The *trans* Influence in [Rh(PH_3)$_3$Cl]: a Density Functional Theory Study*

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Optimised geometries computed using the local density approximation (LDA) of density functional theory (DFT) have been obtained for the Wilkinson's catalyst model complex [Rh(PH_3)$_3$Cl]. The LDA method accurately predicts the 0.09 Å shortening of the Rh–P_{trans} distance relative to Rh–P_{cis} although the Rh–Cl contact is about 0.05 Å too short. These geometrical data are significantly better than single determinant Hartree–Fock (HF) results. In contrast, the Mulliken charge density analyses are very similar and give comparable descriptions of the bonding although small differences in the predicted d-orbital sequences suggest that the LDA method describes a stronger in-plane π-acceptor interaction than does HF theory.

Density functional theory (DFT) is rapidly establishing a reputation for the accurate yet efficient treatment of molecular structure, energetics and reactivity.[1] This is especially true for transition-metal species where DFT promises new and important insights into, for example, the catalytic activity of metal complexes.[2] Such theoretical data are difficult to obtain with conventional Hartree–Fock (HF) or even post Hartree-Fock methods since the important effects of electron correlation are much harder to account for.[3] In addition, HF-based methods scale poorly as a function of molecular size. Density functional theory appears to provide a much better treatment of electron correlation and scales much less severely.

The complex [Rh(PPh_3)$_3$Cl] was the first room-temperature and -pressure catalyst for hydrogenating alkenes and other unsaturated substrates.[4] This molecule, and others derived from it, have spawned an enormous development in synthetic rhodium chemistry and its application to catalysis.[5]

A comprehensive theoretical treatment of the full catalytic cycle for olefin hydrogenation has appeared.[6] This impressive study by Daniel *et al.* models the active three-co-ordinate species [Rh(PH_3)$_2$Cl] and its interaction with H_2 and ethylene. The restricted Hartree–Fock (RHF) energy gradient method was employed to compute the structures of a range of intermediate and transition-state species along the reaction pathway. However, the quality of the basis sets used for the geometry optimisations has been called into question.[7]

Comparable RHF calculations, but employing a wider range of basis sets (including that used by Daniel *et al.*) have been reported by Maseras *et al.*[7] for the parent planar compound [Rh(PH_3)$_3$Cl]. None of the basis sets examined gives a very good description of the *trans* influence in this molecule. Experimentally, the Rh–P_{cis} bond lengths are about 0.09 Å longer than the Rh–P_{trans} contacts. The best RHF results predict about equal Rh–P distances but at the expense of an Rh–Cl contact which is 0.1 Å too short.

The basis set yielding these 'best' data corresponds to that chosen by Daniel *et al.*[6] for studying the catalytic cycle. These authors did not present results on the parent four-co-ordinate molecule presumably because it is not the catalytically active species but the more recent demonstration of the relatively poor performance of this basis with respect to modelling the *trans* influence may cast some doubt on the geometries obtained in the earlier study.

Restricted Hartree–Fock theory appears to be unsuited to the problem particularly where metal–phosphorus bonds are concerned.[8] In contrast, density functional theory (DFT) calculations on the model complex [Rh(PH_3)$_3$Cl] give a good treatment of the Rh–P bond. Geometry optimisations using two relatively modest basis sets yield Rh–P bond lengths within 0.02 Å of experiment while the Rh–Cl contact is about 0.05 Å too short. The shortening of the Rh–P_{trans} distance relative to Rh–P_{cis} is in excellent agreement with experiment. A single-point calculation using a more extended metal basis provides a description of the electronic structure and bonding comparable to best HF results.

Computational Details

All calculations were carried out using the non-relativistic DFT program system of Baerends *et al.*[9] The full Kohn–Sham local density approximation (LDA)[10] was employed with the correlation potential as parameterised by Vosko *et al.*[11] In addition, the correlation energy was corrected as described by Stoll.[12] Slater type orbital (STO) basis sets[13] were used in conjunction with the frozen core approximation[14] (up to 3p on Rh and 2p on P and Cl). Additional STO fit functions for describing the Coulomb potential included all *l* values up to 4.[15] Geometry optimisations employed analytical energy gradients.[16]

Three STO basis sets were examined. The first, B1, is a valence double-ζ expansion for all atoms with the addition of a 5p polarisation function on Rh. The second basis, B2, includes polarisation functions on all atoms (3d on P and Cl, 2p on H) while the third, B3, further expands the Rh 4d orbitals to triple-ζ level. Full listing of basis, core and fit functions have been deposited as supplementary material (SUP 56972).

In order to make comparisons with the geometries computed by Maseras *et al.*,[7] [Rh(PH_3)$_3$Cl] was constrained to C_s symmetry and all P–H distances and Rh–P–H angles were assumed to be equivalent. The number of optimised variables for [Rh(PH_3)$_3$Cl] is therefore six as shown in Fig. 1. Fig. 1 also displays the definition of cartesian axes.

All charge distributions were based on Mulliken population analyses.[17]

Results and Discussion

Optimised Geometries.—Optimised geometrical parameters for [Rh(PH_3)$_3$Cl] are collected in Table 1 along with the RHF results and experimental bond lengths derived from reported

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* *Supplementary data available* (No. SUP 56972, 3 pp.): basis, core and fit function Slater type orbital coefficients. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Optimised LDA, HF and experimental bond lengths (Å) and gross atomic charges ρ for [$Rh(PH_3)_3Cl$]

	Bond lengths			Charges			
Basis	$Rh–P_{cis}$	$Rh–P_{trans}$	Rh–Cl	Rh	*cis*-PH_3	*trans*-PH_3	Cl
B1	2.298	2.247	2.373	−0.44	0.30	0.21	−0.41
B2	2.279	2.204	2.365	0.02	0.18	0.10	−0.48
B3	(2.279)[a]	(2.204)[a]	(2.365)[a]	0.27	0.11	0.01	−0.51
RHF C[b]	2.33	2.31	2.31	−1.70	0.63	0.62	−0.19
RHF F[c]	2.45	2.42	2.46	0.34	0.11	0.09	−0.65
Experimental[d]	2.295	2.203	2.409				
Experimental[e]	2.305	2.224	2.405				
Experimental[f]	2.310	2.230	2.418				

[a] Geometry not optimised. [b] Basis set C from ref. 7. [c] Basis set F from ref. 7. [d] Ref. 18(*a*). [e] Ref. 18(*b*). [f] Ref. 18(*c*).

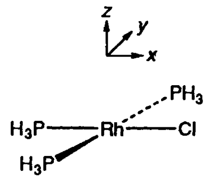

Fig. 1 Molecular structure of [$Rh(PH_3)_3Cl$] in C_s symmetry: the optimised variables are $Rh–P_{cis}$, $Rh–P_{trans}$, Rh–Cl, H–P, H–P–Rh, P_{trans}–Rh–Cl and P_{cis}–Rh–P_{cis}

X-ray crystallographic studies as summarised in Table 1 of ref. 7. The absolute agreement between experiment and the LDA results for all the Rh–P contacts is good for both bases. In addition, basis B1 gives a *trans* shortening of 0.05 Å which increases to 0.08 Å for basis B2. The latter is in excellent agreement with the experimental estimate of 0.09 Å. The Rh–Cl contact is not treated as well and is always about 0.05 Å too short. This might be attributable to various causes.

First, the experimental data invariably refer to substituted phosphine ligands like PPh_3 or PMe_3. There are presumably both steric and electronic differences between these ligands and the PH_3 groups used in the calculations. Experimentally, the RhP_3Cl core displays a small to modest tetrahedral distortion as evidenced by the P_{trans}–Rh–Cl angles which vary from 163.2 to 166.7 to 175.7° for [$Rh(PMe_3)_3Cl$],[18a] [$Rh(PPh_3)_3Cl$][18b] and *trans*-[$Rh(PMe_3)_2(PPh_3)Cl$][18c] respectively. The computed value for basis B2 is comparable (173.2°) suggesting that steric effects are relatively unimportant here. In the absence of calculations on complexes containing the complete ligands, the difference in electronic effects cannot be gauged.

Secondly, non-local corrections to the LDA exchange and correlation potentials[19] have not been added nor has any attempt been made to account for relativistic effects. Either or both of these may account for the discrepancy in the Rh–Cl bond length. Nevertheless, the main molecular features are present in the theoretical data—the shortening of the $Rh–P_{trans}$ relative to the $Rh–P_{cis}$ distance whilst retaining a reasonable Rh–Cl contact. Both of these are missing from the HF treatment.[7]

The remaining aspects of the computed geometries are unremarkable. The molecule is essentially square planar with P–H distances and Rh–P–H angles within expected ranges (about 1.45 ± 0.05 Å and 120 ± 2° respectively). Overall, the LDA description of the ground state structure is good and certainly better than that obtained by single-determinant HF methods. The observation that '*ab initio* (HF) methods might be overridden in the near future by those based on DFT'[7] seems well founded in this instance. Hartree–Fock theory is well known to give a relatively poor description of metal–phosphorus bonding in particular[8] but also of metal–ligand bonding in general.[20] Correction *via* configuration interaction (CI) while possible in principle, would, in practice, be a demanding task even for single-point calculations on moderately sized transition-metal compounds like [$Rh(PH_3)_3Cl$] let alone for full geometry optimisations. Density functional theory-based methods appear to offer a faster, more accurate alternative.

Charge Distribution.—The gross Mulliken charge distribution is quite sensitive to basis set. This is to be expected given the relatively crude assumption of an equal division of the overlap charge. Mulliken population analyses must therefore be interpreted with care.

The LDA B3 data are virtually the same as those obtained from the large basis HF calculations (basis F in Table 1) which were considered[7] to provide a reasonable description of the electronic structure. Note, however, that the latter refer to a geometry rather removed from experiment. The LDA B3 results suggest phosphine is a net charge donor (0.01 to 0.11) although the *trans* PH_3 group is almost neutral. Presumably, the closer approach of this ligand enhances the π-back donation relative to any σ donation. The Cl charge of around −0.5 compares to −0.65 from the HF method. The basis set dependence is particularly marked for the Rh charge. For basis B1 it is negative, for B2 near zero and for B3 moderately positive compared to the formal oxidation state of +1. Evidently, a reasonable charge distribution may require a triple-ζ expansion for the metal valence d orbitals.

Molecular Orbital (*MO*) *Energies and Compositions.*—Molecular orbital (MO) energies from DFT do not have the same interpretation as those from the HF model.[21] Nevertheless, DFT results on metal complexes often give the correct relative ordering of the excited states based solely on the ground state MO energy sequence.[22] The same is often not the case in applications of HF theory.[23]

For the present planar d^8 systems, simple ligand field arguments would predict the following. For $\approx D_{4h}$ [$Rh(PH_3)_4$]$^+$, the lowest unoccupied molecular orbital (LUMO) should correspond to the $d_{x^2-y^2}$ orbital with the sequence $d_{x^2-y^2} \gg d_{xz}, d_{yz} > d_{xy}$. The position of d_{z^2} is more difficult to predict. In other planar systems like [$CuCl_4$]$^{2-}$, d_{z^2} is the lowest energy d orbital.[24] However, Cl is a π donor while PH_3 is a π acceptor. This would tend to push the d_{xz}, d_{yz} and d_{xy} down towards d_{z^2}. The d_{z^2} is probably above the other three functions[25] although this is difficult to verify as any d–d transitions are obscured by intense charge-transfer absorptions.[26]

Replacement of one PH_3 ligand on the *x*-axis by Cl should cause the d_{xz}, d_{yz} orbitals in [$Rh(PH_3)_3Cl$] to split with d_{xz} rising since Cl is a π donor. This will be offset somewhat by increased π acceptance due to the shortening of the $Rh–P_{trans}$ bond. The data in Table 2 indicate the sequence $d_{x^2-y^2} \gg d_{xz} > d_{yz} > d_{xy}$. The d_{z^2} function is placed above d_{xz} in support of previous suggestions.[25]

The extent of the d-orbital involvement in the M–L bonding

Table 2 Valence MO energies and d-orbital compositions

MO	Energy/eV	% d Orbital	ΔE/cm^{-1}*
16a′	−1.418	35.5 ($d_{x^2-y^2}$)	0
15a′	−3.833	77.1 (d_{z^2})	19 479
14a′	−4.201	57.5 (d_{xz})	22 448
9a″	−4.794	68.6 (PH_3)	27 231
8a″	−4.875	79.5 (d_{yz})	27 884
7a″	−6.173	47.0 (d_{xy})	38 354

* Energy relative to 16a′ LUMO (eV ≈ 1.6×10^{-19} J).

is also monitored by the percentage of d-orbital contributions to the valence (antibonding) MOs. In [Rh(PH_3)$_3$Cl], for example, the LUMO has only about 36% d character consistent with the strong M–L σ-bonding role of the $d_{x^2-y^2}$ orbital. Similarly, d_{xy} is the main in-plane M–L π-bonding function with a 47% d contribution. The d_{xz} function is π bonding with respect to Cl and P_{trans} and has about 58% d character compared to a value of 80% for the Rh–P_{cis} and d_{yz} orbital. Evidently, the Cl bonding and the shorter Rh–P_{trans} contact lead to a greater involvement of d_{xz} in the bonding. Finally, d_{z^2} (77%) is also relatively uninvolved, consistent with its interaction being limited to σ bonding using only its 'belly-band'.

The lowest energy d orbital is d_{xy} suggesting a strong in-plane π-acceptor interaction. The HF ordering[7] places d_{xy} between d_{xz} and d_{yz} indicating a reduced in-plane π acceptance relative to the LDA results.

The above discussion describes the nature of the M–L bonding basically from a ligand-field theory viewpoint. This naturally focuses on the essentially antibonding d orbitals in the valence region. However, it is apparent that the frontier orbitals contain additional mainly ligand based MOs such as the phosphine-centred 9a″. The implication for the spectroscopy of these species is that there should be quite low energy charge-transfer (c.t.) absorptions interspersed among the d–d bands. Intense low energy c.t. bands are observed[26] in agreement with this proposition.

Conclusions

The LDA method gives a good account of the *trans* influence in the planar d^8 rhodium(I) complex [Rh(PH_3)$_3$Cl]. The Rh–P distances and the shortening of the Rh–P_{trans} bond length relative to the Rh–P_{cis} contact is in good agreement with experiment. The Rh–Cl distance is 0.05 Å too short. In contrast, HF theory[7] yields a much smaller difference between the two Rh–P distances and at the expense of a Rh–Cl distance some 0.1 Å too short.

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