $Rh_4(CO)_{12}$ ($C_{3v}$ symmetry). The distances are given in Å.

**Table 6.** Theoretical Geometrical Parameters of the Doubly Bridged Isomer of $Ru_3(CO)_{12}$ ($C_{2v}$)

| | BP86 | B3LYP | MPW1PW91 | HF |
|---|---|---|---|---|
| Ru−Ru (unbridged) | 2.891 | 2.898 | 2.842 | 2.890 |
| Ru−Ru (bridged) | 2.831 | 2.842 | 2.790 | 2.827 |
| Ru−C (to bridging CO) | 2.148 | 2.149 | 2.126 | 2.138 |
| Ru−C (to terminal CO) | 1.914 | 1.928 | 1.909 | 1.997 |
| | 1.935 | 1.945 | 1.927 | 1.990 |
| | 1.949 | 1.956 | 1.940 | 1.996 |
| | 1.915 | 1.928 | 1.908 | 1.982 |

the $Ru_3$ isosceles triangle bridged by the two CO groups is 0.05−0.07 Å shorter than the two equivalent unbridged Ru−Ru edges in accord with numerous previous observations on CO bridged versus unbridged metal−metal bonds. The Ru−C distances to the bridging CO groups are ∼0.2 Å longer than those to the terminal CO groups also in accord with previous experience in binuclear and trinuclear metal carbonyl derivatives.

**3.4. $Rh_4(CO)_{12}$.** Possible tetrahedral structures for $Rh_4(CO)_{12}$ can have either all terminal carbonyls (as found experimentally for $Ir_4(CO)_{12}$) or three bridging carbonyls around the base of the tetrahedron and nine terminal carbonyls, as found experimentally for $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$. The relative energetics of these two structures for $Rh_4(CO)_{12}$ are of interest.

The global minimum of $Rh_4(CO)_{12}$ optimized by all the methods is a $C_{3v}$ structure with three edge-bridging carbonyl groups and nine terminal carbonyl groups, namely, $Rh_4(\mu\text{-}CO)_3(CO)_9$ (Figure 6). Our theoretical geometrical parameters predicted by various methods are listed in Table 7. The experimental results[11,68] and the previous theoretical results[17] are also listed for comparison. The experimental (X-ray diffraction) structural parameters, which are slightly distorted

**Table 7.** Comparison of Experimental and Theoretical Geometric Parameters of the Global Minimum $Rh_4(CO)_{12}$ ($C_{3v}$)

|  | BP86 | B3LYP | MPW1PW91 | HF[a] | expt[b] | expt[c] | LDA[17] | GGA[17] |
|---|---|---|---|---|---|---|---|---|
| Rh(apex)−Rh(bas.) | 2.737 | 2.732 | 2.692 | 2.698 (2.697) | 2.715 (2.693−2.746) | 2.673 (2.656−2.690) | 2.683 | 2.996 |
| Rh(bas.)−Rh(bas) | 2.787 | 2.796 | 2.750 | 2.806 (2.798) | 2.749 (2.710−2.804) | 2.724 (2.693−2.767) | 2.695 | 2.992 |
| Rh(bas.)−C(bridg.) | 2.110 | 2.120 | 2.096 | 2.142 (2.137) | 2.00 (1.87−2.24) | 2.101 (2.065−2.137) | 2.065 | 2.120 |
| Rh(bas.)−C(term.) | 1.903 | 1.918 | 1.899 | 1.986 (1.978) | 1.94 (1.69−2.16) | 1.917 (1.878−1.953) | 1.879 | 1.906 |
| Rh(apex)−C | 1.931 | 1.948 | 1.926 | 2.011 (2.002) | 1.99 (1.88−2.11) | 1.943 (1.929−1.962) | 1.905 | 1.933 |
| mean absolute errors | 0.043 | 0.039 | 0.026 | 0.054 |  |  |  |  |

[a] The results predicted using larger basis sets (a set of f functions for Rh is added) are in parentheses. [b] Reference 11. Bond distances are averaged out for the equivalent Rh−Rh bonds with the range indicated in parentheses. [c] Reference 68. Bond distances are averaged out for the equivalent Rh−Rh bonds with the range indicated in parentheses.

**Table 8.** Total Energies (hartrees) and Relative Energies (kcal/mol) for the Two $Rh_4(CO)_{12}$ Isomers

|  | BP86 | B3LYP | MPW1PW91 | HF | HF[a] |
|---|---|---|---|---|---|
| $Rh_4(CO)_{12}$ ($C_{3v}$) | −1803.39125 (0.0) | −1802.90099 (0.0) | −1802.59607 (0.0) | −1791.96822 (0.0) | −1791.99017 (0.0) |
| $Rh_4(CO)_{12}$ ($T_d$) | −1803.34852 (26.8) | −1802.85890 (26.4) | −1802.54890 (29.6) | −1791.91958 (30.5) | −1791.94736 (26.9) |

[a] A set of f functions for Rh are added to DZP basis set.

in the crystal structure, are averaged out in Table 7 to represent the ideal $C_{3v}$ symmetry.

Among the different methods, the predicted bond distances differ slightly (Table 7). For the Hartree−Fock results adding f functions to the Rh basis set has little effect (<0.01 Å). For most of the bonds, the HF method predicts the longest and the MPW1PW91 method predicts the shortest. The MPW1PW91 method predicts bond distances the closest to the most recent X-ray diffraction experimental values.[68]

Our theoretical distances of the basal Rh−Rh bonds with CO bridges range from 2.750 to 2.806 Å, whereas those for the basal-apical Rh−Rh bonds without CO bridges range from 2.682 to 2.737 Å. The basal-apical Rh−Rh bond distances have been found to be consistently longer than those for the basal Rh−Rh bonds by 0.05 Å (DFT methods) or 0.1 Å (the HF method). Using the MPW1PW91 functional, the basal Rh−Rh bond distances were predicted to be 2.692 Å, which is only 0.02 Å different from the experimental value.[68] For the basal-apical Rh−Rh bond distances the MPW1PW91 predicted value (2.750 Å) is also closest to experiment (Table 7). The basal Rh−C distances to the bridging CO groups (2.096−2.142 Å) are significantly longer than those to the terminal CO groups (1.903−1.986 Å) indicating a lower Rh−C bond order for the bridging CO groups relative to the terminal CO groups. The apical Rh−C bond lengths are in the range of 1.926−2.011 Å. The MPW1PW91 predicted Rh−C bond distances are in good agreement with experiment[68] within 0.018 Å.

Besancon and co-workers[17] reported density functional calculations on the bridged ($C_{3v}$) form of $Rh_4(CO)_{12}$ with two different functionals (the LDA and GGA methods with Slater-type basis functions). Their LDA method predicted all bond distances similar to our MPW1PW91 results, while their GGA method predicted almost the same Rh−C bond lengths as our B3LYP and BP86 results but rather long Rh−Rh distances (>2.99 Å).

The $T_d$ structure for $Rh_4(CO)_{12}$ having exclusively terminal CO groups (Figure 7) was optimized using four methods. The energy of the $T_d$ structure was found to be higher than that of the $C_{3v}$ structure by 26.4−30.5 kcal/mol depending upon the method used (Table 8). Our optimized symmetry parameters and theoretical predicted values as well as the

**Table 9.** Comparison of Theoretical Geometrical Parameters of $Rh_4(CO)_{12}$ ($T_d$)

|  | BP86 | B3LYP | MPW1PW91 | HF[a] | LDA[17] |
|---|---|---|---|---|---|
| Rh−Rh | 2.702 | 2.696 | 2.661 | 2.652 (2.655) | 2.601 |
| Rh−C | 1.920 | 1.936 | 1.913 | 1.997 (1.987) | 1.879 |
| C−O | 1.168 | 1.153 | 1.149 | 1.120 (1.120) | 1.149 |

[a] The results predicted by larger basis sets (a set of f functions for Rh is added) are given in parentheses.
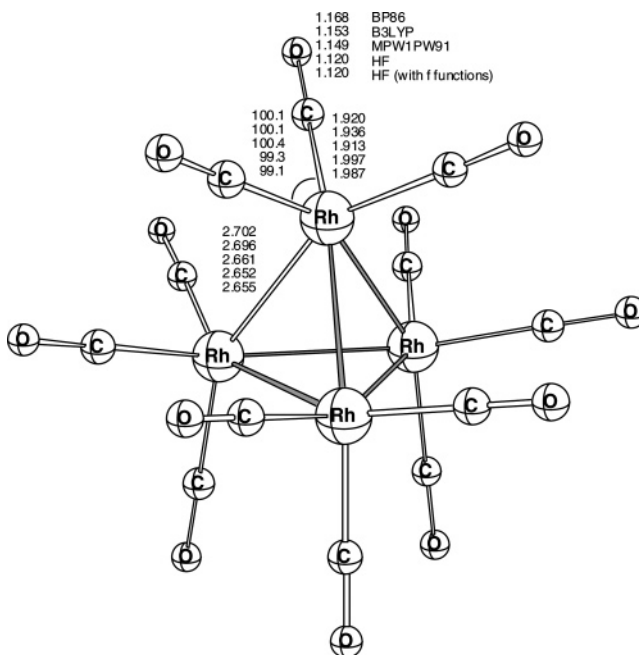


**Figure 7.** The optimized geometry of $Rh_4(CO)_{12}$ ($T_d$ symmetry). The distances are given in Å.

previous theoretical results[17] are summarized in Table 9. The geometrical parameters obtained from the different methods agree reasonably with each other. Again, the effect of the f functions added to Rh atoms is negligible. Our theoretical predicted Rh−Rh bond lengths for the $T_d$ structure of $Rh_4(CO)_{12}$ are in the range from 2.661 to 2.702 Å, while the Rh−C bond lengths are from 1.913 to 1.997 Å. The Rh−Rh distances in the $T_d$ $Rh_4(CO)_{12}$ structure are found to be shorter than the unbridged Rh−Rh distances in the $C_{3v}$ structure of $Rh_4(CO)_{12}$ by 0.031−0.036 Å. Using the MPW1PW91 functional, the Rh−Rh bond distances and the

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***Table 10.*** Comparison of Experimental and Theoretical Geometrical Parameters of $Rh_6(CO)_{16}$ ($T_d$)

| | BP86 | B3LYP | MPW1PW91 | HF | exp.[12] | exp.[73] |
|---|---|---|---|---|---|---|
| Rh−Rh | 2.822 | 2.835 | 2.785 | 2.863 (2.859)[a] | 2.776 (2.762−2.790) | 2.750[a] |
| Rh−C | 1.901 | 1.915 | 1.896 | 1.988 (1.978)[a] | 1.864 (1.849−1.879) | 1.915 (1.900−1.930) |
| C−O | 1.166 | 1.151 | 1.147 | 1.117 (1.117)[a] | 1.155 (1.140−1.170) | 1.126 (1.113−1.139) |
| Rh−C | 2.195 | 2.210 | 2.183 | 2.244 (2.241)[a] | 2.168 (2.156−2.180) | 2.186 (2.182−2.190) |
| C−O | 1.194 | 1.178 | 1.174 | 1.140 (1.141)[a] | 1.201 (1.179−1.223) | 1.153 (1.147−1.159) |
| mean absolute errors | 0.026 | 0.028 | 0.009 | 0.037 | | |

[a] In parentheses are the results predicted by larger basis sets (a set of f functions for Rh is added).
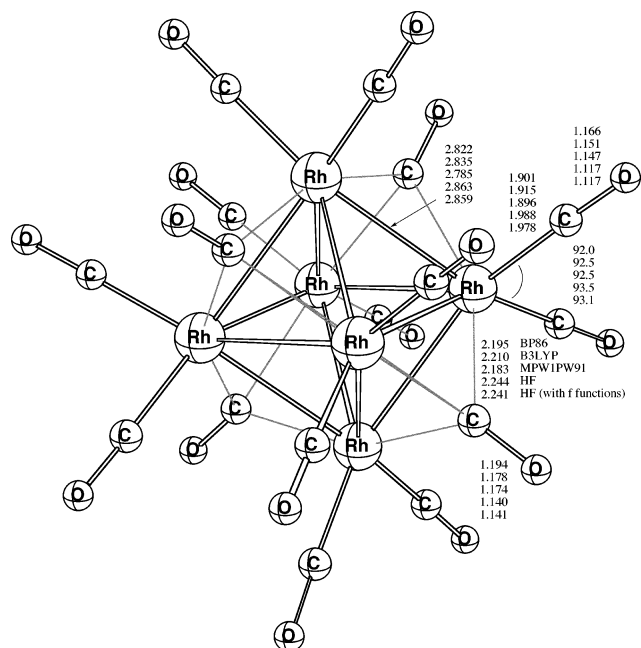


***Figure 8.*** The optimized structure of $Rh_6(CO)_{16}$ ($T_d$ symmetry). The distances are given in Å.

Rh−C bond lengths are predicted to be 2.661 Å and 1.913 Å, respectively. No experimental results are available for comparison. The previous theoretical results[17] for the bond distances predicted by the LDA method are close to but slighter shorter than our MPW1PW91 predictions.

**3.5. $Rh_6(CO)_{16}$.** The molecule $Rh_6(CO)_{16}$ was the first metal carbonyl cluster to be discovered with more than four metal atoms. It is of historical interest related to chemical bonding theories for metal cluster bonding leading to the development of the Wade-Mingos rules.[69−72] Optimization of the structure of $Rh_6(CO)_{16}$ gave an idealized $T_d$ structure with four equivalent face-bridging carbonyl groups and 12 equiv terminal carbonyl groups (Figure 8). The 12 equiv Rh−Rh distances in $Rh_6(CO)_{16}$ (Table 10) are in the range 2.785−2.863 Å predicted by the different methods. These Rh−Rh distances in $Rh_6(CO)_{16}$ are significantly longer than the Rh−Rh distances in $T_d$ $Rh_4(CO)_{12}$ by 0.120−0.211 Å, suggesting a lower effective Rh−Rh bond order in $Rh_6(CO)_{16}$ than in $Rh_4(CO)_{12}$. The MPW1PW91 method predicts the Rh−Rh bond distances to be 2.785 Å, which are the closest to the experimental values[73] (Table 10). The Rh−C distances for the terminal carbonyls fall in the range 1.896−1.988 Å, whereas the C−O bonds are in the range 1.117−1.166 Å. The Rh−C bond distances for the bridging carbonyls fall in the range 2.183−2.244 Å, whereas the C−O bond lengths

***Table 11.*** Comparison of the Experimental and Theoretical Infrared $\nu$(CO) Frequencies for the Metal Carbonyls Studied in This Work

| compound | method | infrared frequencies,[a] cm⁻¹ |
|---|---|---|
| $Mo(CO)_6$ ($O_h$) | Exp[75] | 82m, 367s, 596vs, 2003vvs |
| | BP86 | 84(1), 394(34), 602(96), 1979(1790) |
| | B3LYP | 88(1), 381(51), 611(112), 2057(2080) |
| | MPW1PW91 | 90(1), 401(50), 629(127), 2099(2140) |
| | HF | 100(2), 342(97), 627(181), 2298(2720) |
| $Tc_2(CO)_{10}$ ($D_{4d}$) | Exp[76] | 1984s, 2017vs, 2065s |
| | BP86 | 1978(1100), 2002(2340), 2047(1060) |
| | B3LYP | 2052(1160), 2082(2710), 2120(1380) |
| | MPW1PW91 | 2096(1280), 2125(2770), 2166(1300) |
| | HF | 2292(601), 2329(3560), 2329(3310) |
| $Ru(CO)_5$ ($D_{3h}$) | Exp[77] | 2002s, 2039s |
| | BP86 | 1985(1140), 2017(1290) |
| | B3LYP | 2063(1310), 2100(1470) |
| | MPW1PW91 | 2106(1360), 2144(1510) |
| | HF | 2301(2790), 2372(1710) |
| $Ru_3(CO)_{12}$ ($D_{3h}$) | Exp[78] | 2061s, 2034s, 2015s, 1997m |
| | BP86 | 2042(1790), 2015(2530), 1995(560), 1992(19) |
| | B3LYP | 2118(2340), 2098(2990), 2074(460), 2071(33) |
| | MPW1PW91 | 2163(2380), 2140(3050), 2117(488), 2115(10) |
| | HF | 2351(4220), 2348(4330), 2320(34), 2307(230) |
| $Rh_4(CO)_9$-$(\mu$-CO$)_3$ ($C_{3v}$) | Exp[54] | 1887m, 2044m, 2046m, 2071s, 2076s |
| | BP86 | 1879(689), 1994(51), 2009(283), 2038(1410), 2039(1935) |
| | B3LYP | 1953(867), 2080(31), 2095(362), 2123(1690), 2124(2510) |
| | MPW1PW91 | 1990(902), 2124(49), 2140(300), 2169(1720), 2169(2570) |
| | HF | 2124(49), 2157(1620), 2348(509), 2372(1640), 2392(4390) |
| $Rh_6(CO)_8$-$(\mu$-CO$)_4$ ($O_h$) | Exp[54] | 1819m, 2045w, 2075s |
| | BP86 | 1801(667), 2014(96), 2049(2400) |
| | B3LYP | 1884(834), 2100(56), 2134(2860) |
| | MPW1PW91 | 1921(864), 2142(55), 2177(2860) |
| | HF | 2122(1420), 2364(129), 2395(3730) |

fall in the range from 1.140 to 1.194 Å. Again the MPW1PW91 predictions are in good agreement with the experimental results.

**3.6. Infrared Frequencies.** Table 11 compares the vibrational frequencies found experimentally for the second-row metal carbonyl derivatives with the infrared-active harmonic vibrational frequencies calculated using the four different methods discussed in this paper. For $Mo(CO)_6$, where more experimental data are available, all of the infrared active frequencies are given, whereas for the other metal carbonyl derivatives only the $\nu$(CO) frequencies are given.

The data in Table 11 clearly indicate that the BP86 functional is by far the best for predicting infrared frequencies, as was found earlier for the first-row transition-metal derivatives including $Co_4(CO)_{12}$ and $Co_6(CO)_{16}$ analogous to the rhodium carbonyl derivatives studied in this paper.[74-78] The MPW1PW91 method, which is the most effective for predicting molecular geometries, is not even as effective for predicting $\nu(CO)$ frequencies as the B3LYP method. The Hartree−Fock method predicts $\nu(CO)$ frequencies so far from the experimental values as to be of limited value.

## 4. Concluding Remarks

We report here a systematic comparison between theory and experiment for the six homoleptic second-row transition-metal carbonyls whose structures have been determined by X-ray crystallography. A total of 26 bond distances have been predicted with each of four theoretical methods. The average errors for the different methods are 0.030 Å (BP86), 0.028 Å (B3LYP), 0.018 Å (MPW1PW91), and 0.050 Å (Hartree−Fock).

It is clear that the new generation DFT method MPW1-PW91 is superior to earlier established methods for predicting the structures of these homoleptic second-row transition-metal carbonyls. However, the BP86 method, which is effective for predicting the infrared spectra of first-row transition-metal carbonyl derivatives, is found to be more effective than not only the MPW1PW91 but also the B3LYP method for predicting the infrared spectra of second-row transition-metal derivatives.

**Supporting Information Available:** Harmonic vibrational frequencies (in $cm^{-1}$) and their IR intensities (in km/mol) for $Mo(CO)_6$, $Tc_2(CO)_{10}$, $Ru(CO)_5$, two isomers of $Ru_3(CO)_{12}$ and $Ru_4(CO)_{12}$, and $Rh_6(CO)_{16}$ (Table S1−S8). This material is available free of charge via the Internet at http://pubs.acs.org.

### References

(1) (a) Hawkins, N. J.; Mattraw, H. C.; Sabol, W. W.; Carpenter, D. R. *J. Chem. Phys.* **1955**, *23*, 2422. (b) Jones, L. H. *J. Chem. Phys.* **1962**, *36*, 2375.

(2) Arnesen, S.; Seip, H. M. *Acta Chem. Scand.* **1966**, *20*, 2711.

(3) Mak, T. C. W. *Z. Kristallogr.* **1984**, *166*, 277.

(4) (a) Hileman, J. C.; Huggins, D. K.; Kaesz, H. D. *J. Am. Chem. Soc.* **1961**, *83*, 2953. (b) Wallach, D. *Acta Crystallogr.* **1982**, *15*, 1058.

(5) Bailey, M. F.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1140.

(6) Huang, J.; Hedberg, K.; Davis, H. B.; Pomeroy, R. K. *Inorg. Chem.* **1990**, *29*, 3923.

(7) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655.

(8) Delley, B.; Manning, M. C.; Ellis, D. E.; Berkowitz, J. *Inorg. Chem.* **1982**, *21*, 2247.

(9) Hieber, W.; Lagally, H. *Z. Anorg. Allg. Chem.* **1943**, *251*, 96.

(10) Wei, C. H.; Wilkes, G. R.; Dahl, L. F. *J. Am. Chem. Soc.* **1967**, *89*, 4792.

(11) Wei, C. H. *Inorg. Chem.* **1969**, *8*, 2384.

(12) Corey, E. R.; Dahl, L. F.; Beck, W. *J. Am. Chem. Soc.* **1963**, *85*, 1202.

(13) Heaton, B. T.; Jacob, C.; Podkorytov, I. S.; Tunik, S. P. *Inorg. Chim. Acta* **2006**, *359*, 3557.

(14) Heaton, B. T.; Sabounchei, J.; Kernaghan, S.; Nakayama, H.; Eguchi, T.; Takeda, S.; Nakamura, N.; Chihara, A. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3019.

(15) Evans, J.; Johnson, B. F. G.; Lewis, J.; Norton, J. R.; Cotton, F. A. *J. Chem. Soc., Chem. Commun.* **1973**, 807.

(16) Evans, J.; Johnson, B. F. G.; Lewis, J.; Matheson, T. W.; Norton, J. R. *J. Chem. Soc., Dalton Trans.* **1978**, 626.

(17) Besancon, K.; Laurenczy, G.; Lumini, T.; Roulet, R.; Bruyndonckx, R.; Daul, C. *Inorg. Chem.* **1968**, *37*, 5634.

(18) Farrar, D. H.; Grachova, E. V.; Lough, A.; Patirana, C.; Poë, A. J.; Tunik, S. P. *J. Chem. Soc., Dalton Trans*. **2001**, 2015.

(19) Walter, T. H.; Reven, L.; Oldfield, E. *J. Phys. Chem.* **1989**, *93*, 1320.

(20) Salzmann, R.; Kaupp, M.; McMahon, M. T.; Oldfield, E. *J. Am. Chem. Soc*. **1998**, *120*, 4771.

(21) Wei, C. H.; Dahl, L. F. *J. Am. Chem. Soc.* **1966**, *88*, 1821.

(22) Ehlers, A. W.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 1514.

(23) Delly, B.; Wrinn, M.; Lüthi, H. P. *J. Chem. Phys.* **1994**, *100*, 5785.

(24) Li, J.; Schreckenbach, G.; Ziegler, T. *J. Am. Chem. Soc.* **1995**, *117*, 486.

(25) Jonas, V.; Thiel, W. *J. Phys. Chem.* **1995**, *102*, 8474.

(26) Kaup, M.; Malkin, V. G.; Maklina, O. L.; Salahub, D. R. *Chem. Eur. J.* **1996**, *2*, 24.

(27) Barckholtz, T. A.; Bursten, B. E. *J. Am. Chem. Soc.* **1998**, *120*, 1926.

(28) Jemmis, E. D.; Giju, K. T. *J. Am. Chem. Soc.* **1998**, *120*, 6952.

(29) Niu, S.; Hall, M. B. *Chem. Rev.* **2000**, *100*, 353.

(30) Cotton, F. A.; Gruhn, N. E.; Gu, J.; Huang, P.; Lichtenberger, D. L.; Murillo, C. A.; Van Dorn, L. O.; Wilkinson, C. C. *Science* **2002**, *298*, 1971.

(31) Macchi, P.; Sironi, A. *Coord Chem. Rev.* **2003**, *100*, 353.

(32) Siegbahn, P. E. M. *J. Am. Chem. Soc.*, **2005**, *127*, 17303.

(33) Ziegler, T.; Autschbach, J. *Chem. Rev.* **2005**, *105*, 2695.

(34) Mota, A. J.; Dedieu, A.; Bour, C.; Suffert, J. *J. Am. Chem. Soc.* **2005**, *127*, 7171.

(35) Bühl, M.; Kabrede, H. *J. Chem. Theory Comput.* **2006**, *2*, 1282.

(36) Brynda, M.; Gagliardi, L.; Wimark, P. O.; Power, P. P.; Roos, B. O. *Angew. Chem., Int. Ed.* **2006**, *45*, 3804.

(37) Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.* **2006**, *124*, 224105.

(38) Harvey, J. N. *Ann. Rep. Prog. Chem. Sect. C* **2006**, *102*, 203.

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*J. Chem. Theory Comput., Vol. 3, No. 4, 2007* **1587**

(39) Strickland, N. S.; Harvey, J. N. *J. Phys. Chem. B* **2007**, *111*, 841.

(40) Ignatyev, I.; King, R. B.; Schaefer, H. F., III *J. Am. Chem. Soc.* **2000**, *122*, 1989.

(41) Xie, Y.; King, R. B.; Schaefer, H. F., III *J. Am. Chem. Soc.* **2000**, *122*, 8746.

(42) Li, Q.; Liu, Y.; Xie, Y.; King, R. B.; Schaefer, H. F., III *Inorg. Chem.* **2001**, *40*, 5842.

(43) King, R. B.; Schaefer, H. F., III *Pure Appl. Chem.* **2001**, *73*, 1059.

(44) Kenny, J.; King, R. B.; Schaefer, H. F., III *Inorg. Chem.* **2001**, *40*, 900.

(45) Richardson, N. R.; Xie, Y.; King, R. B.; Schaefer, H. F., III *J. Phys. Chem. A* **2001**, *105*, 11134.

(46) Li, S.; Richardson, N. R.; Xie, Y.; King, R. B.; Schaefer, H. F., III *Faraday Discuss.* **2003**, *124*, 315.

(47) Li, S.; Richardson, N. R.; Xie, Y.; King, R. B.; Schaefer, H. F., III *J. Phys. Chem. A* **2003**, *107*, 10118.

(48) Fuentealba, P.; Preuss, H.; Stoll, H.; v. Szentpaly, L. *Chem. Phys. Lett.* **1989,** *89*, 418.

(49) v. Szentpaly, L.; Fuentealba, P.; Preuss, H.; Stoll, H. *Chem. Phys. Lett.* **1982,** *93*, 555.

(50) Fuentealba, P.; Stoll, H.; v. Szentpaly, L.; Schwerdtfeger, P.; Preuss, H. *J. Phys. B* **1983**, *16*, 1323.

(51) Stoll, H.; Fuentealba, P.; Schwerdtfeger, P.; Flad, J.; v. Szentpaly, L.; Preuss, H. *J. Chem. Phys.* **1984**, *81*, 2732.

(52) Van Wüllen, C. *Int. J. Quantum Chem.* **1996**, *58*, 147.

(53) Hunstock, E.; Mealli, C.; Calhorda, M.; Reinhold, J. *Inorg. Chem.* **1999**, *38*, 5053.

(54) Allian, A. D.; Wang, Y.; Saeys, M.; Kuramshina, G. M.; Garland, M. *Vib. Spectrosc.* **2006**, *41*, 101.

(55) Cotton, F. A.; Gu, J.; Murillo, C. A.; Timmons D. J. *J. Am. Chem. Soc.* **1998**, *120*, 13280.

(56) Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648.

(57) Lee, C.; Yang, W. W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785.

(58) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Perdew, J. P. *Phys. Rev.* **1986**, *B33*, 8822.

(59) Adamo, C.; Barone, V. *J. Chem. Phys.* **1998**, *108*, 664.

(60) Zhao, S.; Wang, W.; Li, Z.; Liu, Z. P.; Fan, K.; Xie, Y.; Schaefer, H. F., III *J. Chem. Phys.* **2006**, *124*, 184102.

(61) Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1993**, *85*, 441.

(62) Bergner, A.; Dolg, M.; Kuechle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431.

(63) Dunning, T. H. *J. Chem. Phys*. **1970**, *53*, 2823.

(64) Huzinaga, S. *J. Chem. Phys*. **1965**, *42*, 1293.

(65) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision C.02*; Gaussian, Inc.: Wallingford, CT, 2004.

(66) Hunstock, E.; Mealli, C.; Calhorda, M. J.; Reinhold, J. *Inorg. Chem.* **1999**, *38*, 5053.

(67) Aime, S.; Dastrù, W.; Gobetto, R.; Krause, J.; Milone, L. *Organometallics* **1995**, 1*4*, 4435.

(68) Farrugia, L. J. *J. Cluster Sci.* **2000**, *11*, 39.

(69) Wade, K. *Chem. Commun. (Cambridge)* **1971**, 792.

(70) Wade, K, *Adv. Inorg. Chem. Radiochem*. **1976**, *18*, 1.

(71) Mingos, D. M. P. *Nat. Phys. Sci.* **1972**, *99*, 236.

(72) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311.

(73) Farrar, D. H.; Grachova, E. V.; Lough, A.; Patirana, C.; Poë, A. J.; Tunik, S. P. *J. Chem. Soc., Dalton Trans.* **2001**, 2015.

(74) Xie, Y.; King, R. B.; Schaefer, H. F., III *Spectrochem. Acta* **2005**, *A61*, 1693.

(75) Jones, L. H.; McDowell, R. S.; Goldblatt, M. *Inorg. Chem.* **1969**, *8*, 2349.

(76) Michels, G. D.; Svec, H. J. *Inorg. Chem.* **1981**, *20*, 3445.

(77) Gregory, M. P.; Poliakoff, M.; Turner, J. J. *J. Mol. Struct.* **1985**, *127*, 247.

(78) Battiston, G. A.; Bor, G.; Dietler, U. K.; Kettle, S. F. A.; Rossetti, R.; Sbrignadello, G.; Stanghellini, P. L. *Inorg. Chem.* **1980**, *19*, 1961.