Structure of trans-Rh(PH3)2(CO)X (X = F, Cl) Using Hartree–Fock/MBPT(2) and Density Functional Theory

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A study of trans-Rh(PH3)2(CO)X (X = F, Cl) using Hartree–Fock/many-body perturbation theory and density functional methods is presented. We report optimized Hartree–Fock and MBPT(2) structures employing effective core potentials with double-ζ plus polarization basis sets including f-type functions. Optimized structures using density functional methods, including those with gradient-corrected exchange-correlation functionals, are also reported. Both ab initio methods yield complexes which have a slightly distorted square-planar structure with moderate bending of the phosphine ligands toward the halide. The predicted structure of the chloro complex is compared with experimental data for trans-Rh(PPh3)2(CO)Cl.

Introduction

Ancillary ligands exert considerable influence on the stability and reactivity of organotransition-metal complexes1–3 in stoichiometric and catalytic transformations of organic compounds. For example, the relative effects of halide σ-donation and π-donation appear to be important factors in the strength of metal–halide and metal–phosphine bonds.4 Experimental and computational studies comparing the chemistry of complexes M–X differing only in the uninegative ligand X− (e.g., halide, carboxylate, isocyanate, isothiocyanate) are therefore of interest. We are particularly interested in the theoretical basis for the polar solvent dichloromethane: NCO− favorably with experiment and with those of traditional Hartree–Fock (HF)16 and the Gaussian92/DFTg computational chemistry programs.

In recent years DFT has become an an important method for routine calculations on medium to large molecules.10–15 DFT geometries and harmonic vibrational frequencies for many small molecules have been found to compare favorably with experiment and with those of traditional Hartree–Fock (HF)16 methods and many-body perturbation theory (MBPT(2)).17–19 A harmonic vibrational frequency calculation, required to establish that a given structure is a local minimum on the potential energy surface, costs roughly the same for DFT methods as for the HF method, and DFT frequencies are often more accurate than the more costly MBPT(2) frequencies. Electron correlation in DFT is incorporated in the density functional itself.20 The inclusion of f-functions on the central metal atom in transition-metal complexes is not expected to have a significant effect on an optimum DFT structure because the density does not require sophisticated basis sets as wave functions do. Our DFT results for the model chloro complex support this claim.

For comparison, we have also computed HF- and MBPT(2)-optimized structures for the model complexes using Gaussian92.21 Studies using HF methods have been conducted on the oxidative addition of H2 to iridium(I) Vaska complexe22,23 without f-type basis functions. We believe f-functions are necessary for the proper correlation of the d electrons of the central metal. In this work we have included f-functions on the central rhodium atom for all HF and MBPT(2) calculations.

Computational Details

All-Electron Calculations. DMol and deMon calculations were performed on an IBM RISC/6000 Model 350. We used the double numerical with polarization (DNP) and the double-ζ with valence polarization (DZVP) basis sets in DMol 2.2 and deMon 1.0, respectively. DMol calculations for the fluoro compound involved 141 basis functions and 104 electrons, while calculations for the chloro compound involved 145 basis functions and 112 electrons. The deMon calculations for the compounds involved 152 and 156 basis functions, respectively. The basis sets do not include f-functions on rhodium. The FINE mesh option was chosen for the numerical integration of matrix elements. The local electron gas exchange-correlation functional of Vosko, Wilk, and Nusair24 (VWN) was used in deMon, and the vonBarth–Hedin25 functional (vBH) was used in DMol. Both VWN and vBH correspond to parametrizations for the uniform electron gas, but they do not yield the same results in practice. No symmetry constraints were imposed during the geometry optimizations. Harmonic vibrational frequencies were computed by finite difference of analytic first derivatives to confirm that local minima had been found.

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Density functional calculations in GAUSSIAN92/DFT were carried out on a Cray C90. We employed the Becke exchange functional26 with the Lee, Yang, and Parr correlation functional27 (B-LYP) and with the local spin density correlation functional of Vosko, Wilk, and Nussair24 (B-VWN); we also used the Slater exchange functional28 (free electron gas) with the VWN correlation functional (S-VWN) for direct comparison with the deMon and DMol results. Studies29,30 have shown that these functionals yield harmonic frequencies with mean absolute errors less than those of MBPT(2) and produce respectable geometries. Single bonds between non-hydrogen atoms tend to be somewhat too short, double bonds are approximately correct, and triple bonds are too long.30 The double-ξ plus polarization basis set31–33 (DZP) was used in all of these calculations; the basis set does not include f-functions on rhodium. B-LYP is the highest quality DFT model used in our study; B-LYP is considered to have the best overall performance, at least for small molecules in the standard 6-31G* basis.30 As a test of the impact of f-functions, we performed a B-LYP optimization on the chloro compound with f-functions included (optimum exponent = 1.10).

The GAUSSIAN92/DFT calculations for the fluoro compound involved a total of 104 electrons and 144 contracted Gaussian basis functions; the chloro complex involved a total of 112 electrons and 148 contracted Gaussian basis functions (155 when augmented with f-functions). The default grid option was chosen for the numerical integration of matrix elements. C2v symmetry was imposed during the geometry optimizations which employed analytic first derivatives in the Bery optimization algorithm. Analytical harmonic vibrational frequencies were computed.

**Pseudopotential Calculations.** The HF and MBPT(2) optimizations were carried out using GAUSSIAN92 on a Cray XMP. Effective core potentials of the LANL1DZ34,35 basis set provided in GAUSSIAN92 were used; valence double-ξ basis sets36 are placed on each atom while an effective core potential is used to describe the core electrons of the Rh, Cl, and P atoms. We augmented the LANL1DZ basis with polarization functions to properly describe the consequences of the full electron-electron interaction by including basis functions of higher angular momentum; i.e., for the d electrons of rhodium, f-functions are required. For basis set balance, an additional unoptimized d-function was added to the rhodium atom as well. The exponents of the polarization functions were determined by optimization of the MBPT(2) energy for each atom or ion. The polarization functions used were as follows: hydrogen, p exponent = 0.70;37 carbon, d exponent = 0.62; oxygen, d exponent = 1.27; fluorine, d exponent = 1.52; chlorine, d exponent = 0.56; phosphorus, d exponent = 0.39; rhodium, f exponent = 1.10, d exponent = 1.00 (unoptimized). An approximate DZP basis set was thereby constructed, denoted as LANL1DZ+P, suitable for MBPT(2) calculations for the complex. Fluoro complex calculations involved 48 electrons and 128 contracted Gaussian functions; the chloro complex calculations involved 46 electrons and 127 contracted Gaussian functions. Analytical first derivatives were not available for the augmented LANL1DZ basis in GAUSSIAN92, so the Fletcher–Powell full optimization algorithm38 was employed in these cases with C2v symmetry imposed. Numerical second derivatives were not computed due to the high computational cost.

**Results and Discussion**

The structural parameters of trans-Rh(PH3)2(CO)X (X = F, Cl) (Figure 1) as determined by our set of computational models are summarized in Table 1. For comparison, the experimental bond angles and bond lengths for trans-Rh(PPh3)2(CO)Cl39 are included in Table 1. Both structures are distorted square-planar; the phosphine groups are shown in an eclipsed conformation in Figure 1 with C2v symmetry. The rotational conformations of the phosphine groups (estimated barrier to rotations < 0.5 kcal/mol) caused difficulties with convergence, and optimizations often yielded structures with one or more imaginary harmonic frequencies, as has been seen previously with similar compounds.32 The fluoro complex was particularly problematic; DMol optimization produced a staggered structure as a stable point on the potential energy surface, while deMon optimization failed to produce a stable structure. By imposing C2v symmetry in all GAUSSIAN calculations, we were able to bypass these difficulties and obtain stable structures in an eclipsed conformation, as confirmed by harmonic frequency calculations. The major structural difference between the compounds is the rhodium–halide bond distance; r(Rh–F) and r(Rh–Cl) are predicted to be 1.92–2.04 and 2.39–2.43 Å, respectively. This is as expected, since fluoride and chloride ionic radii are given as 1.36 and 1.8 Å, respectively.40 In both the fluoro and chloro complexes, the phosphine ligands are bent toward the halide (α(X–Rh–P) = 83–85°) due to electrostatic attraction; each model predicts the bending to be greater by at most 2° in the fluoro complex. In trans-Rh(PPh3)2(CO)Cl, of course, the bulky PPh3 ligands require maximum separation (α(P–Rh–P) = 180°).39 It is also evident from the crystal structure that the phenyl groups are staggered and that the complex is skewed square-planar. The experimental values for α(P–Rh–C) are reported as 95° and 85°; the values for α(P–Rh–Cl) are 93.6° and 86.4°.39 This departure from square-planar symmetry observed in the X-ray structure is most likely due to the intermolecular interaction within the crystal.

The predicted bond lengths agree reasonably well with the values based upon the X-ray crystal data for trans-Rh(PPh3)2(CO)Cl. The best overall agreement with experiment is obtained with the three local spin density results denoted as VWN/DNP, VWN/DZVP, and S-VWN/DZP; differences in the optimum structures are due to the minor differences in the basis sets employed. The B-LYP model produces bond lengths which are systematically longer than other DFT values and longer than expected, considering the experimental values for trans-Rh(PPh3)2(CO)Cl. The Rh–C bond length is 0.10 Å too long, as given by the B-LYP model and 0.06 Å too long by the local
Structure of trans-Rh(Ph3)2(CO)X

TABLE 1: Optimized Structure of trans-Rh(Ph3)2(CO)X (X = F, Cl)

<table>
<thead>
<tr>
<th>X</th>
<th>HF/LANL1DZ + P</th>
<th>MP2/LANL1DZ + P</th>
<th>vBH/DNP</th>
<th>VWN/DZVP</th>
<th>S-VWN/DZP</th>
<th>B-LYP/DZP</th>
<th>expt</th>
</tr>
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<tbody>
<tr>
<td>F</td>
<td>1.915</td>
<td>1.941</td>
<td>1.987</td>
<td>1.969</td>
<td>2.039</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>2.402</td>
<td>2.262</td>
<td>2.287</td>
<td>2.276</td>
<td>2.363</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Values in parentheses denote f-functions included in the basis set for the chloro complex. B-LYP energy = \(-5937.849\) au (F) and \(-5938.492\) au (Cl). MBPT(2) energy = \(-521.668\) au (F) and \(-166.899\) au (Cl).

Approximation methods. All other DFT bond lengths deviate from experiment by less than 0.05 Å. The inclusion of f-type functions in the B-LYP model shortens the Rh–Cl and Rh–C bonds by 0.005 and 0.007 Å, respectively, providing a minor improvement. Although the B-LYP model is the most sophisticated DFT model used, it apparently does not yield the best structure for our particular case. We can not and do not conclude that B-LYP will not be the best overall model in general, and extensive calculations by other groups indicate this to be the best overall model.29,30

The HF/LANL1DZ + P bond lengths are in good agreement with the expected values for the chloro complex; r(Rh–P) and r(Rh–C) are longer than expected by 0.06 Å. The usual bond length expansion upon going from the HF model to the MBPT(2) level of theory is seen for r(P–H), r(C–O) (which expands by 0.06 Å in both complexes), and r(Rh–P) in the fluoro complex (which expands by 0.026 Å). The other metal–ligand bonds in both complexes are contracted at the MBPT(2) level instead. The correlation contraction is surprisingly large (0.14 Å) for the Rh–P and Rh–C bonds in both complexes; the final result is that these MBPT(2) bond lengths are about 0.07 Å shorter than expected. The correlation contraction of transition-metal–neutral ligand bonds has been observed previously for r(M–O) in V(H2O)+ and Sc(H2O)+; for the rest of the series studied (Sc–Zn), the usual r(M–O) correlation expansion was seen.41

Frequencies and intensities of the carbonyl stretch as predicted by the various DFT models are presented in Table 2. In the complexes, the C–O bond distance is known to be longer and the carbonyl stretching frequency is known to be lower than in the unbound CO molecule.42 The experimental values for the carbon monoxide molecule are 1.128 32 Arab and 2169.814 cm\(^{-1}\) (gas phase);43 the fundamental transition in CH2Cl2 is 2143 cm\(^{-1}\).44 The experimental values for the PPh3-based chloro analogue are r(CO) = 1.142(2) Å (solid phase)39 and, for the fundamental transition, \(\nu(CO) = 1980\) cm\(^{-1}\) (CH2Cl2).5 The fundamental transition for the PPh3-based fluoro complex is 1917 cm\(^{-1}\) (CH2Cl2).5 Because of the lower frequency, r(C–O) is expected to be slightly longer in the fluoro complex. These experimental observations are reflected in our computational results in Tables 1 and 2. For example, the B-LYP model predicts 2060.7 cm\(^{-1}\) and 1.160 Å for free carbon monoxide in the gas phase. Our B-LYP calculations predict \(\nu(CO)\) as 1930 and 1935 cm\(^{-1}\) for the fluoro and chloro model complexes; the differences in frequency are comparable to what is observed in experiment, with the fluoro value 5 cm\(^{-1}\) lower than the chloro
TABLE 3: Estimated values for the trans-Rh(PH₃)₃(CO)Cl + F⁻ → trans-Rh(PH₃)₃(CO)F + Cl⁻ Exchange Reaction

<table>
<thead>
<tr>
<th>Method</th>
<th>ΔE</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF/LANL1DZ+P</td>
<td>34.8</td>
</tr>
<tr>
<td>MP2/LANL1DZ+P</td>
<td>27.9</td>
</tr>
<tr>
<td>S-VWN/DPN</td>
<td>63.7</td>
</tr>
<tr>
<td>B-LYP/DPN</td>
<td>24.4</td>
</tr>
<tr>
<td>DZP</td>
<td>27.4</td>
</tr>
</tbody>
</table>


value. The chloro complex C–O bond distance is predicted by B-LYP to be 1.183 Å; the fluoro value is, as expected, longer by 0.002 Å. Indeed, all computational models shown in Table 1 indicate the value of r(C–O) is slightly longer in the fluoro complex, and all DFT models indicate v(CO) is 5–8 cm⁻¹ lower in the fluoro complex (Table 2).

We report estimated ΔE values for the gas phase chlorine–fluoride exchange reaction in Table 3. The highest quality calculations, MBPT(2) using the LANL1DZ+P basis and the B-LYP method using a DZP basis, are in excellent agreement, yielding 27.4 and 27.9 kcal/mol, respectively.

Finally, we note that Mulliken population analysis shows the large charge separation between the rhodium and the halide in our model complexes. The charge difference is, of course, smaller in the chloro complex. For example, the B-LYP Mulliken charges are given by 0.191 (rhodium) and −0.543 (fluorine) and by −0.010 (rhodium) and −0.407 (chlorine), in the respective complexes. The electrostatic attraction between the phosphine ligands and the halide is represented by Mulliken charges as well. The charges of the hydrogen atoms near the halide are 0.020 in the fluoro complex and 0.040 in the chloro complex.

Conclusions

Our calculations for the model phosphine-based Vaska complexes trans-Rh(PH₃)₃(COX) (X = F, Cl) with the MBPT and DFT methods demonstrate that DFT methods afford energetics and structures of comparable quality to that of the more costly MBPT(2) method. Also, vibrational frequencies can be calculated using DFT methods at relatively low computational cost. The intense carbonyl stretching frequency of the fluoro compound is predicted to be 5–8 cm⁻¹ lower than that of the chloro compound; experiment confirms a 9 cm⁻¹ decrease for the PPH₃-based analogues in CH₂Cl₂. The local density approximation yields the overall most favorable structure in comparison with experimental data for trans-Rh(PPh₃)₃(CO)Cl. Little advantage in the structural description of the complex is gained by including f-type functions in the B-LYP method. We expect that considerably larger systems can be successfully studied using DFT methods without f-type basis functions. Results reported in this paper show that the local density approximation is suitable for structures and the B-LYP method produces reliable energetics. We are currently conducting studies of several other rhodium(I) Vaska complexes.