

Ab Initio Molecular Orbital Characterization of the $[\text{Os}(\text{PR}_3)_3\text{H}_5]^+$ Complex

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Abstract: The problem of the structural characterization of $[\text{Os}(\text{PR}_3)_3\text{H}_5]^+$ complexes, which is experimentally unsolved, is considered from the theoretical point of view with a systematic study of the model system $[\text{Os}(\text{PH}_3)_3\text{H}_5]^+$ with the ab initio MO methodology. A fair selection of more than 20 possible isomers, including $[\text{Os}(\text{PH}_3)_3\text{H}(\text{H}_2)]^+$, $[\text{Os}(\text{PH}_3)_3\text{H}_3(\text{H}_2)]^+$, and $[\text{Os}(\text{PH}_3)_3\text{H}_5]^+$ species, is considered, and geometry optimization at the correlated MP2 level is extensively used. The most stable isomer is an eight-coordinate pentahydride complex $[\text{Os}(\text{PR}_3)_3\text{H}_5]^+$, its coordination polyhedron being a dodecahedron with the three phosphine ligands in B sites. Results are compared with available experimental data on other similar species and current general ideas on high coordination number complexes.

I. Introduction

The experimental characterization of polyhydride transition metal complexes has never been easy.¹ The main reason is that the small size of the hydrogen atom makes the determination of its position by X-ray diffraction quite complicated, especially when there are heavy atoms in its proximity. These problems of identification have only been aggravated in the last decade by the discovery of molecular hydrogen complexes.² The existence of these compounds, where a strong interaction between hydrogen atoms is kept despite their coordination to a metallic center, opens a whole new world of isomeric possibilities when the number of hydrogen atoms coordinated to the metallic center is above two or three. The result is the existence at present of a number of complexes of known stoichiometry but unknown coordination number, which can be referred to as "polyhydrides", regardless of their true nature as polyhydrides or molecular hydrogen complexes, which is yet to be clarified.

The challenge posed by the problematic determination of the structure of "polyhydride" complexes has been answered by the chemical community with significant developments in both the application and interpretation of experimental techniques. For instance, a method based on the measurement of spin–lattice relaxation time, T_1 , in NMR experiments, has been proposed³ and later refined.⁴ Previously unknown quantum effects on NMR spectra have been identified.⁵ Novel electrochemical methods have been successfully applied to the prediction of stability of molecular hydrogen complexes.⁶ Nevertheless, these remarkable advances, which will probably be joined by others in the near future, do not alter the fact that the only undisputable identification technique available so far is neutron diffraction, with its major setback of requiring large crystals and sophisticated equipment which are not always available.

The application of theoretical methods to the study of the relationship between true polyhydride and molecular hydrogen complexes also starts to have a certain history of its own.⁷ Apart from the qualitative information obtained from extended Hückel descriptions,⁸ ab initio methods, which are able in principle to provide a quantitative prediction, have also been applied by diverse authors.^{9–15} With very few exceptions,^{12,15} in all of these ab initio calculations the geometries were either taken directly from experiment or optimized at the lower quality RHF level, despite the fact that correlation energy, neglected at this computational level, seems to play a central role in this kind of systems.^{9,13–15} In particular, a study carried out also in our group¹⁵ on the complexes of experimentally known structure $[\text{Os}(\text{PR}_3)_3\text{H}_4]^+$ found that the noncorrelated RHF description gives a poor description of the potential hypersurface of the system, an error which is corrected when the MP2 level of methodology is used instead. Moreover, the MP2 results are not substantially altered by further improvement of the calculations up to the MP4 level. The same study also showed that, despite the necessity of correlation energy in the evaluation of relative stabilities of molecular hydrogen vs dihydride complexes, the RHF description is still valid when the comparison is made between different isomers with the metal in the same oxidation state.

Maybe one of the most representative examples of the activity in the field of characterization of "polyhydride" complexes can

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be found in the case of the $[\text{Os}(\text{PR}_3)_3\text{H}_5]^+$ systems. Their existence was postulated as early as 1970,¹⁶ although no spectroscopic data were available until NMR experiments were carried out by Caulton and co-workers in 1984.¹⁷ Logically, at that time it was considered to be a true polyhydride, since molecular hydrogen complexes were still to gain general acceptance. Things changed in 1988, when this compound was chosen by Crabtree and Hamilton as one of the probes for their original proposal of the T_1 NMR method.³ Their conclusion at the time was that it is not a true pentahydride but it contains a polyhydrogen unit, probably being $[\text{Os}(\text{PR}_3)_3\text{H}_3(\text{H}_2)]^+$, without ruling out the possibilities of $[\text{Os}(\text{PR}_3)_3\text{H}(\text{H}_2)_2]^+$ and $[\text{Os}(\text{PR}_3)_3\text{H}_2(\text{H}_3)]^+$. The last twist so far in this story of experimental data was provided in 1991 by Halpern and co-workers, who in their reassessment of the T_1 NMR method^{4a} concluded that both $[\text{Os}(\text{PR}_3)_3\text{H}_5]^+$ and $[\text{Os}(\text{PR}_3)_3\text{H}_3(\text{H}_2)]^+$ structures are compatible with the experimental data.

The problem of the characterization of the $[\text{Os}(\text{PR}_3)_3\text{H}_5]^+$ systems has also been addressed by Lin and Hall in one of the theoretical papers mentioned above,^{13c} their calculations being included in a general discussion on more than 30 complexes, a fact which obviously precludes a detailed analysis of each of them. In particular, only three isomers are considered for the $[\text{Os}(\text{PR}_3)_3\text{H}_5]^+$ system, their geometries being estimated from experimental and RHF results. Nevertheless, it is worthwhile to mention here their prediction that the pentahydride complex $[\text{Os}(\text{PR}_3)_3\text{H}_5]^+$ is the most stable species, lying below an $[\text{Os}(\text{PR}_3)_3\text{H}_3(\text{H}_2)]^+$ isomer by a small energy difference of 3.7 kcal/mol.

The inconclusiveness that emerges from all these experimental and theoretical studies on the $[\text{Os}(\text{PR}_3)_3\text{H}_5]^+$ complexes prompted us to perform a thorough theoretical study on the $[\text{Os}(\text{PH}_3)_3\text{H}_5]^+$ model system, with extensive use of geometry optimization at the MP2 level, which includes correlation energy. With this study, we expect to bring a fresh view to the already old problem of the characterization of $[\text{Os}(\text{PR}_3)_3\text{H}_5]^+$ complexes from a different perspective. In particular, in comparison with experimental works, the theoretical method applied here should be able to provide a complete description of the geometry of at least qualitative accuracy. The novelties with respect to previous theoretical calculations are the higher computational level and the absence of a priori assumptions on the structure.

After this introduction and a section dealing with the computational method, the results and discussion are going to be presented divided in two blocks. The first is concerned with the determination of the most stable structure, and the second one consists in a detailed analysis of this most stable structure. Finally, a last section collecting the conclusions is also included.

II. Computational Details

All calculations are carried out with the ab initio MO methodology using the Gaussian program.¹⁸ A noncorrelated RHF-SCF description is used for preliminary studies, while the more accurate geometry optimizations are performed at the correlated MP2 level,¹⁹ which seems to be the current state-of-the-art for this kind of system.^{13,15} In these MP2 calculations, excitations involving the full set of occupied orbitals are explicitly considered. Some energy-only calculations at higher computational levels are also performed for a few selected optimized geometries. These are of two different types. One of them is the extension of the same Møller–Plesset scheme¹⁹ up to the fourth order of perturbation theory with inclusion of single, double, and quadruple excitations (MP4SDQ method). The second approach considered is the quadratic

configuration interaction method²⁰ with single and double substitutions plus a correction for the triple substitutions (QCISD(T) method). For these energy-only calculations only excitations concerning the 36 outermost valence electrons are considered, the 19 lower energy orbitals being labeled as frozen core.

Effective core potentials including relativistic contributions are used to represent the 60 innermost electrons of the osmium atom.²¹ The basis set for the metal atom is of valence double- ζ quality,²¹ which is also the case for the 3-21G basis set in the atoms of the phosphine ligands.²² A more extended basis set is used for the hydrogen atoms directly attached to the metal to take account for their eventual hydridic nature. In particular, a triple- ζ basis set²³ with a scale factor of 1.25 is used, complemented with a polarization p shell with an exponent of 1.0.

As far as the geometry optimizations are concerned, an extensive use of symmetry is made, as it will be mentioned during the presentation of the results. Apart from this, full geometry optimizations are carried out, both at the RHF and MP2 levels.

III. Determination of the Most Stable Structure

Since the goal of this study is the theoretical prediction of the geometry of the $[\text{Os}(\text{PR}_3)_3\text{H}_5]^+$ complex, special care must be taken not to exclude a priori any possible isomer from the analysis. That means $[\text{Os}(\text{PH}_3)_3\text{H}(\text{H}_2)_2]^+$, $[\text{Os}(\text{PH}_3)_3\text{H}_3(\text{H}_2)]^+$, and $[\text{Os}(\text{PH}_3)_3\text{H}_5]^+$ complexes, that is, six-, seven-, and eight-coordinate compounds, must be considered, with the complication associated with the lack of definition of a preferred coordination polyhedron in the two latter cases.^{24–26} Since it would be unrealistic to predict the optimization at the highest computational level of all the possible isomers generated by all the possible positions of the ligands in all the different possible coordination polyhedra, the application of a more elaborate strategy is mandatory.

Such a strategy is developed in the following subsections. The first subsection deals with the selection of the starting geometries, and it is followed by other subsections presenting calculations on selected subsets of the complete group of possible geometries. Finally, the last subsection will evaluate the effect that would have on the results, an eventual improvement in the methodological description.

Selection of the Starting Geometries. The large number of possible geometries that can be a priori imagined for this system makes it necessary to set up some kind of classification criterion. The strategy that will be followed uses as a starting point an ideal octahedron. Three of the six coordination sites of this octahedron are occupied by the three phosphine ligands, and the other three by the five hydrogens. The application of this scheme to isomers of the $[\text{Os}(\text{PH}_3)_3\text{H}(\text{H}_2)_2]^+$ type is straightforward, since they are real six-coordinate complexes. Its use with seven- and eight-coordinate complexes relies on the assumption that there are two hydride atoms in one of the octahedron coordination sites. That is, some single coordination sites in the idealized octahedron are split in two, while the other ligands keep an octahedral coordination. This approach to the problem is not unrealistic if one takes into account that this is simply a method to define starting geometries. As will be shown below, the flexibility allowed in the geometry optimizations makes accessible eventually all of the different coordination polyhedra which can be assigned to seven or eight coordination.

Since the number of isomers that could be defined from the octahedron is still very large, two approximations are introduced

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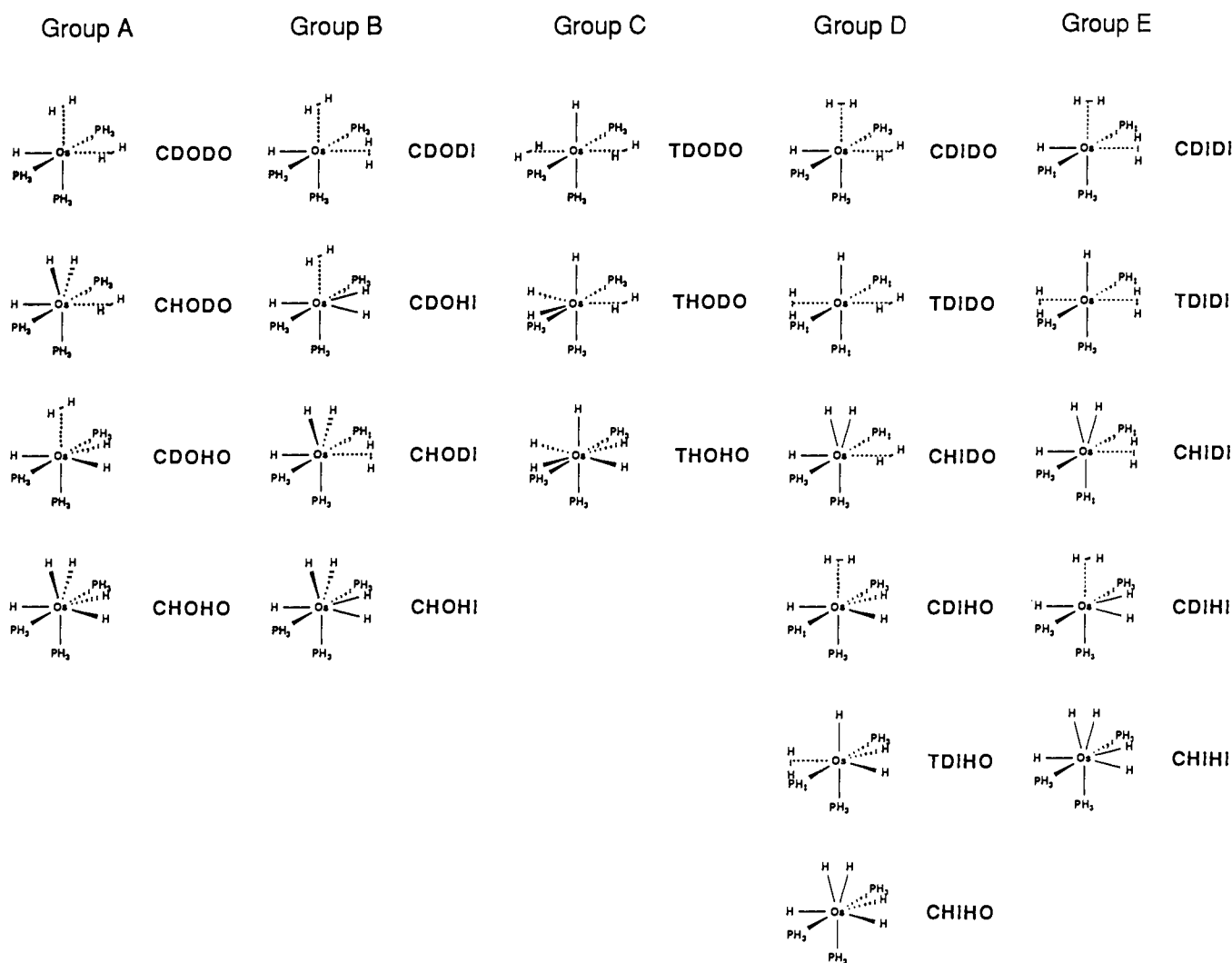
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Chart I



at this point; their validity will be checked later on. The first approximation is concerned with the relative position of the phosphines in the octahedral coordination. It is assumed that they are in a *mer* disposition, that is, approximately in a T shape, with the metal in the vertex, with two of the phosphines being *trans* to each other and *cis* to the third one. The second approximation makes reference to symmetry. The existence of a symmetry plane is assumed, with this plane containing the metal and one of the phosphorus atoms and having one of the other two phosphine ligands on each of its sides. As said above, these approximations are to be checked in light of the results; the symmetry will be relaxed, and the possibility of geometries derived from a *fac* disposition of phosphines will be discussed.

After all these considerations, we are finally able to define a labeling scheme making reference only to the position of the five hydrogen atoms which must be distributed in the three coordination sites not occupied by phosphines. Three criteria are applied: (a) Since two sites must have a pair of hydrogen atoms and another site must have a single one, and since there are two kinds of topologically different sites (one which is *trans* to one of the phosphine ligands and two other sites which are *cis* to the three phosphine ligands), the starting geometries will be classified according to which site is occupied by the single hydrogen atom in T (for *trans*) isomers and C (for *cis*) isomers. (b) Each pair of hydrogen atoms assigned to the same position can be in dihydrogen (D isomers) or in hydride form (H isomers). (c) In each of the positions shared by two hydrogen atoms, these can be in the symmetry plane of the molecule (I isomers) or outside

the symmetry plane of the molecule (O isomers). Of course, in the O isomers, the two hydrogen atoms are related by symmetry.

A final word about the labeling scheme concerns the ordering of the labels. In cases where there is possible confusion between the two sites containing a pair of hydrogen atoms, the first set of labels corresponds to the *trans* position. For instance, in the CDODI structure, the *trans* site is occupied by a dihydrogen ligand with the hydrogen atoms out of plane.

Chart I contains all the possible starting geometries that come out of this classification scheme. There are only 22 structures out of the 32 ($=2^5$) which were in principle possible. This is due to the fact that some labelings lead to chemically equivalent structures, as it would be for instance the case of CHIDO and THIDO labels. Nevertheless, 22 different structures is still a big number, and a further classification between them into five groups is also presented in Chart I. The criterion followed to establish these groups is simply having in the same group the structures that can be easily interconverted in the course of a geometry optimization. That is, each one of the groups contains structures that can be related by formation and breaking of hydrogen-hydrogen bonds and opening or closing of L-M-L angles, without big displacements of atoms or breaking of symmetry.

Group D Complexes. One of the advantages of the classification of the starting geometries in groups is that each of these groups contains a fair representation of the whole set of different coordination numbers. Therefore, calculations within each of the groups provide the possibility to check to what extent the performance of geometry optimizations at the cheaper RHF level

Table I. Energetics Obtained from the Geometries Optimized at the RHF Level of the Complexes Included in Group D of Chart I^a

starting geometry	final geometry	<i>E</i> (RHF)	<i>E</i> (MP2)
CDIDO	CDIDO	0.0	0.0
CDIHO	CDIDO	0.0	0.0
TDIDO	TDIDO	1.9	2.8
TDIHO	TDIDO	1.9	2.8
CHIDO	CHIDO	3.9	-11.4
CHIHO	CHIDO	3.9	-11.4

^a Relative energies with respect to the CDIDO isomer are given in kcal/mol. The total energy of the reference is -1115.045 61 hartree at the RHF level and -1115.613 97 hartree at the MP2 level.

is valid in the $[\text{Os}(\text{PH}_3)_4\text{H}_5]^+$ system. With this idea in mind, the first set of calculations consists of geometry optimizations, both at the RHF and MP2 levels, of all the complexes included in group D. The main reason for choosing group D is that the geometry of a related compound, $[\text{Re}(\text{PMePh}_2)_3\text{H}_5]$, as determined by neutron diffraction would belong to this group.²⁷ In particular, the geometry of the complex, an eight-coordinate deformed dodecahedron, would be derived from the CHIHO structure in Chart I.

The energetics resulting from the geometry optimizations at the RHF level of the complexes belonging to Group D are collected in Table I. It can be seen in the table how of the six different structures proposed initially only three remain as valid after the optimization, the other three not corresponding to local minima in the potential hypersurface at this computational level. In particular, two (CDIDO and TDIDO) of the three remaining structures are bis-molecular hydrogen complexes with octahedron geometries. It is clear that, at the RHF level, the association of hydride ligands to form molecular hydrogen complexes is clearly favored, a fact also exemplified by the instability of the pentahydride CHIHO. From the RHF calculations, the geometry CDIDO would be slightly preferred over the structures TDIDO and CHIDO, but this result is not going to be analyzed in detail because of the dramatic changes introduced by the correlation energy.

The decisive weight of the correlation energy can be already anticipated from Table I, where single-point calculations at the MP2 level on the RHF geometries invert the relative stability of the CHIDO and CDIDO isomers. The change in the global picture introduced by correlation energy is shown to be indeed dramatic when geometry optimization at the MP2 level is performed. While the RHF method leads to the results presented in Table I, with three different local minima, the geometry optimization at the MP2 level of the complexes belonging to group D produces in all the cases the same structure, regardless of the starting point. Moreover, this geometry corresponds to the pentahydride complex CHIHO, which was not stable at the RHF level. Its energy comes out to be 24.5 kcal/mol below that of the RHF-optimized CDIDO presented in Table I.

Therefore, it can be concluded from these calculations on complexes of group D that the inclusion of correlation energy is essential for the right prediction of geometries. Actually, it so happens that the most stable isomer at the higher computational level is not even a minimum at the RHF level. Another conclusion that is hinted at here is the preference of the system for the pentahydride $[\text{Os}(\text{PH}_3)_3\text{H}_5]^+$ coordination, although this will have to be checked against calculations on complexes of the other groups.

RHF Calculations on $[\text{Os}(\text{PH}_3)_3\text{H}(\text{H}_2)_2]^+$ Complexes. It has just been demonstrated that introduction of correlation energy is necessary in order to obtain optimized geometries with a certain chemical meaning. Still, the fact that calculations at the MP2 level are computationally much more expensive than those at the RHF level should not be overlooked. Therefore, it would be

Table II. Energetics Obtained from the Geometries Optimized at the RHF Level of Bis-Molecular Hydrogen Complexes^a

group	isomer	<i>E</i> (RHF)	<i>E</i> (MP2)
A	CDODO	3.3	29.5
B	CDODI	3.9	30.6
C	TDODO	7.8	38.7
D	CDIDO	0.0	24.5
D	TDIDO	1.9	27.3
E	CDIDI	0.5	27.3

^a Initial geometries did not change the general topology after optimization. Relative energies are given in kcal/mol referred to the most stable isomers, which are CDIDO at the RHF level and CHIHO at the MP2 level. The total energy of the references is -1115.045 61 hartree at the RHF level and -1115.652 94 hartree at the MP2 level.

Table III. Energetics Obtained from the Geometries Optimized at the MP2 Level Starting from the Pentahydride Isomers of Chart I^a

group	starting geometry	final geometry	<i>E</i> (MP2)
A	CHOHO	CDOHO	17.7
B	CHOHI	CHOHI	13.1
C	THOHO	TDODO	32.9
D	CHIHO	CHIHO	0.0
E	CHIH I	CHIDI	16.4

^a Relative energies with respect to the CHIHO isomer are given in kcal/mol. The total energy of the reference is -1115.652 94 hartree.

highly desirable to find some way to apply the lower level calculations. In fact, the simple RHF methodology can still be helpful for the comparison of the relative energies of complexes from different groups. The justification for this approach is that, as it has already been mentioned in the introduction, RHF calculations are fairly reliable when comparing different isomers with the same oxidation number.¹⁵

From the previous subsection, it is obvious that the coordination number preferred at the RHF level is six, corresponding to octahedral bis-molecular hydrogen species, those with DD labels in Chart I. According to that, the geometry of one bis-molecular hydrogen complex belonging to each group has been optimized, the resulting energetics being presented in Table II. Inspection of this table demonstrates that energetic differences between the different groups do not seem to be substantial. The RHF energies of the six different isomers are in a range of only 8 kcal/mol, while MP2 energies coming from single-point calculations present a somehow larger but still small spread of 15 kcal/mol.

This conclusion attains full meaning when complemented by those obtained in the previous subsection on the complexes of group D. Certainly, since different groups seem to be roughly similar, one must not expect to find molecular hydrogen complexes $[\text{Os}(\text{PH}_3)_3\text{H}_3(\text{H}_2)]^+$ with an energy very different from that previously found for CHIDO. Therefore, these hypothetical stable $[\text{Os}(\text{PH}_3)_3\text{H}_3(\text{H}_2)]^+$ complexes would still have an energy more than 10 kcal/mol above that of the pentahydride $[\text{Os}(\text{PH}_3)_3\text{H}_5]^+$ labeled as CHIHO. Since the concern of this paper is the determination of the most stable form or forms within the thermally accessible range of a few kcal/mol, $[\text{Os}(\text{PH}_3)_3\text{H}_3(\text{H}_2)]^+$ complexes can be reasonably skipped to focus exclusively on true pentahydride complexes.

MP2 Calculations on $[\text{Os}(\text{PH}_3)_3\text{H}_5]^+$ Complexes. The results presented so far allow a substantial simplification of the computational problem in the sense of justifying a restriction to the true pentahydride complexes $[\text{Os}(\text{PH}_3)_3\text{H}_5]^+$. They have however the rather unpleasant secondary result that calculations to distinguish between them have to be done completely at the computer time consuming MP2 level. Nevertheless, this has been done, and the results are presented in this subsection. In particular, Table III shows the results obtained from MP2 optimizations carried out using as starting points the pentahydride complexes presented in Chart I, one per group.

The first striking feature of Table III is that MP2 optimizations starting from pentahydride species only stay in this coordination

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mode in two of the five complexes (CHIHO and CHOHI), going in two other cases to $[\text{Os}(\text{PH}_3)_3\text{H}_5(\text{H}_2)]^+$ isomers (CDOHO and CHIDI) and even to a $[\text{Os}(\text{PH}_3)_3\text{H}(\text{H}_2)_2]^+$ species in another case (TDODO). Does that mean that the reasoning just exposed about the stability of $[\text{Os}(\text{PH}_3)_3\text{H}_5]^+$ forms is not correct? This would be a wrong conclusion. One must take into account that all these geometry optimizations are carried out within the frame of C_2 symmetry, and therefore the failure to optimize certain pentahydride structures only means that they do not exist for these specific symmetry requirements, within this group, in the terminology used in this paper.

The results of Table III provide indeed further evidence for the stability of eight-coordinate $[\text{Os}(\text{PH}_3)_3\text{H}_5]^+$ complexes with respect to other coordination numbers. The two complexes with lower energies are the eight-coordinate CHIHO and CHOHI, trailed by the seven-coordinate CHIDI and CDOHO, and much further, by the six-coordinate TDODO. Actually, the geometries of CHIDI, CDOHO, and TDODO isomers may even be unstable if symmetry were relaxed, evolving to either CHIHO or CHOHI. Nevertheless, this point has not been checked, since it does not seem important for the main goal of this study, which is the determination of the most stable structure.

The main conclusion from this subsection must be therefore that the species labeled as CHIHO in Chart I is the most stable of all those considered in that chart. Moreover, it is so by a difference of more than 10 kcal/mol. This formally concludes the study of the molecules presented in Chart I.

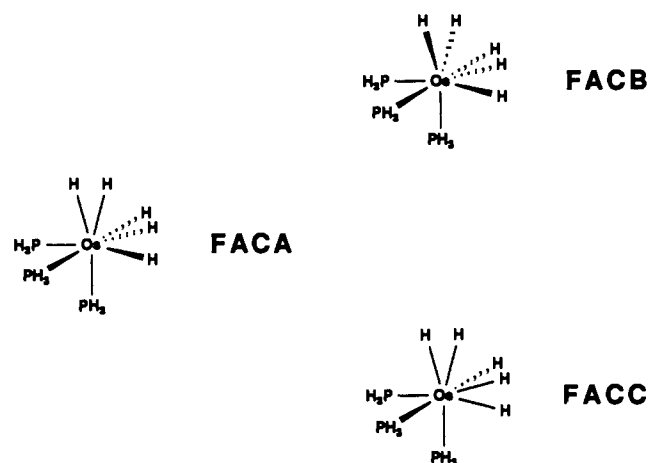
Checking of the Assumptions of Chart I. At the beginning of this section, when the selection of the starting geometries was being discussed and Chart I defined, we already warned that the approach to the problem relied on two assumptions, namely, the use of C_2 symmetry and the *mer* disposition of phosphine ligands. After the strategy defined there was fully applied and led to the determination of the most stable form, it is time to check the validity of those assumptions.

Although the use of symmetry simplifies and accelerates geometry optimizations, caution must always be taken in the interpretation of the results, because it can lead to the location of spurious local minima in the potential hypersurface. In order to prevent this problem, a simple check of the nature of the localized stationary points is performed. It consists simply in relaxing the symmetry restrictions and making a small displacement from the geometry that is being checked, starting a new geometry optimization from there. If the initial geometry corresponds to a local minimum, it will be recovered in a few steps. If on the contrary it does not, the geometry optimization is going to lead to a completely different geometry.

The results of applying this procedure to the two lowest energy isomers obtained in the previous section, CHIHO and CHOHI, reveal that both of them are real minima in the potential energy hypersurface. Therefore, the most stable of them, CHIHO, confirms its position as the most stable form for this complex, while CHOHI happens to be another isomeric form of higher energy.

Making reference to the second approximation introduced in the confection of Chart I, the restriction to *mer* isomers, the method to check it is of course the consideration of *fac* isomers. The procedure to deal with them is much simpler than that followed for the *mer* isomers, in part because of the data obtained from the study on the *mer* forms and in part because of intrinsic reasons. Certainly, the results of the previous sections are very useful in the sense that they allow us to restrict the calculations to the pentahydride $[\text{Os}(\text{PH}_3)_3\text{H}_5]^+$ forms. Another simplification comes from the fact that in the *fac* forms the three positions not occupied by phosphines in the coordination sphere of the metal are in principle equivalent, each of them *cis* to two of the phosphines and *trans* to the third one. The application of these considerations to an analysis similar to that applied in the

Chart II



construction of Chart I leads to the three possible starting geometries presented in Chart II. In this case, since there are only three of them, no elaborate labeling scheme is applied.

Calculations are only performed in one of them, the one called FACA in Chart II. The main reason for this choice is that this structure seems to be the *fac* equivalent of CHIHO, with the H-H lines oriented in perpendicular directions. Optimization of this isomer at the MP2 level yielded an energy 5.1 kcal/mol above that of the most stable isomer CHIHO.

Thus, it is confirmed that the most stable form in the $[\text{Os}(\text{PR}_3)_3\text{H}_5]^+$ system is a pure pentahydride $[\text{Os}(\text{PR}_3)_3\text{H}_5]^+$, in particular, an isomer that derives from the structure labeled as CHIHO in Chart I. This structure is going to be analyzed in detail in the next section.

MP4 and QCISD Calculations. As has been repeatedly mentioned above, the MP2 methodological level seems to be currently accepted as sufficient for the description of these kinds of systems.^{13,15} Nevertheless, it is always interesting to check the validity of the results against an improvement in the methodological description, namely a more accurate computation of the correlation energy.

With this goal, some energy-only calculations are performed at more sophisticated levels of methodology. These include higher levels of the many-body perturbational theory with the same Møller-Plesset partition¹⁹ (MP3 and MP4SDQ calculations), as well as the quadratic configuration interaction method²⁰ (QCISD(T) calculations), based on a rather different approach. The species on which these calculations are performed are the three local minima identified at the MP2 level, the pentahydride species CHIHO, CHOHI, and FACA, plus two other complexes, one, CHIDO, with a single molecular hydrogen ligand and the other one, CDIDO, containing two molecular hydrogen ligands. The optimized MP2 geometries are used in the first three cases. For the CHIDO and CDIDO complexes the RHF geometries are used instead, since they were not local minima at the MP2 level.

Table IV presents the results coming from these energy-only calculations. The general view¹⁵ on the role of electron correlation in these "polyhydride" systems is again confirmed. There is an important change in going from the RHF to the MP2 description, while the more accurate methods introduce minor corrections to the MP2 results. Therefore, it seems adequate to put aside the RHF data from the discussion that follows.

If the RHF results are not taken into account, it comes out that CHIHO is predicted to be the most stable species in all the cases. Its energy difference with the other two pentahydride species, CHOHI and FACA, is roughly independent of the methodology, with values which are respectively around 13 and 4 kcal/mol. Changes are more significant in the cases of the CHIDO and CDIDO isomers, which involve an alteration in the oxidation state of the metal atom. In both cases, the energetic difference

Table IV. Results of the Energy-Only Calculations at Higher Computational Levels for Some Selected Species^a

species	RHF	MP2	MP3	MP4SDQ	QCISD(T)
CHIHO	0.0	0.0	0.0	0.0	0.0
CHOHI	+13.0	+12.5	+13.6	+12.6	+12.8
FACA	+0.1	+4.5	+3.4	+3.9	+3.6
CHIDO	-10.5	+9.3	+3.7	+4.9	+3.8
CDIDO	-13.9	+20.3	+10.9	+13.4	+11.4

^a Geometries for the CHIHO, CHOHI, and FACA isomers come from the MP2 optimizations, while those for CHIDO and CDIDO systems are from RHF optimizations. Relative energies with respect to the CHIHO isomer are given in kcal/mol. The total energy in hartree of the reference is -1115.022 65 at the RHF level, -1115.540 04 at the MP2 level, -1115.558 263 at the MP3 level, -1115.597 91 at the MP4SDQ level, and -1115.612 141 at the QCISD(T) level.

with respect to the absolute minimum CHIHO is reduced approximately by half as one goes from the MP2 level to the most accurate QCISD(T). One may say that MP2 overestimates the correlation effect in the energy change for going from one H₂ bond and a d lone pair to two M-H bonds. While the bis-molecular hydrogen complex CDIDO stays well over the absolute minimum (11.3 kcal/mol), the mono-molecular hydrogen complex CHIDO becomes closer to it (3.8 kcal/mol). Actually, CHIDO becomes far more stable than the CHOHI isomer and of the same order of stability as the FACA complex. Nevertheless, the energetic difference of still *ca.* 4 kcal/mol practically rules it out as the absolute minimum of the system.

The results in this subsection can be summarized by saying that the improvement in the methodological description does not lead to a substantial alteration of the results. Therefore, the MP2 geometries obtained in the previous subsections are accepted as satisfactory, and they are the only ones which are going to be discussed in the next section.

IV. Detailed Study of the Most Stable Isomer

The previous section has been exclusively concerned with the search for the most stable form of the [Os(PH₃)₃"H₅"]⁺ system. Because of that, a stress has been put on the energetics, while few details have been discussed on the geometries, which have been used essentially as labels referring to very schematic pictures presented in charts. Now that the most stable structure has been identified as the one that was labeled as CHIHO, a complete analysis of its geometry and other features is going to be presented in this section.

The MP2-optimized geometry of the species that has been labeled so far as CHIHO is shown in Figure 1. The definition of the axis is such that the C_s symmetry plane is YZ and contains the atoms Os(1), P(2), H(7), H(8), and H(9), while the pairs P(3)/P(4) and H(5)/H(6) are symmetric with respect to this plane. The drawing is presented from two different orientations: the first one, 1a, shows how it actually derives from the schematic octahedron CHIHO depicted in Chart I; the second view, 1b, stresses its nature as a dodecahedron. The dodecahedron is indeed one of the most common polyhedra for eight-coordinate monomeric compounds.^{25,26,28} Its basic analysis dates back to the 60s,²⁸ the main aspects being recalled here in order to provide the necessary background for the following discussion. The dodecahedron receives its name from its 12 triangular faces and, in a completely symmetric case with eight identical spheric ligands, would have a D_{2d} symmetry. Maybe the most simple way to visualize it is as a superposition of two tetrahedra, one of them elongated with respect to one of the S₄ axes and the other one flattened with respect to this same axis. There are two different types of ligand sites, characterized by these two tetrahedra: the four sites from the elongated tetrahedron are A sites, while the four from the flattened one are B sites. These features can be easily visualized in Figure 1b for our optimized geometry, despite

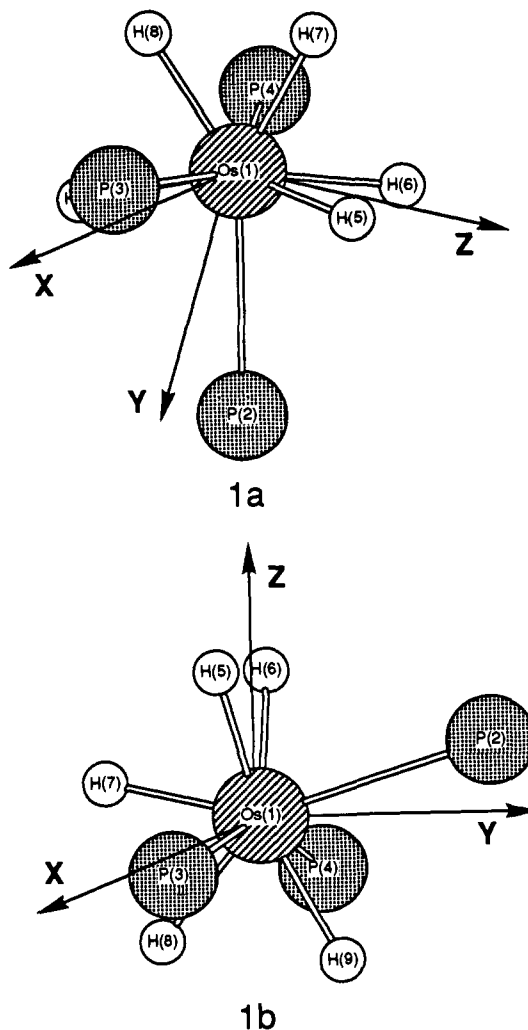


Figure 1. MP2-optimized geometry of the most stable isomer, labeled as CHIHO, seen from two different views. Hydrogen atoms of phosphine ligands have been suppressed for the sake of clarity.

the reduction in symmetry caused by the nonequivalence of the eight ligands. In particular, the pseudo-S₄ axis is Z, the A sites being occupied by H(5), H(6), H(8), and H(9) atoms, with P(2), P(3), P(4), and H(7) in the B sites. Another helpful view of this coordination figure is as two mutually perpendicular trapezoids intersecting in the S₄ axis. Referring again to Figure 1, one of these trapezoids would be defined by P(2), H(7), H(8), and H(9) in the YZ symmetry plane, and the other one by P(3), P(4), H(5), and H(6) approximately in the XZ plane.

The more meaningful parameters of the geometry optimized for the absolute minimum are collected in Table V. Distances seem to be in reasonable agreement with those considered to be average in organometallic compounds.²⁹ The Os-H distances we report are between 1.60 and 1.64 Å, comparing fairly well with osmium-hydride distances like the ones reported in the neutron diffraction study of the [Os(PMe₂Ph)₃H₄] complex,³⁰ the average of which is 1.66 Å. Agreements are a little worse for the phosphine ligands, which we find to be separated from the metal by distances of 2.41 and 2.45 Å. In this case, comparison with experiment is more difficult because of the existence of different values depending on the substituent R of phosphines PR₃. Some average values that can be mentioned are 2.33 Å for PMe₃ and 2.39 Å for PPh₃.²⁹ Our values seem to overestimate slightly the value of the metal-phosphorus distance, a result which

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Table V. MP2-Optimized Geometrical Parameters (in Å and deg) of the Most Stable Isomer of the $[\text{Os}(\text{PH}_3)_3\text{H}_5]^+$ Complex^a

Bond Distances			
Os(1)–P(2)	2.451	Os(1)–H(7)	1.602
Os(1)–P(3)	2.410	Os(1)–H(9)	1.638
Os(1)–H(5)	1.619		
Bond Angles			
P(2)–Os(1)–P(3)	96.9	P(3)–Os(1)–H(8)	77.8
P(2)–Os(1)–H(5)	81.3	P(3)–Os(1)–H(9)	80.2
P(2)–Os(1)–H(7)	151.1	H(5)–Os(1)–H(6)	58.2
P(2)–Os(1)–H(8)	146.4	H(5)–Os(1)–H(7)	73.4
P(2)–Os(1)–H(9)	77.4	H(5)–Os(1)–H(8)	127.0
P(3)–Os(1)–P(4)	152.9	H(5)–Os(1)–H(9)	143.8
P(3)–Os(1)–H(5)	73.7	H(7)–Os(1)–H(8)	62.5
P(3)–Os(1)–H(6)	131.6	H(8)–Os(1)–H(9)	69.1
P(3)–Os(1)–H(7)	89.6		

^a The atomic labels are the same as those in Figure 1.

is actually quite common in theoretical calculations.^{9b,13b,31} Nevertheless, comparison of optimized interatomic distances with available experimental data is good enough to rely on the qualitative accuracy of the predicted geometry.

Values for the L–M–L angles, also presented in Table V, can also be satisfactorily compared to experimental data for related complexes. In this case, comparison can be made with the neutron diffraction studies of two other eight-coordinate dodecahedral complexes with hydride and phosphine ligands: $[\text{Re}(\text{PMePh}_2)_3\text{H}_5]^{27}$ and $[\text{Os}(\text{PC}_{12}\text{H}_{19})_2\text{H}_6]^{32}$. Though, for reasons of space, it is impossible to discuss the values of all of the angles, it may be interesting to mention that our smaller H–Os–H angle (H(5)–Os(1)–H(6)), with a value of 58.2°, is on the same order of magnitude as the values of 65.4° and 60.5° found in the two just mentioned experimental studies and that the larger P–Os–P (P(3)–Os(1)–P(4)), with a value of 152.9°, lies precisely between the reported values of 148.0° and 155.2°.

The distortion introduced in our $[\text{Os}(\text{PH}_3)_3\text{H}_5]^+$ system by the presence of a hydride ligand H(7) in one of the B sites can be clearly observed both in Figure 1 and in Table V. The hydride ligand seems to claim a smaller space in the coordination sphere than the phosphine ligands occupying the other three B coordinations sites. This can be exemplified by the comparison of the bond angles involving H(7) and those involving P(2), which is the phosphine in the position that by symmetry should be equivalent. The bond angles with the other B ligands P(3) and P(4) are 89.6° in the case of H(7) and 96.9° in the case of P(2). The angles with the A ligands in the perpendicular plane, H(5) and H(6), are 73.4° for H(7) and 81.3° for P(2). Finally, the angle with the closer A ligand in the symmetry plane is 62.5° for H(7) and 77.4° for P(2). In all the cases, the angles with the hydride ligand are smaller than those implying the phosphine ligand, a result which we attribute to a steric effect, expected to be especially critical in crowded coordination spheres like that of the system under discussion.

Nevertheless, and despite the distortion, the general molecular shape has to be qualified definitely as dodecahedral, with all the features associated with this coordination polyhedron. The four A positions correspond to positions with four neighboring ligands (angles inferior to 100 degrees), while the four B positions have five neighbor ligands. Also, the A positions are more sterically crowded than the B positions. For instance, H(5), an A ligand, forms with its four closer ligands bond angles of 58.2°, 73.4°, 73.7°, and 81.3°, while the angles associated to H(7), a B ligand, are 62.5°, 73.4°, 73.4°, 89.6°, and 89.6°.

The molecular orbitals resulting from our calculation are in good agreement with the general features of eight-coordinate systems proposed by the extended Hückel method.^{25b} The most

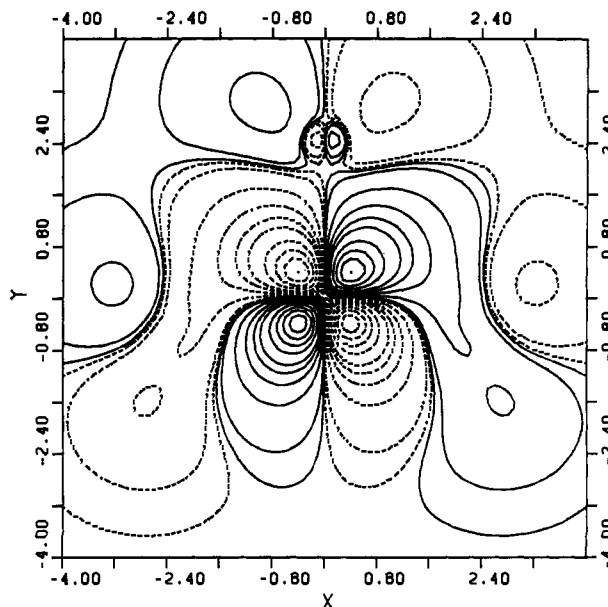


Figure 2. Plot in the XY plane of the higher energy occupied molecular orbital of the most stable isomer as obtained at the RHF level.

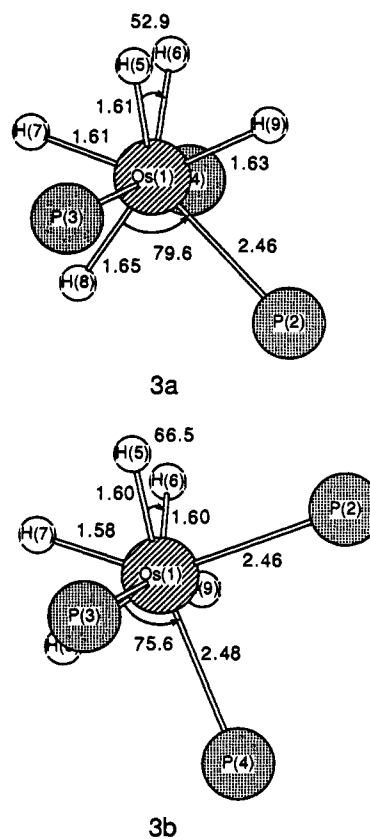


Figure 3. Optimized geometry of the two higher energy species corresponding to local minima CHOHI (3a) and FACA (3b). Hydrogen atoms of phosphine ligands have been suppressed for the sake of clarity.

significant agreement is probably the nature of the HOMO. According to these studies, the orbital picture associated with dodecahedral coordination contains only a single low energy d orbital, which would correspond to d_{xy} in the axis orientation depicted in Figure 1. Since $[\text{Os}(\text{PH}_3)_3\text{H}_5]^+$ is formally an Os(VI) system, that is, formally d^2 , one would expect this orbital to be occupied in the complex. And that is actually what happens in our calculation, the HOMO obtained at the RHF level being presented in Figure 2.

So far, this section has been fully devoted to the discussion of

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the most stable isomer of the system, as announced in the title, and no mention has been made of the other two structures which were also found in the previous section to be stable at the best computational level. The geometry of these MP2-optimized structures, which were labeled at the time as CHOHI and FACA and had relative energies of 13.1 and 5.1 kcal/mol with respect to CHIHO, is presented in Figure 3. They happen to also be dodecahedral, though with a different arrangement of the ligands. Certainly, both structures are characterized by having three hydride ligands in A positions and two in B positions, a different distribution from that in CHIHO, that has four hydrides in A coordination sites and only one in B sites. Nevertheless, the relationship between the three structures can be easily observed by comparing Figures 1 and 3. In particular, CHOHI can be obtained from CHIHO by exchanging the positions of P(2) and H(9), while the corresponding change for the structure FACA would be between P(4) and H(9).

The fact that the three isomers that have been found to be stable involve the same coordination polyhedron fits nicely within the general picture we have obtained for this system, in the sense that the coordination must be dodecahedral. Moreover, the superior stability of the CHIHO isomer, the only one with all the phosphines in B positions, can also be rationalized in terms of simple steric effects, which place the phosphine ligands in the less crowded B sites.

V. Conclusions

The theoretical study of the $[\text{Os}(\text{PR}_3)_3\text{H}_5]^+$ system has led

to its characterization as an eight-coordinate pentahydride complex $[\text{Os}(\text{PR}_3)_3\text{H}_5]^+$, the associated coordination polyhedron being a dodecahedron. Several stable isomers with this general coordination shape have been found to be stable, local minima in the potential hypersurface. The most stable of them, which we identify as the most stable form for this complex, has the three phosphine ligands in B coordination sites, with four hydride ligands in A positions and another one in the remaining B site. The existence of other higher energy pentahydride isomers, especially with a dodecahedral geometry, cannot be ruled out. Nevertheless, our results do make quite unlikely the existence as stable species in this system of isomers containing molecular hydrogen units H_2 as ligands.

Note Added in Proof: Prof. Caulton has recently informed us that a neutron diffraction study (Koetzle, T.; Albinati, A.; Caulton, K. G. Unpublished work.) has confirmed the present prediction of the structure of the complex.

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