Comparison of the Becke−Lee−Yang−Parr and Becke−Perdew−Wang Exchange-Correlation Functionals for Geometries of Cyclopentadienyl−Transition Metal Complexes

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Complete all-electron density functional geometry optimizations have been performed on six “half-sandwich” cyclopentadienyl−transition metal complexes using both the Becke−Lee−Yang−Parr (BLYP) and Becke−Perdew−Wang functionals (BPW91). The two functionals agree very well with each other for bond distances not involving the metal. In a double-ζ plus polarization quality basis, both overestimate these distances by amounts similar to those observed in small molecules with equivalent basis sets. For the single first series complex examined, BPW91 gives comparable agreement for all the bonds, but for complexes of the second transition series, BPW91 consistently overestimates the metal−Cp C distances by 0.06−0.07 Å. Metal f functions shorten these slightly. After estimated relativistic contractions are applied, the BPW91 metal−Cp C overestimates for the second series complexes would be reduced to levels comparable to the first series or small molecules without metals. However, BLYP consistently gives significantly longer values than BPW91 for all distances involving the metal in both the first and second series complexes, so that even after applying all the previous corrections, overestimates ≥ 0.07 Å relative to experiment would persist for the metal−Cp C bonds. Consistent disagreements of this magnitude between the two functionals for normal chemical bonds appear to be unprecedented in the literature.

1. Introduction

Cyclopentadiene (Cp, C_5H_5) is a ubiquitous ligand in organotransition metal chemistry. One extremely important general class of Cp complexes are the “half-sandwich” complexes containing one η^5-Cp in a piano stool geometry with 1−4 legs formed by additional ligands such as halogens, CO, NO, NS, or alkyl groups.[1] Such complexes are of widespread interest for their relevance in areas such as homogeneous catalysis, and they often display a number of interesting structural features which may play important roles in such applications, namely, (a) high sensitivity of the ring orientation to the other ligands; (b) pronounced ring “slippage,” or unequal metal−ring carbon distances; (c) significant distortion of the ring from pentagonal symmetry. From a theoretical viewpoint, the ability to predict quantitatively these features presents not only a major goal but also a major computational challenge due to the mere size and number of electrons as well as the presence of a transition metal.

The Kohn−Sham formulation of density functional theory[2] holds considerable promise for predicting theoretically the quantitative properties of large molecules in general and such complexes in particular.[3] Unfortunately, except for isolated special cases (*e.g.*, two-electron atoms), accurate exchange and correlation functionals are known only for systems of uniform electron density. Use of these functionals in calculations on systems of nonuniform electron density leads to the local density approximation (LDA).

In order to achieve higher accuracy, there has been considerable effort directed toward the development of improved exchange and correlation functionals by incorporating gradients of the electron density. Several of these generalized gradient approximations (GGA) have found widespread use in molecular calculations.

One of the most common examples is the exchange functional of Becke[4] combined with the correlation functional of Lee, Yang, and Parr[5] to yield the exchange-correlation functional referred to as BLYP. There have been several systematic studies in which self-consistent solution of the Kohn−Sham equations with the BLYP functional was used for predicting the geometries of molecules composed of first row atoms. In particular, in an extensive test involving 32 such molecules the BLYP functional was found to give bond lengths which are systematically too long by ∼0.02 Å.[6]

Recently, Perdew and Wang have presented a new correlation functional,[7] which has been shown[8] to satisfy more formal constraints on the exact correlation functional than do a number of others. Combined with the Becke exchange functional, this yields the BPW91 exchange-correlation functional. Salahub *et al.*[9] have tested the PW91 functional for the geometries of 21 diatomic and 26 polyatomic molecules composed of first and second row atoms. They found mean absolute bond distance errors of 0.022 and 0.011 Å in the diatomic and polyatomic cases, respectively, only slightly better than Becke exchange plus the earlier 1986 Perdew[10] correlation functional (BP86) and comparably accurate to BLYP.

While there have been a number of density functional studies of transition metal complexes, relatively few have reported optimized geometries for complexes containing cyclopentadiene as a ligand, and most of these have involved full-sandwich Cp_2 complexes of the first transition series.[11−13] The focus of this

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work has been on elucidating the mechanism of Ziegler−Natta type catalysis, so neither the complexes chosen for study nor the geometry optimizations performed were intended to permit detailed comparisons of predicted with experimental structures for different functionals.

DFT studies of half-sandwich complexes are even more sparse, but recently Field *et al.*[14] have published a combined experimental−theoretical study of CpNi(NO). Optimized LDA and BP86 geometries were determined; however, neither the BLYP nor the BPW91 functional was investigated.

In none of these studies—nor in any others of which we are aware—has a systematic comparison been made between different GGA functionals in terms of their ability to predict the geometries of a general class of complexes containing cyclopentadiene as a ligand. In particular, we are unaware of any work in which BLYP and BPW91 have been compared systematically for such complexes.

We recently undertook a study of several cyclopentadienyl−ruthenium complexes using both the BLYP and BPW91 functionals. We found that for bond distances not involving the metal the two functionals gave computed geometries in good agreement with each other and in comparable agreement with experiment to that found in the various small molecule studies. However, metal−ligand distances were systematically overestimated, and this overestimation was particularly severe for distances between the Ru and the carbons in the Cp ring. Moreover, BLYP consistently gave values for these distances approximately 0.05 Å larger than those of BPW91. As will be discussed, one might expect nonrelativistic calculations to overestimate metal−ligand distances in second transition series complexes by amounts comparable to those we observed with BPW91; however, with BLYP the overestimation seems well outside the range of plausible relativistic contractions.

This level of disagreement between the two functionals is in marked contrast to the good agreement between them for bonds involving nonmetal atoms, including the other atoms in our complexes. In order to determine if this is an isolated instance or a more general phenomenon, we have carried out calculations on several additional complexes. The results of this study are reported here. The primary purpose of this paper is to determine if systematic disagreements exist between BLYP and BPW91 geometries for complexes of this type. No RHF or LDA results are included since many other studies have shown that systematic differences do exist between RHF, LDA, and GGA geometries even for much simpler molecules. To keep the comparison as unambiguous as possible, the introduction of further approximations (*e.g.*, effective core potentials) has been avoided as well.

It would, of course, be possible for BLYP and BPW91 to disagree significantly and still be comparably accurate if they bracketed the experimental geometry. Therefore, a comparison with experiment is an essential component of this study, and the major criterion for choosing the complexes included was that they have well-defined X-ray crystal structures with low standard error and no disorder. Secondary criteria were that several geometries had to be represented and that the other ligands had to be relatively simple for computational efficiency. Only first and second transition series complexes were considered; third series metals were excluded due to the lack of adequate basis sets and the inevitability of large, uncertain relativistic corrections.

The X-ray structures apply, of course, to the solid phase, whereas our computed structures are analogous to the gas phase. However, in cases where the X-ray structures of Cp−transition metal complexes can be compared with gas phase microwave or electron diffraction structures,[15] the bond lengths are found to agree much better than the discrepancies between theory and experiment we observe. Therefore, errors due to crystal-packing effects should not be a significant factor.

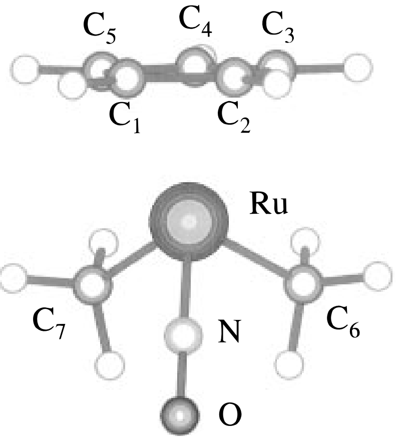

Figure 1. Structure of $CpRu(NO)(CH_3)_2$.

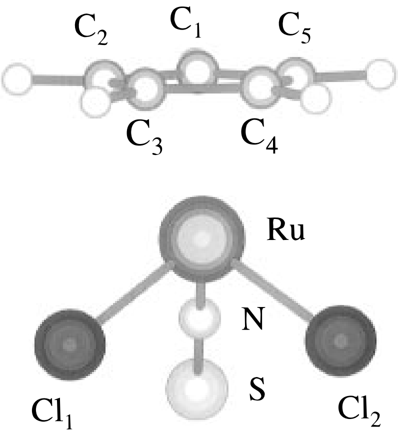

Figure 2. Structure of $CpRu(NS)Cl_2$.

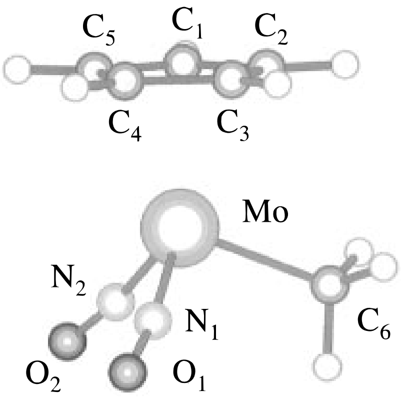

Figure 3. Structure of $CpMo(NO)_2CH_3$.

The three-legged stool complexes included in this study are two Ru complexes, $CpRu(NO)(CH_3)_2$ (Figure 1) and $CpRu(NS)Cl_2$ (Figure 2), and two Mo complexes, $CpMo(NO)_2CH_3$ (Figure 3) and $CpMo(NO)_2Cl$ (Figure 4). The X-ray structures of the Cp* (pentamethylcyclopentadiene, C_5Me_5) analogs of these complexes have been determined by Hubbard and coworkers.[16]

The two-legged stool complexes considered are $CpCo(CO)_2$ (Figure 5) and $CpRh(CO)_2$ (Figure 6), which differ only in the replacement of the first series Co with the corresponding second series Rh. The X-ray structures of the Cp* analogs have been determined by Byers and Dahl[17] and Lichtenberger, Blevins, and Ortega,[18] respectively.

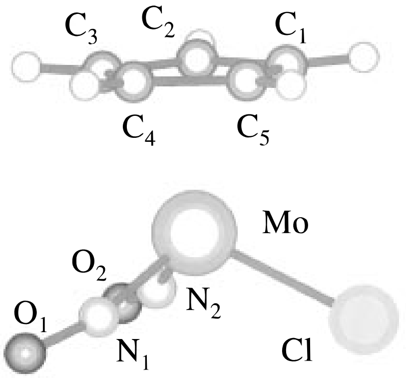

Figure 4. Structure of $CpMo(NO)_2Cl$.

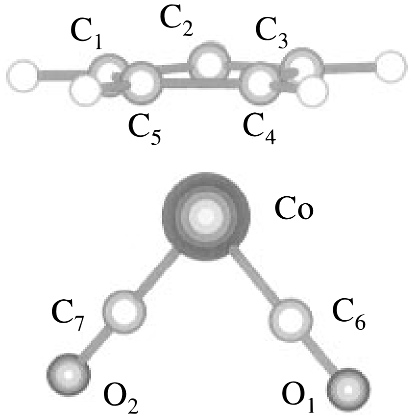

Figure 5. Structure of $CpCo(CO)_2$.

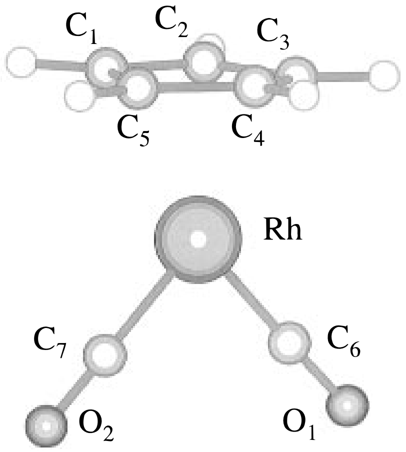

Figure 6. Structure of $CpRh(CO)_2$.

Note that all of these are normal 18-electron complexes and would not appear to involve any unusual electronic structure or bonding.

2. Methods

Fully self-consistent, nonrelativistic, all-electron, complete geometry optimizations were performed in C_1 symmetry using Gaussian basis sets. For the transition metals, basis sets developed collaboratively by the Cray Research and University of Montreal groups[19] were adopted; these are of double-ζ valence plus polarization (DZVP) quality except for the absence of f functions on the metal. In some calculations a single set of f primitives (exponents: Co 2.0, Ru 0.90, Rh 0.93) was added; these are denoted by +f in the text and tables. For the remaining atoms, we used the correlation consistent double-ζ plus polarization basis sets developed by Dunning and coworkers (cc-pvdz).[20]

The charge density fitting procedure of Dunlap *et al.*[21] was used for the approximate evaluation of the Coulomb potential in order to decrease the computational time. The auxiliary basis sets were taken from the same source as the transition metal basis sets given above.[19] An additional set of f and g functions was added to the metal basis set to improve the accuracy in the evaluation of the fitted Coulomb potential; the new set of f exponents is equal to the old d exponents, whereas for the g exponents we have used only two of the d exponents.

The calculations were carried out with the NWChem computational chemistry package,[22] which is targeted to exploit the aggregate computing power of massively parallel processors. The calculations were performed on 32−64 nodes of the IBM SP at the Maui High Performance Computing Center (MHPCC) or the KSR-2 at Pacific Northwest National Laboratory. For a representative calculation using 9711 grid points/atom for the numerical integration of the exchange-correlation functional, 229 orbital basis functions and 579 fitting functions, a 20-step geometry walk required an average of 12 min per step (energy plus gradients) on 39 SP nodes.

3. Results

The optimized geometries and total energies at the minima are shown in Tables 1−6. The experimental structures of the Cp* analogs also are tabulated. The theoretical geometries are converged to ~0.002 Å. The standard errors in the experimental geometries are uniformly <0.01 Å, typically 0.005 Å.

Since the experimental structures are all for Cp* complexes, the effect of substituting Cp for Cp* was tested. Optimized geometries were determined for the Cp* variants of the two Ru complexes using BPW91+f. These results are included in Tables 1 and 2.

In order to assess the possible geometric error introduced by the charge density fitting procedure, the geometry optimization for $CpRh(CO)_2$ was repeated using exact N^4 evaluation of the Coulomb potential. These results also are shown in Table 6.

To test the adequacy of the basis sets, the geometry of $CpRu(NO)(CH_3)_2$ was reoptimized in several extended basis sets using the BPW91 functional. Table 7 shows the results.

4. Discussion

For every complex, BLYP and BPW91 give computed geometries that are in excellent qualitative agreement with experiment. In particular, the same pattern of unequal metal−Cp C and Cp C−C distances observed experimentally is found in all the calculations. However, the calculations differ quantitatively from experiment and from each other in systematic ways. In Table 8 we show the mean absolute deviations from experiment in the distances between (a) the metal and the five ring carbons, (b) the metal and the other (nonring) ligands, and (c) intra-ring carbons. We use the mean absolute error in the individual metal−Cp C distances rather than the metal−Cp centroid distance because the former is much more sensitive to slippage or inequality of individual distances. The slippage is quite pronounced for many of these complexes, especially $CpRu(NS)Cl_2$, where the longest and shortest Ru−Cp C bonds differ by >0.1 Å.

Note that the replacement of Cp* by Cp causes very small changes in an average sense. The maximum effect is seen in the ring C−C distances for $CpRu(NO)(CH_3)_2$, which are ~0.01 Å smaller than in its Cp* analog. Thus, this computation-time-saving simplification appears to be an excellent approximation unless very high accuracy is required.

One sees that f functions have a negligible effect on the geometry of the first series complex and only a small effect for

TABLE 1: Energies and Bond Distances for CpRu(NO)(CH$_3$)$_2$[a]

			BPW91+f		
	BLYP	BPW91	Cp	Cp*	Cp* exptl
energy	−4846.029 08	−4846.427 33	−4846.438 54	−5042.966 05	
lengths					
Ru−C$_6$	2.174	2.154	2.146	2.150	2.118
Ru−C$_7$	2.174	2.154	2.146	2.148	2.118
Ru−N	1.783	1.759	1.761	1.767	1.719
Ru−C$_1$	2.437	2.383	2.371	2.356	2.295
Ru−C$_2$	2.438	2.386	2.371	2.350	2.295
Ru−C$_3$	2.379	2.333	2.318	2.319	2.277
Ru−C$_4$	2.318	2.277	2.268	2.273	2.238
Ru−C$_5$	2.377	2.329	2.318	2.325	2.277
C$_1$−C$_2$	1.446	1.442	1.442	1.454	1.436
C$_2$−C$_3$	1.427	1.425	1.425	1.434	1.415
C$_3$−C$_4$	1.445	1.443	1.443	1.454	1.430
C$_4$−C$_5$	1.445	1.443	1.443	1.455	1.430
C$_5$−C$_1$	1.427	1.425	1.425	1.434	1.415

[a] Energies in hartrees; distances in angstroms.

TABLE 2: Energies and Bond Distances for CpRu(NS)Cl$_2$[a]

			BPW91+f		
	BLYP	BPW91	Cp	Cp*	Cp* exptl
energy	−6009.736 40	−6010.124 42	−6010.137 57	−6206.709 23	
lengths					
Ru−Cl$_1$	2.413	2.390	2.380	2.394	2.406
Ru−Cl$_2$	2.413	2.389	2.380	2.390	2.396
Ru−N	1.798	1.786	1.774	1.776	1.772
Ru−C$_1$	2.287	2.233	2.223	2.218	2.192
Ru−C$_2$	2.318	2.271	2.260	2.252	2.191
Ru−C$_3$	2.399	2.358	2.350	2.363	2.300
Ru−C$_4$	2.400	2.358	2.351	2.366	2.317
Ru−C$_5$	2.320	2.271	2.260	2.256	2.211
C$_1$−C$_2$	1.443	1.442	1.447	1.451	1.438
C$_2$−C$_3$	1.450	1.448	1.448	1.461	1.445
C$_3$−C$_4$	1.419	1.416	1.415	1.424	1.399
C$_4$−C$_5$	1.449	1.447	1.447	1.459	1.460
C$_5$−C$_1$	1.443	1.443	1.442	1.451	1.427

[a] Energies in hartrees; distances in angstroms.

TABLE 3: Energies and Bond Distances for CpMo(NO)$_2$(CH$_3$)[a]

	BLYP	BPW91	Cp* exptl
energy	−4470.508 31	−4470.857 67	
lengths			
Mo−C$_6$	2.227	2.214	2.170
Mo−N$_1$	1.868	1.858	1.815
Mo−N$_2$	1.867	1.855	1.806
Mo−C$_1$	2.464	2.424	2.359
Mo−C$_2$	2.481	2.438	2.398
Mo−C$_3$	2.464	2.422	2.377
Mo−C$_4$	2.445	2.404	2.339
Mo−C$_5$	2.445	2.405	2.337
C$_1$−C$_2$	1.431	1.429	1.416
C$_2$−C$_3$	1.433	1.431	1.426
C$_3$−C$_4$	1.441	1.439	1.409
C$_4$−C$_5$	1.431	1.429	1.411
C$_5$−C$_1$	1.442	1.440	1.433

[a] Energies in hartrees; distances in anstroms.

TABLE 4: Energies and Bond Distances for CpMo(NO)$_2$Cl[a]

	BLYP	BPW91	Cp* exptl
energy	−4890.889 64	−4891.229 21	
lengths			
Mo−Cl	2.438	2.414	2.412
Mo−N$_1$	1.872	1.859	1.829
Mo−N$_2$	1.873	1.861	1.833
Mo−C$_1$	2.458	2.414	2.349
Mo−C$_2$	2.419	2.381	2.312
Mo−C$_3$	2.433	2.393	2.356
Mo−C$_4$	2.456	2.413	2.363
Mo−C$_5$	2.470	2.425	2.371
C$_1$−C$_2$	1.442	1.439	1.425
C$_2$−C$_3$	1.439	1.437	1.420
C$_3$−C$_4$	1.430	1.428	1.418
C$_4$−C$_5$	1.443	1.440	1.437
C$_5$−C$_1$	1.428	1.425	1.415

[a] Energies in hartrees; distances in angstroms.

the second series complexes. Table 7 shows that the effect of increasing the number of s, p, and d functions on Ru (column TZVP) or increasing the flexibility of the ligand basis (column aug-cc-pvdz) appears to be insignificant even for the second series. Since the purpose of this paper is to compare BLYP and BPW91 geometries in the same basis set for a variety of complexes, and since the differences between the two functionals are considerably larger than even the effect of f functions, it was not felt necessary to include f functions in all the calculations or conduct extensive basis set investigations for all the complexes.

Also note that although there is a significant total energy error introduced by the charge density fitting procedure (Table 6), the geometric error is insignificant.

From Table 8 one sees that for every complex BLYP and BPW91 give very similar Cp C−C distances; the average difference between them is only 0.001−0.003 Å. Both functionals tend to overestimate these distances by 0.01−0.02 Å, which is consistent with the behavior observed for small molecules.[6,9]

In contrast, the two functionals give very different values for bond distances involving the metal, and these differences are

TABLE 5: Energies and Bond Distances for CpCo(CO)$_2$[a]

	BLYP	BPW91	BPW91+f	Cp* exptl
energy	−1802.819 44	−1802.983 75	−1802.987 84	
lengths				
Co−C$_6$	1.757	1.740	1.741	1.724
Co−C$_7$	1.758	1.740	1.741	1.732
Co−C$_1$	2.108	2.068	2.068	2.062
Co−C$_2$	2.148	2.102	2.103	2.102
Co−C$_3$	2.108	2.069	2.068	2.072
Co−C$_4$	2.156	2.113	2.109	2.101
Co−C$_5$	2.156	2.113	2.109	2.105
C$_1$−C$_2$	1.434	1.433	1.433	1.407
C$_2$−C$_3$	1.433	1.433	1.433	1.414
C$_3$−C$_4$	1.460	1.457	1.456	1.445
C$_4$−C$_5$	1.415	1.416	1.416	1.392
C$_5$−C$_1$	1.460	1.457	1.456	1.447

[a] Energies in hartrees; distances in angstroms.

most extreme for the bonds to the carbons in the Cp ring. In every case BLYP consistently gives metal−Cp C distances 0.04−0.05 Å longer than those of BPW91. Since the present calculations involve a variety of metals, ligands, and geometries, it seems safe to conclude that this disagreement is a general feature of calculations on piano stool Cp complexes with transition metals. To our knowledge, a consistent disagreement of this magnitude between BLYP and BPW91 is unprecedented in the literature.

For all the second series complexes, the BPW91 metal−Cp C distances themselves are too long by 0.06−0.07 Å. Metal f functions reduce these by ∼0.01 Å, leaving a residual discrepancy of 0.05−0.06 Å. As noted, this almost certainly is not due to crystal-packing effects. Instead, compelling evidence that a significant part of the discrepancy has a relativistic origin is provided by comparing calculations on the first series complex CpCo(CO)$_2$ with its second series analog CpRh(CO)$_2$. The Rh−Cp C distances exhibit the same level of error found for the other second series complexes, whereas the Co−Cp C distances are in (probably fortuitously) good agreement with experiment. Ziegler *et. al.* have published a quasi-relativistic DFT study of several η-bonded ethene complexes.[23] They calculate a relativistic contraction in the metal−ethene distance of 0.02 Å for Ru and 0.04 Å for Pd. If, as a first approximation, these contractions simply are subtracted from our BPW91+f metal−Cp C distances for the Ru and Rh complexes, respectively, the discrepancy with respect to experiment would be reduced to an overestimation of 0.02−0.03 Å. This is only slightly greater than the overestimation observed for bonds between nonmetal atoms. However, even after these corrections are made, the BLYP distances would still exhibit errors ≥0.07 Å, approximately three times larger than typically found for nonmetal atoms.

The most obvious feature of the metal−Cp bonds is that they are usually the longest bonds in these complexes. A detailed examination of all the distances in Tables 1−6 reveals an interesting trend. With only one exception, BLYP gives larger values than BPW91 for *all* of these distances regardless of the atom pair involved, and the amount by which BLYP exceeds BPW91 appears correlated to some extent with the distance itself. To illustrate this, in Figure 7 we show a graph of the difference between the BLYP and BPW91 distances versus the

TABLE 6: Energies and Bond Distances for CpRh(CO)$_2$[a]

		BPW91			
	BLYP	cd fit	exact N^4	BPW91+f	Cp* exptl
energy	−5107.883 10	−5108.252 36	−5108.228 76	−5108.260 38	
lengths					
Rh−C$_6$	1.915	1.896	1.896	1.891	1.863
Rh−C$_7$	1.915	1.895	1.895	1.892	1.845
Rh−C$_1$	2.340	2.290	2.288	2.285	2.234
Rh−C$_2$	2.394	2.344	2.345	2.338	2.281
Rh−C$_3$	2.340	2.290	2.289	2.285	2.222
Rh−C$_4$	2.412	2.357	2.357	2.349	2.278
Rh−C$_5$	2.412	2.357	2.357	2.350	2.276
C$_1$−C$_2$	1.433	1.432	1.432	1.432	1.412
C$_2$−C$_3$	1.433	1.432	1.431	1.433	1.410
C$_3$−C$_4$	1.462	1.458	1.457	1.457	1.445
C$_4$−C$_5$	1.412	1.412	1.412	1.412	1.384
C$_5$−C$_1$	1.462	1.458	1.457	1.456	1.447

[a] Energies in hartrees; distances in angstroms.

TABLE 7: BPW91 Basis Set Study for CpRu(NO)(CH$_3$)$_2$[a]

Ru basis ligand basis	DZVP cc-pvdz	DZVP+f cc-pvdz	TZVP cc-pvdz	DZVP aug-cc-pvdz	Cp* exptl
energy	−4846.427 33	−4846.438 54	−4846.437 73	−4846.451 53	
lengths					
Ru−C$_6$	2.154	2.146	2.151	2.154	2.118
Ru−C$_7$	2.154	2.146	2.151	2.155	2.118
Ru−N	1.759	1.761	1.771	1.770	1.719
Ru−C$_1$	2.383	2.371	2.382	2.382	2.295
Ru−C$_2$	2.386	2.371	2.384	2.384	2.295
Ru−C$_3$	2.333	2.318	2.331	2.332	2.277
Ru−C$_4$	2.277	2.268	2.277	2.278	2.238
Ru−C$_5$	2.329	2.318	2.329	2.329	2.277
C$_1$−C$_2$	1.442	1.442	1.441	1.442	1.436
C$_2$−C$_3$	1.425	1.425	1.424	1.425	1.415
C$_3$−C$_4$	1.443	1.443	1.442	1.443	1.430
C$_4$−C$_5$	1.443	1.443	1.442	1.443	1.430
C$_5$−C$_1$	1.425	1.425	1.424	1.425	1.415

[a] Energies in hartrees; distances in angstroms.

TABLE 8: Mean Absolute Deviations of Bond Lengths from Experiment[a]

complex/ bonds	BLYP	BPW91	BPW91+f	
			Cp	Cp*
CpRu(NO)(CH$_3$)$_2$/				
Ru−ring C	0.113	0.065	0.053	0.048
Ru−other ligands	0.059	0.037	0.033	0.037
ring C−C	0.013	0.010	0.010	0.021
CpRu(NS)Cl$_2$/				
Ru−ring C	0.103	0.056	0.047	0.049
Ru−other ligands	0.017	0.012	0.015	0.007
ring C−C	0.011	0.011	0.011	0.016
CpMo(NO)$_2$(CH$_3$)/				
Mo−ring C	0.098	0.057		
Mo−other ligands	0.057	0.045		
ring C−C	0.017	0.015		
CpMo(NO)$_2$Cl/				
Mo−ring C	0.097	0.055		
Mo−other ligands	0.036	0.020		
ring C−C	0.013	0.011		
CpCo(CO)$_2$/				
Co−ring C	0.047	0.006	0.005	
Co−other ligands	0.030	0.012	0.013	
ring C−C	0.019	0.018	0.018	
CpRh(CO)$_2$/				
Rh−ring C	0.121	0.069	0.063	
Rh−other ligands	0.061	0.042	0.038	
ring C−C	0.021	0.019	0.018	

[a] Deviations in angstroms.

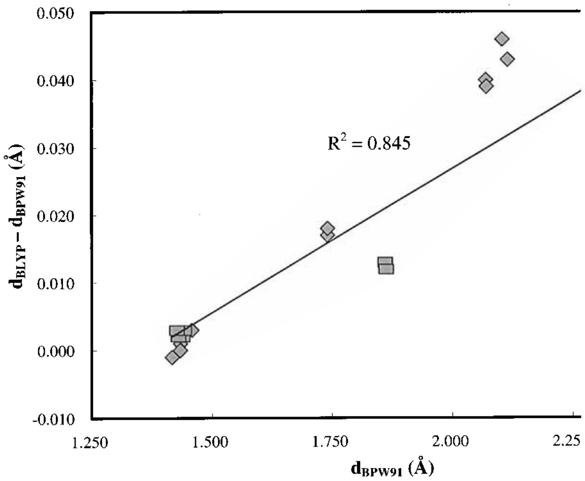

Figure 7. Distance differences BLYP-BPW91 versus BPW91 distance for CpMo(NO)$_2$Cl(□) and CpCo(CO)$_2$(◇).

BPW91 distance for CpCo(CO)$_2$ and CpMo(NO)$_2$Cl for all the bonds listed in Tables 4 and 5. Combining the different types of bonds for two complexes with different metals and different numbers and types of ligands into a single figure undoubtedly is a gross oversimplification. Thus the regression line probably should be taken more as a indicator of general trends rather than a precise statistical relationship. Nevertheless, a rather high correlation ($R^2 = 0.845$) is obtained for these two rather dissimilar complexes.

Whether the difficulty BLYP is experiencing with the metal−ligand bonds is strictly a result of distance or arises from some more subtle aspects of the electron density is unclear. It is well-known that most of the current GGA functionals have difficulties with weakly interacting systems such as van der Waals complexes, but the metal−Cp interaction is comparable to normal chemical bonds and is by no means weak. However, in their analysis of the bonding in Cr(CO)$_6$, Kunze and Davidson[24] proposed that dispersion interaction contributions to the bonding may become appreciable at normal bond lengths, and this was confirmed by subsequent correlated calculations.[25] A difference in dispersion interactions would not be inconsistent with the fact that since BLYP and BPW91 share a common exchange potential, the source of their disagreement must lie in the correlation potentials. One possibility is the long range behavior of the respective correlation potentials. Umrigar and Gonze[26] have compared the correlation potentials obtained from a number of approximate functionals with essentially exact results for atomic helium. They find that both the LYP functional and the PW91 functional give comparably poor correlation potentials in the region of maximum electron density. However, the PW91 potential at least begins to decay rapidly at essentially the same distance as the exact potential, whereas the LYP potential has a much longer tail and extends roughly twice as far. This sort of behavior could provide an explanation for the differences we observe.

In summary, we have shown that for complexes of this type BPW91 and BLYP agree very well with each other for bond distances not involving the metal. In a double-ζ plus polarization quality basis, both overestimate these distances by amounts similar to those observed in small molecules with equivalent basis sets. For the single first series complex examined, BPW91 gives comparable agreement for all the bonds; however, for complexes of the second transition series, BPW91 consistently overestimates the metal−Cp C distances by 0.06−0.07 Å. Metal f functions shorten these slightly (∼0.01 Å). After estimated relativistic contractions (0.02−0.04 Å) are applied, the BPW91 metal−Cp C overestimates for the second series complexes would be reduced to levels comparable to the first series or small molecules without metals. Thus a relativistic version of BPW91 would appear to be a promising candidate for geometry calculations on such complexes.

On the other hand, BLYP consistently gives significantly longer values than BPW91 for all distances involving the metal in both the first and second series complexes, 0.04−0.05 Å longer for the metal−Cp C bonds, so that even after applying all the previous corrections, overestimates ≥0.07 Å relative to experiment would persist. Consistent disagreements of this magnitude between the two functionals for normal chemical bonds appear to be unprecedented in the literature. Regardless of its success for small molecules, it seems clear that the BLYP functional has problems describing the metal−ligand bonds in this general class of organotransition metal complexes, especially the bonds to the Cp ring. In addition to geometries, BLYP has been show to give very good energetics for small molecules. We have not examined any energetics; however, the large geometry errors would suggest that the use of BLYP for energetic calculations on these complexes should be approached with due caution.

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