



## Scalar Relativistic Study of the Structure of Rhodium Acetate

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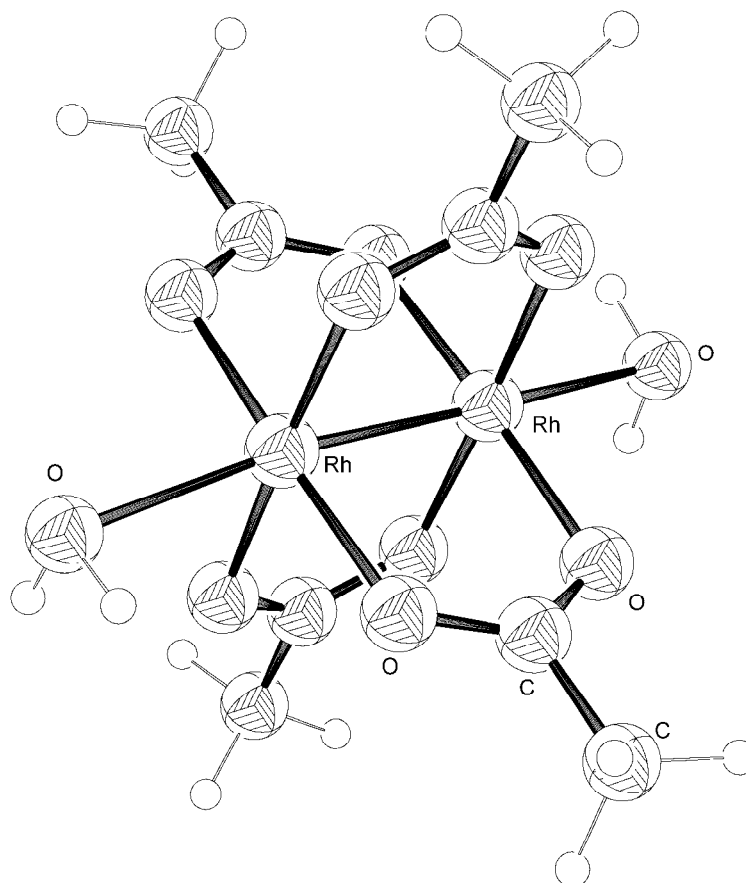
**Abstract:** Rhodium acetate, related rhodium carboxylates, and rhodium amide complexes are powerful catalysts for carbene chemistry. They readily promote the decomposition of diazo compounds and transfer the resulting carbene to a variety of substrates. There have been several quantum chemistry studies of these compounds, particularly of the acetate. These have all used non-relativistic methods, and all have shown optimized Rh-Rh bond lengths significantly longer than the experimental value. In this study we have surveyed several scalar relativistic DFT methods using Gaussian, Slater, and numerical basis functions (in DGAUSS, ADF, and DMOL3). Several combinations of exchange-correlation functionals with relativistic and non-relativistic effective core potentials (ECP) were investigated, as were non-relativistic and all electron scalar relativistic methods. The combination of the PW91 exchange and PW91 correlation functional with the Christiansen-Ermiler ECP gave the best results: 2.3918 Å compared to the experimental value of 2.3855±0.0005 Å.

**Keywords:** DFT, relativity, rhodium acetate, structure.

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### Introduction

The chemistry of rhodium acetate and related compounds as catalysts for carbene chemistry has been well established [1]. This paper is concerned mostly with the diaquo complex of rhodium acetate, shown in Figure 1. This figure shows the structure optimized in ADF with the PW91-PW91 energy functional. Computed structures (and particularly the Rh-Rh bond length) were chosen for study since they can be compared to highly accurate experimental data that can be measured without ambiguity.



**Figure 1.** The structure of diaquo rhodium acetate; representative atoms have been labeled.

The structure of this complex was measured by Cotton et al. [2], who found the Rh-Rh bond length to be  $2.3855 \pm 0.0005$  Å. This bond length is consistent with many other structural measurements on related compounds. A search of the Cambridge Crystallography database found 165 similar rhodium carboxylates; the average Rh-Rh bond for this set is 2.39 Å with a standard deviation of 0.16 Å. There have been several computational quantum chemistry studies of similar compounds [3]. Many of the recent studies used DFT methods and have found bond lengths significantly longer than this, for example 2.439 Å for BLYP (this study) or 2.454 Å (B3LYP for diaquo rhodium formate) [4]. These studies have not explicitly considered relativistic effects, in fact, a recent search of Chemical Abstracts found over 900 hits for rhodium acetate (CAS 15956-28-2); none of these included the concepts of relativistic effects or relativity. It is commonly observed that inclusion of relativistic effects decreases computed lengths of bonds involving heavy atoms when compared to similar non-relativistic calculations [5]. Even though rhodium is not as heavy as third row transition metals, relativistic effects may still be anticipated to play a role in its properties: early Dirac-Fock calculations by Desclaux [6] show anomalously large relativistic effects near  $Z=45$  (Rh). Dienfanbach [7] has shown that inclusion of relativistic effects improved the computation of reaction barriers in Pd ( $Z=46$ ) reactions.

In this study we present the results of a comparison of DFT methods for computing the structure of

the diaquo complex of rhodium acetate. We compare non-relativistic calculations to calculations that include scalar relativistic effects either via effective core potentials, or all electron methods; in addition we compare results from Gaussian, Slater, and numerical basis sets. In the calculations described here, those that are relativistic were scalar in nature: this means that no attempt was made to solve the complete Dirac equation with four-component wavefunctions, and spin-orbit coupling was not explicitly included. Faegri [8] has shown that including these scalar effects reproduces most of the relativistic bond contraction seen in fully relativistic four-component calculations.

## Computations

The computations described here were done using DFT methods with either DGAUSS, DMOL3, or ADF [9]. DGAUSS uses Gaussian basis sets that have been optimized for solving the Kohn-Sham equations. All of the DGAUSS calculations were done with an all electron double zeta valence polarized (dzvp) basis set and the A1 auxiliary basis set, except that in some cases, 28 core electrons on the Rh atoms were replaced with an effective core potential (ECP), often one that was derived from solving the Dirac-Fock equation. Such a potential is referred to as a relativistic effective core potential (RECP). DMOL3 uses a numerical basis set; the calculations here used one such set (DNP) that is comparable in quality to the dzvp basis set in DGAUSS. DMOL3 has a facility that applies scalar relativistic corrections to this basis set [10]; this method was used for the relativistic calculations in DMOL3. ADF uses Slater functions in its basis sets; the smallest polarized basis set in the ADF distribution that includes rhodium is a triple zeta polarized set; this set (TZP) was used in the ADF calculations. Geometry optimizations in DGAUSS were done with the medium geometry convergence and medium scf convergence criteria; a few test calculations were done with both of these criteria set to tight. In these tests, the resulting change in the Rh-Rh bond length was very small, and was never more than 0.001 Å. In all cases the high accuracy option for the numerical integrals was set. The DMOL3 calculations were done with either  $1 \times 10^{-6}$  scf energy combined with  $1 \times 10^{-5}$  geometry convergence criteria, or  $1 \times 10^{-8}$  scf energy combined with  $1 \times 10^{-6}$  geometry convergence criteria. These tighter criteria were used in an attempt to improve the vibrational frequencies calculated with DMOL3; as in DGAUSS they had an insignificant effect on the Rh-Rh bond length. The ADF geometry optimizations were done with the numerical integration accuracy set to 5.0 (number of significant digits required for the integrals), and the gradient tolerance set to  $1 \times 10^{-3}$  hartree/Å. The results were compared to a calculation with these tightened to 6.0 and  $3 \times 10^{-4}$ ; as with the other programs this had only a very small effect on the bond length. All of the ADF calculations used the small frozen core approximation for all atoms. This kept 28 electrons in the core for Rh (similar to the DGAUSS ECP methods), and 2 electrons in core for C and O. Scalar relativity was included using the ZORA [11] method. The exchange-correlation potential was included in a self-consistent fashion in all calculations. All DGAUSS calculations were run on a Silicon Graphics Origin 2400 computer using

either 4 or 8 processors; all of the DMOL3 calculations were done on a parallel IBM SP computer, usually on 20 processors, except for the calculations with the PBE functional which were done on the SGI Origin. The ADF calculations were done on the SGI Origin. None of the calculations with any of the programs assumed or used any symmetry for the diaquo rhodium acetate.

The DGAUSS calculations used the following ECP's: Stevens-Krauss [12], Christiansen-Ermler [13], Hay-Wadt [14], Stuttgart [15], and DGAUSS [16]. The scalar relativistic method in DMOL3 is due to Delley [10]. While most of the functionals in this study are in common use, the BOP [17] and PBE [18] functionals in DMOL3 and rPBE [19] and revPBE [20] in ADF are not. It should be noted that DMOL3 refers to the PW91-PW91 functional as GGA.

## Results and Discussion

The bond lengths predicted by the various methods surveyed are shown in the Tables 1-3 below. The experimental value is  $2.3855 \pm 0.0005$  Å [2]. The results are summarized in the three tables below. For each program, the best agreement with the experimental value is given in italics. The tables give the Rh-Rh bond length in Å.

**Table 1.** Rh-Rh bond lengths (Å) using DMOL3.

Functional	PBE	PW91-PW91	BOP	BLYP
Relativistic Bond Length	2.411	<i>2.409</i>	2.439	2.438
Non-Relativistic Bond Length	2.421	2.42	2.451	2.449

**Table 2.** Rh-Rh bond lengths (Å) using ADF.

Functional	PBE	rPBE	revPBE	PW91-PW91*	BLYP	BP
ZORA Relativistic Bond Length	2.402	2.411	<i>2.407</i>	<i>2.401</i>	2.430	2.405
Non-Relativistic Bond Length	2.416	2.428	2.425	2.416	2.446	2.420

\*In order to check the geometry convergence, the PW91-PW91 ZORA calculation was repeated with a gradient tolerance of  $3 \times 10^{-4}$  hartree/Å and integration accuracy of 6.0; the Rh-Rh bond length was virtually unchanged, 2.402 Å.

**Table 3.** Rh-Rh bond lengths (Å) using DGAUSS.

Functional	BP	BLYP	B88-PW91	PW91-PW91
Effective Core Potential				
Stevens-Krauss, Relativistic	2.423	2.443	2.423	2.420
Christiansen-Ermler, Relativistic	2.393	2.413	2.393	2.392
Hay-Wadt, Relativistic	2.420	2.440	2.420	2.419
Stuttgart, Relativistic	2.415	2.436	2.415	2.415
DGAUSS, Non-Relativistic	2.471	2.488	2.466	2.466
All Electron, Non-Relativistic (no ECP)	2.418	2.439	2.417	2.416*

\*When the DGAUSS dzvp basis set and PW91-PW91 was used in Gaussian98 [21], the resulting bond length was 2.420 Å.

The results in Table 1 show that in DMOL3 the all electron scalar relativistic corrections produces a contraction of the Rh-Rh bond for all of the functionals considered, with the PW91-PW91 functional coming closest to matching the experimental bond length. The ADF results in Table 2 show that the ZORA relativistic correction also produces a contraction of the Rh-Rh bond length, and that with the PW91-PW91 functional this contraction best matches the measured bond length. The results in Table 3 show that with DGAUSS, all of the relativistic ECP's produce also show a contraction of this bond, when compared to a similar non-relativistic ECP, but they do not always show similar contraction compared to a non-relativistic all-electron calculation. The Christiansen-Ermler RECP shows the greatest contraction and comes closest to reproducing the experimental bond length when it is used with the PW91-PW91 functional.

We interpret these results as showing that the Rh-Rh bond length in diaquo rhodium acetate is at least in part determined by relativistic effects, and that of the methods surveyed, the combination of the PW91-PW91 functional with the Christiansen-Ermler RECP is the best at reproducing these effects. As mentioned previously the above DGAUSS results were obtained with somewhat relaxed convergence criteria yielding a bond length of 2.3918 Å; when the most stringent criteria were used, this best method gave 2.3924 Å, a difference of less than 0.001 Å.

In order to check the apparent accuracy of this method, the Christiansen-Ermler RECP was used with PW91-PW91 to predict the Rh-Rh bond length in diaquo rhodium trifluoroacetate; the result was 2.4156 Å, which agrees fairly well with the experimental [22] value of  $2.409 \pm 0.001$  Å. A survey of the Cambridge Crystallography database which found 59 structures containing the rhodium trifluoroacetate unit gave an average Rh-Rh bond length of 2.414 Å with a standard deviation of 0.018 Å; the calculation is in excellent agreement with this average value. The same functional without the Christiansen-Ermler RECP gave a bond length of 2.4419 Å; this calculation used all of the compound's electrons (no ECP on Rh or other atoms).

There seems to be less relativistic improvement for bond lengths other than the Rh-Rh bond. For example, the experimental value for the average Rh-O bond to the axial water ligands is  $2.310 \pm 0.003$  Å [2], while some computed values are: 2.444 (all electron, PW91-PW91, non-relativistic in DGAUSS), 2.421 (DGAUSS non-relativistic ECP, PW91-PW91 in DGAUSS), 2.435 (PW91-PW91, non-relativistic in ADF), 2.503 (BLYP, non-relativistic in ADF), 2.436 (Christiansen-Ermler relativistic ECP, PW91-PW91 in DGAUSS), 2.412 (PW91-PW91, relativistic ZORA in ADF), and 2.480 (BLYP, relativistic ZORA in ADF). There is some relativistic contraction, but even in the best case (PW91-PW91 ZORA in ADF) the bond is still 0.1 Å too long. Similarly, the average length of the eight Rh-O bonds to the acetate ligands is  $2.039 \pm 0.008$  Å [2]; the closest match to this is 2.056 Å (Christiansen-Ermler relativistic ECP, PW91-PW91 in DGAUSS). While less satisfactory than the Rh-Rh bond results, these Rh-O results are still consistent with the recommendation for the use of the PW91-PW91 functional, combined with the Christiansen-Ermler RECP if available.

In some cases the geometry optimizations in DMOL3 and DGAUSS did not converge to equilibrium structures, instead structures with one (or in a few cases more than one) imaginary vibrational frequencies were found. In most cases when this happened, the imaginary frequencies were eliminated by re-optimizing the structure guided by the Hessian from the frequency calculation. In a few cases, this process was not successful and the imaginary frequencies were still present. The vibrational modes for these were always hindered rotational modes for one or more of the methyl groups. In order to investigate this further, a scan of the methyl dihedral angle (for the methyl group with the imaginary frequency) was carried out with DGAUSS, where the energy and gradient norm were evaluated for a sequence of structures differing only in the orientation of the methyl group relative to the rest of the molecule. The scan included the angle for the optimized structure. This scan showed that the angle with the lowest gradient norm was about  $9^\circ$  different from the angle with the minimum energy. For an exact wavefunction, the energy minimum must occur where the gradient norm is zero; the discrepancy here may indicate a defect in the DFT approximations used here. Since the geometry optimization process in DGAUSS converges on the gradient only, it is probably not possible to avoid this optimization problem. In any case, the problem is not serious for this study, since the Rh-Rh bond is not involved in any of the imaginary frequency vibrational modes. Frequency calculations were not carried out with ADF; some of the DMOL3 structures were investigated with frequency calculations. These did not indicate any problems that did not seem related to the choice of step size for the required numerical second derivatives (DGAUSS uses analytic second derivatives).

## Conclusions

Of the methods surveyed, the combination of the Christiansen-Ermler ECP with the PW91-PW91 functional in DGAUSS did a better job of predicting the Rh-Rh bond length in rhodium acetate, and this ECP combined with most functionals was more accurate than most of the other methods. The ZORA relativistic corrections in ADF were a close second, and the PW91-PW91 functional was consistently the best with the relativistic corrections available in any of these DFT packages.

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