

An ab Initio Molecular Orbital Study of the $[\text{Os}(\text{PR}_3)_3\text{H}_4]$ System: Peeking into the Peculiarities of Seven-Coordination

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Abstract: General features of seven-coordination are investigated through an ab initio study of the $[\text{Os}(\text{PR}_3)_3\text{H}_4]$ complex. After an assessment of the validity of different methods for the description of the generic $[\text{Os}(\text{PR}_3)_3\text{H}_4]$ system, the characteristics of the two different sites of the preferred coordination polyhedron, a pentagonal bipyramid, are examined. It is found that formally neutral ligands prefer axial sites, while formally negative ligands prefer equatorial sites. The energy decomposition analysis (EDA) explains this result as a consequence of the anisotropy in electron distribution associated with the metal nonbonding d orbitals.

I. Introduction

Despite the fact that seven-coordinate discrete transition metal complexes have been known for a long time^{1,2} and are present in a number of topics of current active research,³ seven-coordination remains a subject where general principles are scarce and arguable. Diversity seems to be the main problem in this study. With the existence of three different common coordination polyhedra,^{1,4} even the assignment of an experimental structure to one of them is not trivial.⁵ Chelation, steric effects, and π -bonding are also usually intermixed, further complicating the topic.

The most successful theoretical approach to the subject so far seems to be the ligand repulsion method devised by Kepert,⁴ which is based in the VSEPR theory⁶ and stresses the importance of steric effects of polydentate ligands. Application of the molecular orbital extended Hückel (EH) method, certainly efficient for lower coordination numbers,^{7,8} looks more problematic in the case of seven-coordination.^{9,10} Indeed, the probably most significant paper on this concern⁹ ends up admitting that "predictions do not differ significantly from those that would be based solely on steric arguments". Application of more precise ab initio methods has also been carried out, though in most cases the seven-coordinate system is just seen as an intermediate with the particular stereochemistry not being considered as an issue by

itself. For instance, a number of heptacoordinate species are present in ab initio studies of molecular hydrogen/polyhydride systems.¹¹⁻¹³ Some significant ab initio calculations have also been performed on systems containing only main group elements.¹⁴⁻¹⁶

The present paper applies the ab initio methodology to the study of a particular heptacoordinate transition metal complex, with the objective of contributing to the clarification of the role played by electronic effects in this type of system. The complex chosen for this study is $[\text{Os}(\text{PH}_3)_3\text{H}_4]$, which stands as a model for $[\text{Os}(\text{PR}_3)_3\text{H}_4]$ systems. Availability of neutron diffraction data for the $[\text{Os}(\text{P}(\text{CH}_3)_2\text{Ph})_3\text{H}_4]$ complex¹⁷ will permit the calibration of the methodology, and the presence of two different σ -donor ligands will allow the comparison of different coordination sites.

A problem associated with the selection of this particular system is the eventual interference of molecular hydrogen complexes,¹⁸ which have been demonstrated to be likely in this type of system from both experimental^{18,19} and theoretical^{11,12,13,20,21} studies. Therefore, before beginning the discussion of the specific features

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- (1) Drew, M. G. B. *Progr. Inorg. Chem.* **1977**, *23*, 67-210.
- (2) Melnik, M.; Sharrock, P.; *Coord. Chem. Rev.* **1985**, *65*, 49-85.
- (3) (a) Lindmark, A. F. *Inorg. Chem.* **1992**, *31*, 3507-3513. (b) Philipp, C. C.; White, P. S.; Templeton, J. L. *Inorg. Chem.* **1992**, *31*, 3825-3830. (c) Carnahan, E. M.; Protasiewicz, J. D.; Lippard, S. J. *Acc. Chem. Res.* **1993**, *26*, 90-97.
- (4) (a) Kepert, D. L. *Progr. Inorg. Chem.* **1979**, *25*, 41-144. (b) Kepert, D. L. *Inorganic Stereochemistry*; Springer-Verlag: Berlin, 1982.
- (5) (a) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748-1756. (b) Kouba, J. K.; Wreford, S. S. *Inorg. Chem.* **1976**, *15*, 1463-1465.
- (6) (a) Gillespie, R. J.; Hargittai, I. *The VSEPR Model of Molecular Geometry*; Allyn and Bacon: Boston, 1991. (b) Gillespie, R. J. *Chem. Soc. Rev.* **1992**, 59-69.
- (7) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365-374.
- (8) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.
- (9) Hoffmann, R.; Beier, B. F.; Muetterties, E. L.; Rossi, A. R. *Inorg. Chem.* **1977**, *16*, 511-522.
- (10) Hoffmann, R.; Wilker, C. N.; Lippard, S. J.; Templeton, J. L.; Brower, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 146-147.

(11) (a) Hay, P. J. *J. Am. Chem. Soc.* **1987**, *209*, 705-710. (b) Pacchioni, G. *J. Am. Chem. Soc.* **1990**, *112*, 80-85. (c) Maseras, F.; Duran, M.; Lledós, A.; Bertrán, J. *J. Am. Chem. Soc.* **1992**, *114*, 2922-2928.

(12) (a) Haynes, G. R.; Martin, R. L.; Hay, P. J. *J. Am. Chem. Soc.* **1992**, *114*, 28-36. (b) Lin, Z.; Hall, M. B. *J. Am. Chem. Soc.* **1992**, *114*, 6102-6108. (c) Lin, Z.; Hall, M. B. *Inorg. Chem.* **1992**, *31*, 4262-4265.

(13) Lin, Z.; Hall, M. B. *J. Am. Chem. Soc.* **1992**, *114*, 2928-2932.

(14) Bartell, L. S.; Rothman, M. J.; Gavezzotti, A. *J. Chem. Phys.* **1982**, *76*, 4136-4143.

(15) Christie, K. O.; Curtis, E. C.; Dixon, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 1520-1526.

(16) Christie, K. O.; Dixon, D. A.; Mahjoub, A. R.; Mercier, H. P. A.; Sanders, J. C. P.; Seppelt, K.; Schrobilgen, G. J.; Wilson, W. W. *J. Am. Chem. Soc.* **1993**, *115*, 2696-2706.

(17) Hart, D. W.; Bau, R.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 7557-7564.

(18) (a) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451-452. (b) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120-128. (c) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299-338. (d) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155-284. (e) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913-928.

(19) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173-4184.

(20) (a) Jean, Y.; Eisenstein, O.; Volatron, F.; Maouche, B. Sefta, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 6587-6592. (b) Burdett, J. K.; Eisenstein, O.; Jackson, S. A. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: Weinheim, 1991; pp 149-184. (c) Maseras, F.; Duran, M.; Lledós, A.; Bertrán, J. *J. Am. Chem. Soc.* **1991**, *113*, 2879-2884.

(21) (a) Plitt, H. S.; Bär, M. R.; Ahlrichs, R.; Schnöckel, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 832-834. (b) Lin, Z.; Hall, M. B. *Organometallics* **1992**, *11*, 3801-3804.

of seven-coordination in this system, the ability of the methodology to predict this coordination number will be assessed. We have recently carried out a similar analysis for $[\text{Os}(\text{PR}_3)_3\text{H}_5]^{2+}$ to predict the most stable isomer to be an eight-coordinate pentahydride complex with dodecahedral coordination.²²

II. Computational Details

All the ab initio calculations are performed with the Gaussian program.²³ The 60 innermost electrons of the osmium atom are represented by an effective core potential (ECP) including relativistic contributions, and this ECP is used with a corresponding triple- ζ basis set.²⁴ For most of the other atoms under consideration, the valence double- ζ 3-21G basis set²⁴ is used, with the only exception being the hydrogen atoms directly attached to the metal. For these hydrogen atoms, a more extended basis set is applied to take account of their eventual hydridic nature. Specifically, it is a basis set of triple- ζ quality,²⁵ using a scale factor²⁶ of 1.25 complemented with a polarization p shell with an exponent of 1.0.

Although most of the discussion is done on results at the RHF level, correlation energy is also contemplated through various orders of Møller-Plesset perturbational approach²⁷ (MP2, MP3, and MP4 calculations). In the case of the MP2 geometry optimization, excitations concerning the full space of orbitals are considered, while single-point MP2, MP3, and MP4 calculations use the frozen core (FC) approximation. MP4 calculations include single, double, triple, and quadrupole excitations (MP4SDTQ).

Geometry optimization makes extensive use of C_s symmetry unless stated otherwise. In the case of the parent molecule $[\text{Os}(\text{PH}_3)_3\text{H}_4]$, complete optimization is performed with the only exceptions being the dihedral angle of one hydrogen atom of each phosphine ligand, which is fixed to avoid rotation around the M-P bond. When other ligands are considered, limited geometry optimization involving only metal-ligand distances is carried out. Further details are given in the corresponding sections.

III. Theoretical Characterization of $[\text{Os}(\text{PH}_3)_3\text{H}_4]^{2+}$ as $[\text{Os}(\text{PH}_3)_3\text{H}_4]$

At first we would like to examine what level of theory is required for theoretical prediction of the coordination number in this species. It has been demonstrated that electron correlation plays a substantial role in the characterization of the dihydride *vs* molecular hydrogen complex equilibrium.^{12,13,21} We have optimized a representative set of geometries at both the RHF and MP2 levels and performed energy-only calculations at MP3 and MP4 levels on some selected optimized geometries.

Selection of the Starting Geometries. For systematic search of possible structures of the complex, we have used an ideal octahedron as the starting point of geometry optimization. The seven-coordination is accomplished by making two hydrides share one site. In order to make full use of C_s symmetry, the three phosphine ligands are placed in a *mer* disposition with one of the phosphorus atoms in the symmetry plane; this assumption will be discussed again in a later section. The four hydrogen atoms are then distributed in the remaining three positions, and the resulting species are labeled according to the following three criteria concerning the site shared by a pair of hydrogen atoms: (i) their site can be *trans* (T) to one of the phosphine ligands or *cis* (C) to all of them; (ii) they can be in the form of dihydrogen (D) or hydrides (H); and (iii) they can be in (I) or out of (O)

(22) Maseras, F.; Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1993**, *115*, 8313–8320.

(23) GAUSSIAN90, Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. GAUSSIAN Inc.: Pittsburgh, PA, 1990.

(24) (a) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939–947. (b) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797–2803.

(25) Dunning, T. J. *J. Chem. Phys.* **1971**, *55*, 716–723.

(26) CADPAC Version 4.0, Amos, R. D.; Rice, J. E.

(27) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

Chart I

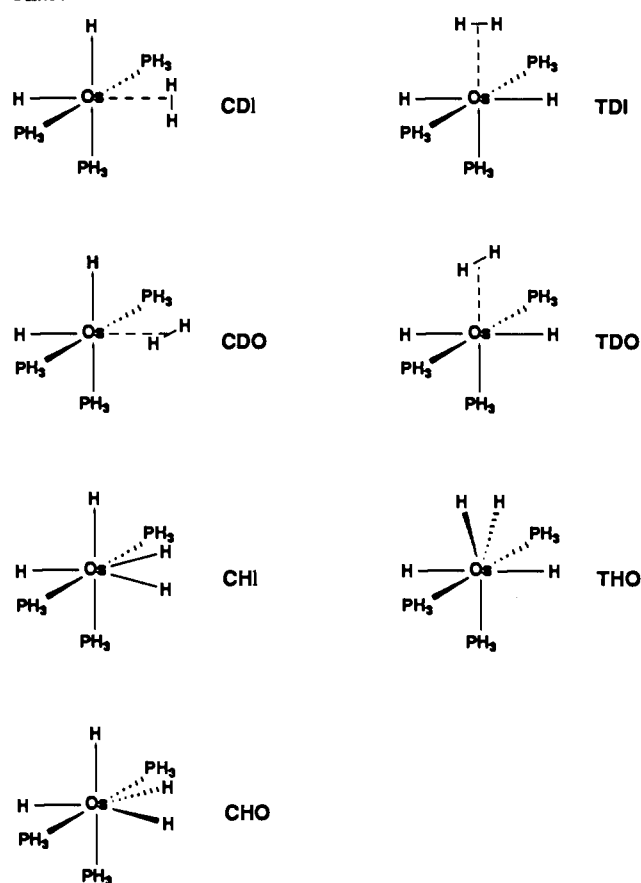


Table I. Results of Geometry Optimization at the RHF Level of the Isomers Included in Chart I^a

initial	C_s optimiz	energy	C_1 optimiz	energy
CDI	CDI	6.2	CDI	6.2
CDO	CDO	10.5	CDI	6.2
CHI	CHI	0.0	CHI	0.0
CHO	CHO	15.8	CHO	15.8
TDI	CHI	0.0	CHI	0.0
TDO	TDO	18.5	CHI	0.0
THO	TDO	18.5	CHI	0.0

^a Relative energies with respect to the CHI isomer are given in kcal/mol. The total energy of the reference is -1114.65277 hartrees.

the molecular symmetry plane. This labeling scheme leads to the seven distinct geometries presented in Chart I.

First, the seven geometries in Chart I are fully optimized within the C_s symmetry. Then geometry optimization without symmetry restrictions is performed from slightly distorted structures derived from the optimized C_s geometries to check whether they are true local minima. If they are not, this should lead to a different C_1 optimized geometry. All possible isomers of six- and seven-coordination with *mer* disposition of three phosphines should be accessible with this scheme.

RHF Calculations. Table I summarizes the results of RHF optimization. Two of the seven starting geometries, TDI and THO, do not even correspond to local minima within the C_s symmetry and collapse to CHI and TDO, respectively. The number of candidates for local minima is further reduced when symmetry is relaxed, with the disappearance of the CDO and TDO structures from the list. The final result is that only the three structures CHI, CDI, and CHO are local minima at the RHF level.

While only three of the seven starting geometries were hepta-coordinate true polyhydride complexes, two of the three species remaining after optimization belong to this class, including the

Table II. Results of Geometry Optimization at the MP2 Level of the Isomers Included in Chart I^a

initial	C ₂ optimiz	energy	C ₁ optimiz	energy
CDI	CHI	0.0	CHI	0.0
CDO	CHO2 ^b	7.9	CHO2	7.9
CHI	CHI	0.0	CHI	0.0
CHO	CHO2	7.9	CHO2	7.9
TDI	CHI	0.0	CHI	0.0
TDO	TDO	34.3	CHI	0.0
THO	TDO	34.3	CHI	0.0

^a Relative energies with respect to the CHI isomer are given in kcal/mol. The total energy of the reference is -1115.24475 hartrees. ^b CHO2 corresponds to a geometry substantially different from that referred in Table I as CHO.

Table III. Results of the Frozen Core Energy-Only Calculations at Higher Computational Levels for Some Geometries Optimized at the RHF Level^a

species	RHF	MP2	MP3	MP4
CDI	6.2	15.0	14.4	12.4
CDO	10.5	19.9	19.3	16.8
CHI	0.0	0.0	0.0	0.0
CHO	15.8	12.4	13.5	12.1
TDO	18.5	38.3	32.5	34.
CHO2	16.6	8.1	10.4	7.6

^a Relative energies with respect to the CHI isomer are given in kcal/mol. The total energy of the reference is -1114.65277 hartrees at the RHF level, -1115.22259 hartrees at the MP2 level, -1115.23442 hartrees at the MP3 level, and -1115.30222 hartrees at the MP4 level.

most stable one CHI. The experimental structure,¹⁷ a pentagonal bipyramid with the four hydride ligands in the equatorial plane, is nothing but CHI in Chart I.

MP2 Calculations. In order to assess the effect of electron correlation, we have carried out the same set of calculations at the MP2 level. MP2 single-point calculations on RHF-optimized geometries have been previously considered reliable by other authors¹³ for addressing the real nature of "polyhydride" complexes.

The results of geometry optimization at the MP2 level, presented in Table II, are remarkably different from those obtained above with the RHF method. The predicted absolute minimum is still the same, CHI, but this is practically the only thing that remains unchanged. There are no molecular hydrogen complexes stable at the MP2 level. The energy difference between the absolute minimum CHI and the C₂-optimized molecular hydrogen complex TDO is almost twice as large at the MP2 level as at the RHF level (34.3 vs 18.5 kcal/mol). Moreover, optimization of the CHO structure leads to a species, labeled as CHO2, which is topologically different from the one that was obtained at the RHF level; CHO is a pentagonal bipyramid, while CHO2 is a capped octahedron.

Therefore, despite the coincidence in the nature of the predicted absolute minimum, the remarkable differences between Tables I and II suggest the necessity of geometry optimization at the MP2 level.

Higher Level Calculations. The previous two subsections have demonstrated that the correlated MP2 optimization significantly changes the results obtained at the RHF level. This does not mean necessarily that the MP2 results are satisfactory. This subsection presents the energies obtained at higher order MP3-(FC) and MP4(FC) levels for five structures obtained by symmetry restricted RHF optimization as well as for the capped octahedron CHO2 reoptimized at this level for consistency. Geometries optimized at the RHF level are chosen instead of those optimized at the MP2 level essentially because their larger number provides better grounds for comparison.

The most remarkable feature of results shown in Table III is definitely the high resemblance of the MP3 and MP4 results with the MP2 values, in sharp contrast with the larger discrepancy of

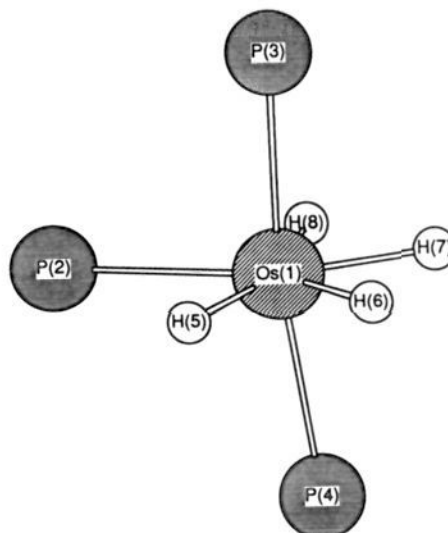


Figure 1. MP2 optimized geometry of the most stable isomer, labeled as CHI. Hydrogen atoms of phosphine ligands are omitted for the sake of clarity. C₁ optimization gave a C₂ structure. Geometrical parameters are given in Table IV.

the RHF numbers. The largest difference between MP2 and MP4 relative energies is 3.5 kcal/mol for TDO. The RHF-MP4 differences are larger in all cases with values up to 16.3 kcal/mol. Though we have not carried out more elaborate calculations for the present system, our previous study on the [Os(PR₃)₃"H₅"]⁺ complex has shown that MP4SDQ results are in excellent agreement with the most elaborate QCISD(T) results.²² Therefore, one can consider that in the present system the MP2 level gives satisfactory relative energetics, higher levels bringing only minor corrections.

Maybe more significant is the fact that at the RHF level the molecular hydrogen complexes CDI, CDO, and TDO are systematically overstabilized by about 10 kcal/mol with respect to polyhydride complexes. This error can probably be attributed to the poor description of back-donation at the RHF level. Whatever is its origin, RHF energetics cannot deal with the problem of equilibrium between molecular hydrogen and dihydride complexes.

Nevertheless, the fact that the error is systematic has some advantage. The RHF energetics gives a good estimation of relative energies within species of the same coordination number, or even better within the same coordination polyhedron. The energy difference between the two PBP species CHI and CHO is 15.8 kcal/mol at the RHF level and 12.1 kcal/mol at the MP4 level. The comparison of different pentagonal bipyramidal isomers is the main topic of the rest of this paper. For this purpose we will later use RHF as the main computational tool.

IV. The Problem of the Coordination Polyhedron

There are three different coordination polyhedra associated with seven-coordination: the pentagonal bipyramid (PBP), the capped octahedron (CO), and the capped trigonal prism (CTP). This section classifies the geometries optimized in the previous section, plus some others added for completeness, according to this criterion.

The Most Stable Isomer. Figure 1 presents the geometry of the pentagonal bipyramidal CHI isomer, the most stable structure of the complex. Numerical details are given in Table IV, where a comparison of the results of geometry optimization at both the RHF and MP2 levels is made with the experimental data for [Os(P(CH₃)₂Ph)₃H₄].¹⁷ The largest difference appears in the Os-P(2) distances, which are off by up to 0.13 Å in the RHF calculation. This error is partially corrected in the MP2

Table IV. Selected Geometrical Parameters of the Optimized Absolute Minimum CHI for the $[\text{Os}(\text{PH}_3)_3\text{H}_4]$ Complex, Compared with Experimental Neutron Diffraction Data for the $[\text{Os}(\text{P}(\text{CH}_3)_2\text{Ph})_3\text{H}_4]$

parameter ^a	RHF	MP2	expt ^b
Os(1)–P(2)	2.479	2.412	2.35
Os(1)–P(3)	2.397	2.342	2.31–2.32
Os(1)–H(5)	1.671	1.649	1.66–1.68
Os(1)–H(6)	1.616	1.608	1.64–1.65
P(2)–Os(1)–P(3)	94.3	95.6	96.9–97.1
P(2)–Os(1)–H(5)	79.7	78.4	73.0–79.7
P(3)–Os(1)–H(5)	90.8	91.3	89.6–92.7
P(3)–Os(1)–H(6)	86.3	85.4	83.7–84.9
H(5)–Os(1)–H(6)	69.1	69.7	69.4–70.0
H(6)–Os(1)–H(7)	64.9	66.3	67.9

^a The labeling of the atoms is that defined in Figure 1. C_1 optimization converged to a C_1 structure. ^b The range provided in the experimental data corresponds to taking into account the values for "pseudosymmetric" ligands.

optimization, when the difference comes down to 0.06 Å. Indeed, one cannot expect a perfect agreement in the Os–P distance because we have used PH_3 in place of experimental $\text{P}(\text{CH}_3)_2\text{Ph}$. The Os–H distances are better described, especially at the MP2 level, where differences are never larger than 0.03 Å. Angles, which are the most significant parameters in defining the coordination polyhedron, are predicted with an error always smaller than 4°.

Other Local Minima. Since it has been demonstrated in the previous section that the RHF computational level is sufficient for the comparison of species with the same coordination number, only species optimized at this level are considered here. Figure 2 shows four optimized geometries different from the CHI isomer. Two of these structures, CHO and FAC, correspond to the PBP coordination mode. In the FAC species the phosphines are not on different sides of the ideal octahedron. Despite noticeable deformations, probably associated to steric effects, both geometries fit well into the PBP description. This can be appreciated for instance in the presence of five coplanar ligands, which is incompatible with CO or CTP coordination polyhedra. Features of PBP coordination will be discussed in detail in Sections V and VI.

As seen in Figure 2, the species CHO2 is a capped octahedron, the capping ligand being H(5). This is a C_{3v} -like geometry, with the symmetry axis passing through the metal and the capping ligand. Though the orientation of phosphines is not exactly in C_{3v} geometry,²⁸ the proximity to this symmetry can be appreciated in the dihedral angles P(3)–Os(1)–H(5)–P(2) and H(6)–Os(1)–H(5)–H(8), which are respectively of 120.3° and 120.1°, very close to the ideal value of 120°.

Finally, the species CTP in Figure 2, belonging to the capped octahedron, was not found during the search for the most stable isomer and does not correspond to a local minimum. We forced the CTP geometry by optimizing the four Os–H distances and P(2)–Os–H angles as single values. The result is a structure with a relative energy of 43.7 kcal/mol, remarkably higher than the energy of the other species. The existence of other CTP isomers of lower energy cannot be completely ruled out, but it seems clear that this is not the preferred coordination polyhedron for this system.

In summary, theoretical calculations confirm the pentagonal bipyramid as the preferred coordination polyhedron for this system, in agreement with the experimental data. The preference of a d^4 system with pure σ -donor ligands for this coordination can in fact be deduced from the theoretical results of the previously mentioned study with the EH method.⁹ The pentagonal bipyramid is the only one of the three possible polyhedra where the two

lower energy d orbitals are strictly nonbonding, being weakly antibonding in the other cases. In line with this preference of the present system for the PBP geometry, the rest of the paper is focused on the characteristics of this coordination mode.

V. Equatorial and Axial Ligands in PBP Coordination. Evaluation of "Interaction Energies"

The presence of two topologically different coordination sites in a pentagonal bipyramid provides an interesting problem for study. This type of situation is not so common in lower coordination numbers, with the remarkable exception of five-coordination, where nevertheless patterns for the preference of different ligands can be established in a satisfactory way from EH calculations.⁷ Things are not as clear for the PBP geometry.^{6,9,15}

The analysis presented here starts with the quantification of the complex–ligand interaction in different species through a magnitude referred to as interaction energy. This value is calculated as the difference between the total energy of the $\text{ML}_6\text{L}'$ complex and the energy of the two separated fragments ML_6 and L' . A regular PBP geometry with angles of 90.0° and 72.0° is fixed for the $\text{ML}_6\text{L}'$ system, while the ML_6 and L' fragments are kept rigid at the same geometry they have in the complex. Hydrogen atoms of phosphine ligands are kept in the same geometries they have in the CHI isomer, and a single M–L bond distance is used regardless of the coordination site, this being 2.4243 Å for Os–P and 1.6457 Å for Os–H. These values are the averages of bond distances obtained in RHF optimization of the most stable isomer CHI. The interaction energy computed in this way is only remotely related to the experimental binding energy,²⁹ but it is still a very meaningful measure of bonding between a ligand and a metal center.

The $[\text{Os}(\text{PH}_3)_3\text{H}_4]$ System. Figure 3 collects the interaction energies of four different PBP isomers of the $[\text{Os}(\text{PH}_3)_3\text{H}_4]$ complex. Some of the numbers are trivial results which deserve little comment. For instance, the fact that the interaction energies of the hydride ligands (over 200 kcal/mol) are much larger than those of the phosphine ligands (under 50 kcal/mol) is a mere reflection of the intrinsic instability of free H^- with respect to PH_3 . The hydride donates a large fraction of an electron to form a covalent metal–H bond, which may still be polarized like $\text{M}^{+\delta}-\text{H}^{-\delta}$. Another expected result is the presence of a trans effect in the axial position, the bonds *trans* to phosphine being more than 10 kcal/mol stronger than those *trans* to hydride.

More significant to the discussion under way is the comparison of axial and equatorial interaction energies for each ligand. The case of hydride is clear, with stronger bonds in equatorial (from 230.8 to 245.2 kcal/mol) than in axial sites (from 200.9 to 216.0 kcal/mol). The case of phosphine ligands is not so clear. Steric effects are surely playing some role. This is likely to be at least one of the reasons that the weakest of all metal–phosphine bonds, only 7.9 kcal/mol, is formed when there are two other close phosphines in equatorial positions in the THO complex. Nevertheless, it also seems that electronic effects do not favor the equatorial position to the extent they do in the case of the hydride ligand. It can serve as an example that the stronger metal–phosphine ligand appears in the axial position (39.6 kcal/mol in CHI), while the weakest is the aforementioned equatorial bond (7.9 kcal/mol) of the THO complex. The different behavior between hydride and phosphine ligands is quite unexpected, since both ligands are considered to be essentially pure σ -donors and should show a similar pattern of axial/equatorial preference.

The General $[\text{Os}^{\text{IV}}(\text{PH}_3)_2\text{H}_3]^+\text{L}_2$ System. Though both hydride and phosphine share a common classification as pure σ -donors, there are a number of differences between the two ligands, like the size, the formal charge, and the different hybridization of the donor orbital. In order to pinpoint which of these characteristics

(28) This geometry could indeed be strictly C_{3v} if the hydrogens of phosphine ligands were properly oriented. They are not so because their dihedral angles are fixed in orientations related to the octahedral models defined in Chart 1.

(29) Simões, J. A. M.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629–688.

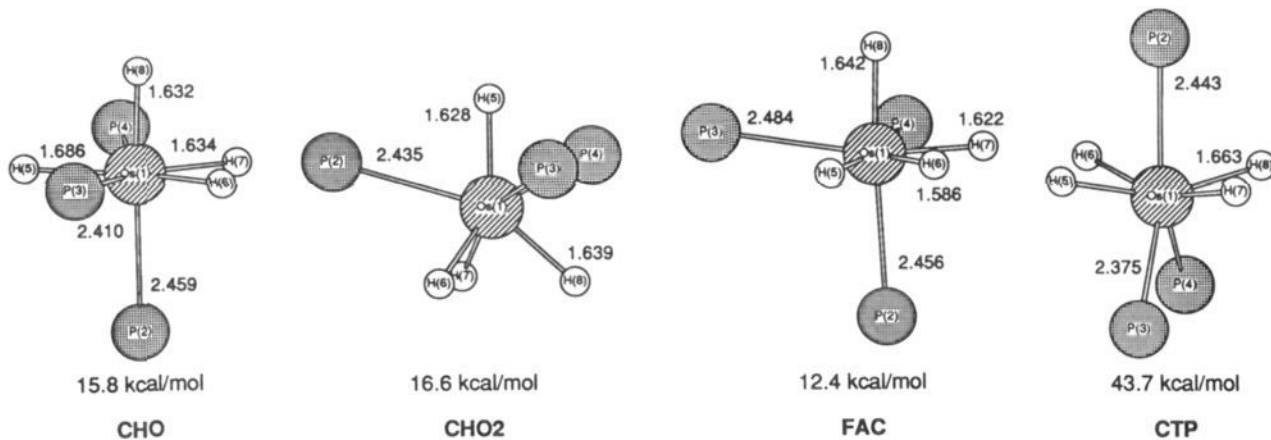


Figure 2. RHF optimized geometry of the CHO, CHO2, FAC, and CTP isomers. Relative energies (kcal/mol) with respect to the absolute minimum and the values of some selected distances (Å) are also provided. Hydrogen atoms of phosphine ligands are omitted for the sake of clarity.

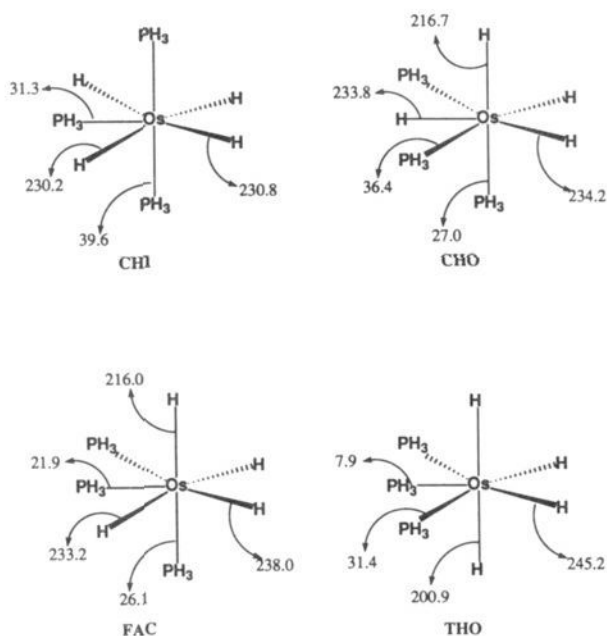
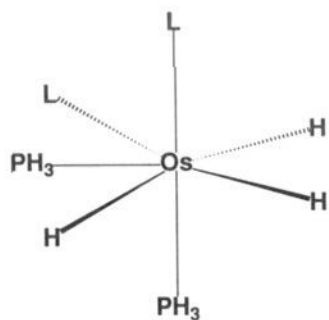


Figure 3. Interaction energies (kcal/mol) for different isomers of the $[\text{Os}(\text{PH}_3)_3\text{H}_4]$ complex, computed with the algorithm described in the text.

Chart II



is responsible for their different behavior in PBP complexes, other hypothetical ligands formally related to H^- and PH_3 are investigated. These ligands are SiH_3^- , NH_3 , CH_3^- , He , Li^- , Be , BH , and BeH^- .

The interaction energy in equatorial and axial positions of a generic ligand L is evaluated with RHF calculations on a model complex $[\text{Os}^{\text{IV}}(\text{PH}_3)_2\text{H}_3]^+\text{L}_2$ of the form depicted in Chart II. In each case, the $[\text{Os}^{\text{IV}}(\text{PH}_3)_2\text{H}_3]^+$ fragment is kept rigid as above,

Table V. Interaction Energies (kcal/mol) Corresponding to Different Ligands (L) in $[\text{Os}^{\text{IV}}(\text{PH}_3)_2\text{H}_3]^+\text{L}_2$ Complexes As Depicted in Scheme I

ligand	$\Delta E(L_{\text{ax}})$	$\Delta E(L_{\text{eq}})$	$\Delta E(L_{\text{ax}}) - \Delta E(L_{\text{eq}})$
PH_3	47.3	31.6	+15.7
BH	105.2	90.6	+14.6
NH_3	56.0	43.2	+12.8
Be	38.9	29.8	+9.1
He	4.2	1.4	+2.8
SiH_3^-	76.8	80.0	-3.2
CH_3^-	100.5	105.3	-4.8
BeH^-	101.3	113.7	-11.4
H^-	103.8	115.6	-11.8
Li^-	7.7	22.4	-14.7

and the Os-L distance is optimized with the restriction of both Os-L_{eq} and Os-L_{ax} being the same, while the internal geometrical parameters of the ligand are frozen to the values they have in the free ligand. Os-L distances are optimized to provide an even ground for comparison, which could not be reached otherwise because of the lack of reliable standard values for all the ligands under consideration. The total charge of the complex is chosen so that the metal keeps a formal oxidation state of IV.

Results presented in Table V show that the leading factor in the preference of axial or equatorial positions in pentagonal bipyramidal coordination is the formal charge of the ligand. Formally neutral ligands, like phosphine, prefer axial positions; formally negative ligands, like hydride, prefer equatorial positions. All of the ten ligands that have been checked, five neutral and five negative, follow this rule. Though steric factors also play a minor role, they are definitely not the main contribution. Neither hybridization of the donor orbital nor donor strength seem to be relevant.

Reliability of this result with respect to the introduction of energy correlation is checked through an additional set of calculations for H^- and PH_3 ligands at the MP2 level. Despite significant differences in absolute values, the trend in the axial/equatorial preference is the same, with the phosphine preferring the axial position by 13.9 kcal/mol and the hydride preferring the equatorial site by 8.0 kcal/mol.

VI. Equatorial and Axial Ligands in PBP Coordination. Decomposition of the "Interaction Energies"

The just identified relationship between the formal charge of σ -donor ligands and their site preference in PBP coordination demands some kind of qualitative explanation. This section provides such an explanation through the application of the energy

Table VI. Results of the Energy Decomposition Analysis of the Complex-Ligand Interaction for Different Ligands (L) in Pentagonal Bipyramidal $[Os(PH_3)_2H_3]L_2$ Complexes^a

ligand	site	ES	EX	BCTPLX	FCTPLX + R	-ΔE
PH ₃	ax	-73.3	+72.7	-7.9	-38.8	-47.3
	eq	-86.4	+108.5	-9.9	-43.8	-31.6
	diff	13.1	-35.8	+2.0	+5.0	-15.7
Be	ax	-43.5	+87.3	-22.2	-60.5	-38.9
	eq	-60.6	130.8	-23.2	-76.8	-29.8
	diff	+17.1	-43.5	+1.0	+16.3	-9.1
SiH ₃ ⁻	ax	-130.7	+138.2	-5.9	-78.4	-76.8
	eq	-173.3	+197.3	-7.8	-96.2	-80.0
	diff	+42.6	-59.1	+1.9	+17.8	+3.2
H ⁻	ax	-136.1	+138.6	-9.3	-97.0	-103.8
	eq	-166.4	+167.8	-11.1	-105.9	-115.6
	diff	+30.3	-29.2	+1.8	+8.9	+11.8

^a Energies are in kcal/mol.

decomposition analysis (EDA) method.^{30,31} This scheme is applied to four of the ten ligands that were considered in the previous section: the two parent ligands of this study (PH₃ and H⁻) plus Be and SiH₃⁻. Be and SiH₃⁻ are chosen because of their formal relationship to the other two ligands. Silyl is isoelectronic with phosphine and, in a sense, it is the closest one can get to a phosphine ligand with a negative charge. In the case of hydride, the simplest choice for a "neutral hydride", that is, He, is skipped because its small binding energies would hamper the interpretation of the decomposition analysis. Instead, Be is used, with the hope that 2p orbitals do not play a substantial role.

EDA Results. The total interaction energy is defined as a positive value in accord with its definition used in the preceding section. The attraction energy, -ΔE, is decomposed in the EDA partition³² into the following terms: (i) ES, the electrostatic interaction; (ii) EX, the exchange term, representing the always repulsive interaction between the occupied shells of both fragments; (iii) FCTPLX, the donative interaction, which includes the charge transfer from the ligand to the complex and the polarization this process induces in the orbitals of the latter; (iv) BCTPLX, the back-donative interaction, involving the charge transfer from the complex to the ligand and the polarization caused on the ligand orbitals; and (v) R, the remainder, a collection of the contributions not included in the previous terms. A slight modification had to be done to the scheme in this application to this particular system. Since EDA is a method devised especially for cases with relative small interaction energies, its application to systems with large interactions may preclude the convergence of some of the terms. This happens indeed for the FCTPLX term in some of the cases considered in this paper. The solution used to overcome this problem is to consider together the donative interaction and the remainder, giving a global term FCTPLX + R, which must be dominated by the FCTPLX part. This FCTPLX + R term is the one that is used in the following discussions as the donative interaction, regardless of the fact that in some cases the FCTPLX term itself could be computed. In these cases, the magnitude of the remainder R was satisfactorily small always below 10 kcal/mol. A certain pattern can be readily observed in the EDA results presented in Table VI. Putting aside the always negligible back-donation contribution, each of the other three terms is analyzed in detail in the following subsections.

The Donative Interaction. The extended Hückel (EH) method,^{32,33} with its stress on orbital interactions, seems well suited for the study of this term. This method, which achieves a very

low computational cost through the use of substantial approximations, has its strong point in the evaluation of orbital interactions which are expected to be the gist of the donative term. The inability of this method to describe properly the repulsion between occupied inner shells and electrostatic effects is an advantage in this particular case.

The conclusion from a previous EH calculation⁹ on a PBP complex with pure σ-donors was 2-fold: (i) from the overlap population, it appeared that the axial bond was marginally stronger, and (ii) from the charge distribution, it was concluded that the better σ-donors should enter the equatorial sites. On the other hand, one would expect the stronger σ-donors to go to the positions forming the stronger σ-bonds. To solve this apparent contradiction, new EH calculations using the weighted H_{ij} scheme³⁴ are performed on the D_{5h} symmetry $[OsH_7]^{3-}$ system, with an Os-H distance of 1.6457 Å. The results for the charges and population overlaps are comparable to those reported in the aforementioned paper,⁹ and the contradiction, not surprisingly, persists. The EH binding energy is evaluated with a preference of 4.0 kcal/mol for the equatorial position being found. The EH method thus predicts a stronger bond for the equatorial sites and reproduces the trend of the EDA donation term. The apparent contradiction of the overlap populations must be associated with a shortcoming of the Mulliken population analysis.

The analysis of these EH results allows for a rationalization of the larger magnitude of the donative term for the equatorial position. In short, it is due to the high energy of the symmetry adapted combination of the orbitals of the equatorial ligands donating to $\{d_{xy}, d_{x^2-y^2}\}$ orbitals, and these equatorial ligands also give electrons to the metal d_{z^2} orbital. The destabilization introduced in each of the donor orbitals of the five equatorial ligands by the presence of the other four in-plane ligands is therefore a substantial factor enhancing its interaction with the empty metal d orbitals.

The Exchange Term. The exchange term is shown in Table VI to favor strongly the axial position, with preferences ranging from 29.2 to 59.1 kcal/mol. The study of the reasons for this behavior is complicated by the difficulty of quantifying this effect apart from the EDA method itself. Nevertheless, this limitation can be overcome by accepting an intuitive explanation, which goes in the same direction of the observed result. This explanation relies on the assumption that in a sterically crowded coordination complex the exchange interaction must be associated with ligand-ligand interactions more than with ligand-metal interactions, an assumption based on the fact that the existence itself of a chemical bonding between metal and ligands precludes the presence of significant overlap between their occupied shells. Once this is accepted, the reasoning becomes straightforward. Equatorial ligands are closer to each other than to the axial ligands as a direct consequence of the different L-M-L angles. The closer the ligands are to each other, the larger their interaction and the larger the repulsive EX term. Therefore, the equatorial ligands must have a much larger repulsive term. This is precisely what is found in the EDA results.

The Electrostatic Term. Some of the features concerning the ES term which can be observed in Table VI have little mystery. One certainly expects to have an attractive electrostatic term in the metal-ligand interaction of a coordination complex. After all, the crystal field approach³⁴ yields satisfactory results in a number of cases. Another predictable result is the magnification of the electrostatic effects when charged ligands are considered. Electrostatic effects must indeed be directly proportional to the electric charge.

The result that is not so trivial is the preference that electrostatic interactions grant to the equatorial positions. Still, a qualitative explanation can be obtained from the nonspherical space distribution

(30) (a) Kitaura, K.; Morokuma, K. *Int. J. Quantum Chem.* 1976, 10, 325-340. (b) Morokuma, K. *Acc. Chem. Res.* 1977, 10, 294-300.

(31) (a) Kitaura, K.; Morokuma, K. In *Chemical Applications of Atomic and Molecular Electrostatic Potentials*; Politzer, P., Truhlar, D. G., Eds.; Plenum: New York, 1981; pp 215-242. (b) Kitaura, K.; Sakaki, S.; Morokuma, K. *Inorg. Chem.* 1981, 20, 2292-2297.

(32) Hoffmann, R. *J. Chem. Phys.* 1963, 39, 1397-1412.

(33) Ammeter, J. H.; Bürgi, H.-B.; Thibault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* 1978, 100, 3686-3692.

(34) Ballhausen, C. J. *Introduction to Ligand Field Theory*; McGraw-Hill: New York, 1962.

Scheme I

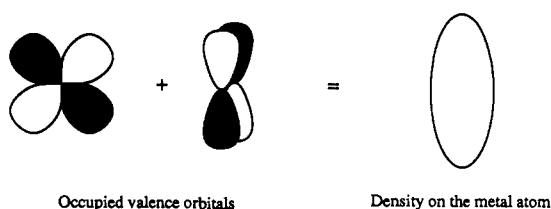


Table VII. Interaction Energies (kcal/mol) for the Ligands (L) in Pentagonal Bipyramidal $[\text{Os}^{\text{VIII}}(\text{PH}_3)_2\text{H}_3]^{5+}\text{L}_2$ Complexes As Estimated with the "Frozen Orbitals" Approach (See Text for Explanation)

ligand	$\Delta E(L_{\text{ax}})$	$\Delta E(L_{\text{eq}})$	$\Delta E(L_{\text{ax}}) - \Delta E(L_{\text{eq}})$
PH_3	200.4	131.3	+69.1
Be	524.0	481.0	+43.0
SiH_3^-	832.1	369.6	+462.5
H^-	726.1	605.1	+121.0

of the nonbonding metal d^4 electrons. Its likely asymmetry is confirmed by the computation of the quadrupole moment of a hypothetical atomic system containing only these four electrons. Such a calculation yields values of $-2.14 \text{ D}\cdot\text{\AA}$ for the axial Q_{zz} component and $+1.07 \text{ D}\cdot\text{\AA}$ for the equatorial Q_{xx} and Q_{yy} components, indicating a prolate ellipsoidal density of the type depicted in Scheme I. As a result, the screening of nuclear charge by these electrons is smaller in the equatorial region, allowing for a stronger electrostatic bond in these sites. In order to further confirm the validity of this explanation, calculations are performed with a system $[\text{Os}^{\text{VIII}}(\text{PH}_3)_2\text{H}_3]^{5+}\text{L}_2$ where these four nonbonding d electrons are eliminated. Execution of this plan of calculations on the $[\text{Os}^{\text{VIII}}(\text{PH}_3)_2\text{H}_3]^{5+}\text{L}_2$ complex is not that simple. Not surprisingly, RHF calculations on a system of this stoichiometry do not converge to the desired electronic state, the ligands also acquiring part of the positive charge. The strategy applied here to bypass this limitation consists of using the frozen orbitals of the corresponding $[\text{Os}(\text{PH}_3)_2\text{H}_3]^+\text{L}_2$ complex. This procedure does not provide the real energy of the system, but it should be helpful in clarifying the role of the four subtracted d electrons in the binding of the complex.

Putting aside the expected spectacular increase in the absolute interaction energies, the significant result in Table VII is that in all cases, regardless of the formal charge of the ligand, the axial position is preferred. This results confirms the decisive role played by the nonbonding d metal electrons on transition metal PBP complexes. The differential screening of these electrons in the equatorial and axial regions, through the magnification of the

electrostatic term associated with charged ligands, is indeed ultimately responsible for the correlation between formal charge and site preference in these systems.

Though the validity of the present EDA analysis can be called into question on grounds of the arguable accuracy of the heterolytic complex–ligand bond-breaking scheme that is applied, we feel that this is not a serious limitation. If one were to apply a homolytic scheme, the partition of the interaction energy would admittedly put more stress on the donative and less on the electrostatic term, but the global trends would remain unchanged, and the origin of the difference in this homolytic FCTPLX term probably could also be traced back to the orbitals presented in Scheme I.

VII. Conclusions

The detailed study of the particular system $[\text{Os}(\text{PR}_3)_3\text{H}_4]$ leads to an improved understanding of seven-coordination, which might have implications concerning far more general fields.

Introduction of dynamic electron correlation is shown to be necessary for the study of the equilibrium of complexes containing molecular hydrogen and hydride ligands. Performance of geometry optimization at the correlated level is the most desirable, since the limitations of the RHF description do not even warrant the qualitative determination of the local minima in the potential energy hypersurface. The MP2 approach seems to be sufficient for a qualitative description, since improvement up to MP4 level does not alter substantially the results. Despite the importance of correlation energy, RHF methodology alone still provides acceptable results in the comparison of isomers with the same coordination number.

A relationship is found between the formal charge of a pure σ -donor ligand and its site preference in d^4 pentagonal bipyramidal complexes. Its origin is the nonspherical distribution of the nonbonding metal d electrons, which enhances the electrostatic bond in the equatorial plane relative to that in the axial direction. Though possibly outweighed in some cases by other contributions absent in this particular system, like π -bonding or steric interactions, this space distribution of nonbonding metal electrons is likely to be a general factor affecting the site preference in transition metal seven-coordinate complexes.

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