Organometallics **2001,** *20,* 5297−5309

Synthesis and Characterization of Mixed-Phosphine Osmium Polyhydrides: Hydrogen Delocalization in $[OsH_5P_3]^+$ Systems

Miguel A. Esteruelas,*[‡] Agustí Lledós,*[†] Marta Martín,[‡] Feliu Maseras,[†]
Raquel Osés,[‡] Natividad Ruiz,[‡] and Jaume Tomàs[†]

Departament de Química, Edifici Cn, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain, and Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza, CSIC, E-50009 Zaragoza, Spain

Received March 2, 2001

The hexahydrido complex $OsH_6(P^iPr_3)_2$ (**1**) reacts with $PHPh_2$ to give molecular hydrogen and the tetrahydride $OsH_4(PHPh_2)(P^iPr_3)_2$ (**2**). However, the formation of $OsH_2(PHPh_2)_2(P^iPr_3)_2$ (**3**) as a consequence of the substitution of a second hydrogen molecule from **2** by $PHPh_2$ does not occur. The treatment of **2** with 1.0 equiv of $PHPh_2$ in toluene at 80 °C leads after 3 days to $OsH_2(PHPh_2)_3(P^iPr_3)$ (**4**). The preparation of **3** requires the previous acidolysis of **2** with HBF_4, which gives $[OsH_5(PHPh_2)(P^iPr_3)_2]BF_4$ (**5**). In contrast to **2**, the addition of $PHPh_2$ to **5** affords $[OsH_3(PHPh_2)_2(P^iPr_3)_2]BF_4$ (**6**) and molecular hydrogen. Deprotonation of **6** with Et_3N yields **3**. The skeleton of the cation of **5** has been determined by X-ray diffraction. The configuration is consistent with a Y-shaped OsP_3 disposition with the osmium atom in the common vertex. Complex **5** also reacts with methanol and water to give $[OsH_5\{P(OMe)Ph_2\}(P^iPr_3)_2]BF_4$ (**7**) and $[OsH_5\{P(OH)Ph_2\}(P^iPr_3)_2]BF_4$ (**8**), respectively. The addition of Et_3N to **7** affords $OsH_4\{P(OMe)Ph_2\}(P^iPr_3)_2$ (**9**). A theoretical study on the $OsH_5(PH_3)_3^+$ model complex reveals that although a static description is fully consistent with a classical pentahydride assignment, the formation of a dihydrogen is a very low energy costing process, on both thermodynamic and kinetic grounds. Thus, these polyhydride systems might be better described as possessing delocalized hydrogen atoms. A further QM/MM IMOMM study on the actual $OsH_5(PR_3)^+$ systems indicates that the inclusion of bulky phosphine substituents plays a role against the stability of dihydrogen forms, because of the higher steric congestion of lower coordination number complexes arising from repulsions between bulky phosphines. Although IMOMM calculations improve significantly the agreement with experimental structures, they do not change the validity of the aforementioned statement concerning delocalization.

Introduction

After the discovery that, in addition to the classical hydride form, hydrogen atoms can be present in the coordination sphere of a transition metal as a dihydrogen ligand, much effort has been devoted to the structural characterization of transition metal hydrides.[1] Although experimental location of H atoms presents significant difficulties, neutron diffraction determinations[2] and NMR (T_1(min) and J_{HD}) measurements have led to accurate structural assignments for a large series of compounds. Moreover, since computational chemistry is nowadays a low-cost high-quality technique for precisely locating H nuclei and predicting classical versus nonclassical structures, theoretical calculations are being widely used to this purpose.[3] However there is an increasing number of species that are difficult to classify from a structural point of view because their H−H distances fall between the dihydrogen (0.8−1.0 Å) and dihydride (>1.6 Å) limits. This third class of complexes has been called elongated or stretched dihydrogen complexes. J_{HD} values are useful indicators of the presence of an elongated dihydrogen ligand,[4,5] and some of them have been characterized by neutron diffraction techniques, but their chemical properties are not fully understood with purely structural arguments.[6]

LMH_n polyhydrides with $n > 4$ have attracted the interest of theoreticians.[3,7,8] The $[OsH_5(PMe_2Ph)_3]^+$

[†] Universitat Autònoma de Barcelona.

[‡] Universidad de Zaragoza.

(1) (a) Kubas, G. *J. Acc. Chem. Res.* **1988**, *21*, 120. (b) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95. (c) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155. (d) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913.

(2) Bau, R.; Drabnis, M. H. *Inorg. Chim. Acta* **1997**, *259*, 27.

(3) Maseras, F.; Lledós, A.; Clot, E.; Eisenstein, O. *Chem. Rev.* **2000**, *100*, 601.

(4) (a) Klooster, W. T.; Koetzle, T. F.; Jia, G.; Fong, T. P.; Morris, R. H.; Albinati, A. *J. Am. Chem. Soc.* **1994**, *116*, 7677. (b) Maltby, P. A.; Schlaf, M.; Steinbeck, M.; Lough, A. J.; Morris, R. H.; Klooster, W. T.; Koetzle, T. F.; Srivastava, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 5396. (c) Heinekey, D. M.; Luther, T. A. *Inorg. Chem.* **1996**, *35*, 4396. (d) Luther, T. A.; Heinekey, D. M. *J. Am. Chem. Soc.* **1997**, *119*, 6688.

(5) (a) Bacskay, G. B.; Bytheway, I.; Hush, N. S. *J. Am. Chem. Soc.* **1996**, *118*, 3753. (b) Hush, N. S. *J. Am. Chem. Soc.* **1997**, *119*, 1717.

(6) (a) Gelabert, R.; Moreno, M.; Lluch, J. M.; Lledós, A. *J. Am. Chem. Soc.* **1997**, *119*, 9840. (b) Gelabert, R.; Moreno, M.; Lluch, J. M.; Lledós, A. *J. Am. Chem. Soc.* **1998**, *120*, 8168. (c) Barea, G.; Esteruelas, M. A.; Lledós, A.; López, A. M.; Tolosa, J. I. *Inorg. Chem.* **1998**, *37*, 5033. (d) Barea, G.; Esteruelas, M. A.; Lledós, A.; López, A. M.; Oñate, E.; Tolosa, J. I. *Organometallics* **1998**, *17*, 4065.

10.1021/om010173c CCC: $20.00
Publication on Web 11/10/2001

complex, extensively studied by Caulton et al.,[9] shows interesting features concerning hydride arrangement. An early paper suggested that it is a dihydrogen trihydride complex.[9a] This characterization was based on a short T_1(min) measured by solution NMR techniques. Although this has often been considered a valid criterion for the detection of a dihydrogen moiety, the structure was later reevaluated through neutron diffraction techniques, and finally it was best described as a dodecahedral pentahydride. This assignment, however, posed the problem of the anomalously short T_1(min), which might indicate that some residual H···H interaction is present between a pair of hydrides. Indeed, the neutron diffraction structure located two hydrides at 1.49 Å from each other,[9b] a large distance for a typical dihydrogen unit, but shorter than the sum of their van der Waals radii. This indicates that the complex $[OsH_5(PMe_2Ph)_3]^+$ may belong to the rather diffuse range of elongated dihydrogen complexes. It shows also remarkable reactivity patterns, hydrogenating ethylene under mild conditions (25 °C, 1 atm) to generate $[OsH(C_2H_4)_2(PMe_2Ph)_3]^+$ and alkane.[9b] The saturated character of the pentahydride requires the dissociation of at least a hydrogen molecule before the coordination of the hydrogenated olefin. This step of the hydrogenation process can be formally viewed as the substitution of a π-acceptor H_2 ligand by ethylene. Thus, although the neutron diffraction study indicates the absence of H_2 ligands in the solid at 11 K, the whole of the experimental data is compatible with the formation in solution of dihydrogen species in the $[OsH_5(PMe_2Ph)_3]^+$ systems at a very low energy cost.

Early calculations for the $[OsH_5(PH_3)_3]^+$ model system from Lin and Hall predicted the pentahydride complex to be the most stable species.[10a] Later Maseras et al. analyzed exhaustively the structural features of this model complex.[10b] In their systematic approach, 22 different initial structures were carefully examined through ab initio calculations. This analysis led to the description of five low-lying isomers, the lowest of them being a dodecahedral pentahydride complex, in very good agreement with the actual neutron diffraction of $[OsH_5(PMe_2Ph)_3]^+$, published one year later.[9b]

Despite the success of theoretical calculations in the determination of the most stable structures in several polyhydride complexes, an accurate description of these systems is still lacking. On one hand, most of the calculations have been carried out in model systems, replacing the actual PR_3 ligands by PH_3, and this simplification may lead to a significant error in some cases. For instance, experimental results on $ReH_7(PR_3)_2$ derivatives have shown an extreme dependence of one H–H distance on the nature of the PR_3 ligands.[11] On the other hand, high-level theoretical methods that give a balanced description in all the regions of the potential energy surface (polyhydride, dihydrogen, bisdihydrogen) are required to study the energetics of the H motion in polyhydrides. The experimental values of the dihydrogen/dihydride equilibrium in the Kubas complex have been reproduced only theoretically by using CCSD(T) calculations.[12]

As a part of our study on the chemical properties of the hexahydride $OsH_6(P^iPr_3)_2$,[6d,13] we have observed that, in addition to $[OsH_5(PMe_2Ph)_3]^+$, mixed-phosphine $[OsH_5(PR_3)_2(PR_3')]^+$ complexes can be prepared. In this paper we report (i) the synthesis of $[OsH_5(PHPh_2)(P^iPr_3)_2]BF_4$ and $[OsH_5\{P(OMe)Ph_2\}(P^iPr_3)_2]BF_4$ and related tetra-, tri-, and dihydride compounds; (ii) the X-ray-determined structure of $[OsH_5(PHPh_2)(P^iPr_3)_2]BF_4$; and (iii) theoretical studies on $[OsH_5(PH_3)_3]^+$, $[OsH_5(PHPh_2)(P^iPr_3)_2]^+$, $[OsH_5\{P(OMe)Ph_2\}(P^iPr_3)_2]^+$, and $[OsH_5(PMe_2Ph)_3]^+$ by means of high-level quantum mechanical (QM) and hybrid quantum mechanics/molecular mechanics (QM/MM) IOMOMM calculations.

Results and Discussion

1. Reactions of $OsH_6(P^iPr_3)_2$ with $PHPh_2$. $OsH_6(P^iPr_2Ph)_2$ has been characterized by neutron diffraction as a classical hexahydride with a typical dodecahedral coordination geometry.[14] Although these $OsH_6(PR_3)_2$ complexes do not contain any dihydrogen ligand, B3LYP calculations gave a low value for the dissociation energy of molecular hydrogen (15.4 kcal/mol),[13i] while our high-level CCSD(T)//B3LYP calculations gave an even smaller value (10.0 kcal/mol). This suggests that the elimination of molecular hydrogen from the hexahydride is easy. In agreement with this, the treatment of $OsH_6(P^iPr_3)_2$ (**1**) with 1.0 equiv of diphenylphosphine in toluene at 80 °C leads after 1 h to the tetrahydride $OsH_4(PHPh_2)(P^iPr_3)_2$ (**2**), which was isolated as a white solid in 71% yield, according to eq 1.

---

(7) (a) Hlatky, G. G.; Crabtree, R. H. *Coord. Chem. Rev.* **1985**, *65*, 1. (b) Lin, Z.; Hall, M. B. *Coord. Chem. Rev.* **1994**, *135/136*, 845.

(8) (a) Maseras, F.; Li, X.-K.; Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1993**, *115*, 10974. (b) Barea, G.; Maseras, F.; Jean, Y.; Lledós, A. *Inorg. Chem.* **1996**, *35*, 6401. (c) Bayse, C. A.; Couty, M.; Hall, M. B. *J. Am. Chem. Soc.* **1996**, *118*, 8916. (d) Bosque, R.; Maseras, F.; Eisenstein, O.; Patel, B. P.; Yao, W.; Crabtree, R. H. *Inorg. Chem.* **1997**, *36*, 5505. (e) Bayse, C. A.; Hall, M. B.; Pleune, B.; Poli, R. *Organometallics* **1998**, *17*, 4309.

(9) (a) Johnson, T. J.; Huffman, J. C.; Caulton, K. G.; Jackson, S. A.; Eisenstein, O. *Organometallics* **1989**, *8*, 2073. (b) Johnson, T. J.; Albinati, A.; Koetzle, T. F.; Ricci, J.; Eisenstein, O.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 4966.

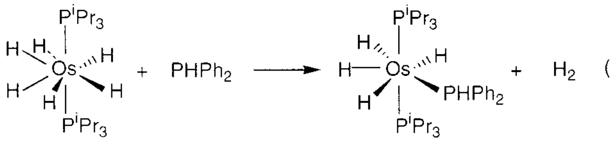
(10) (a) Lin, Z.; Hall, M. B. *J. Am. Chem. Soc.* **1992**, *114*, 6102. (b) Maseras, F.; Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1993**, *115*, 8313.

(11) (a) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126. (b) Costello, M. T.; Walton, R. A. *Inorg. Chem.* **1988**, *27*, 2563. (c) Howard, J. A. K.; Mason, S. A.; Johnson, O.; Diamond, I. C.; Crennell, S.; Keller, P. A.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1988**, 1502. (d) Luo, X.-L.; Crabtree, R. H. *Inorg. Chem.* **1989**, *28*, 3775. (e) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 4813. (f) Luo, X.-L.; Baudry, D.; Boydell, P.; Charpin, P.; Nierlich, M.; Ephritikhine, M.; Crabtree, R. H. *Inorg. Chem.* **1990**, *29*, 1511. (g) Brammer, L.; Howard, J. A. K.; Johnson, O.; Koetzle, T. F.; Spencer, J. L.; Stringer, A. M. *J. Chem. Soc., Chem. Commun.* **1991**, 241. (h) Haynes, G. R.; Martin, R. L.; Hay, P. J. *J. Am. Chem. Soc.* **1992**, *114*, 28. (i) Michos, D.; Luo, X.-L.; Howard, J. A. K.; Crabtree, R. H. *Inorg. Chem.* **1992**, *31*, 3914.

(12) Tomàs, J.; Lledós, A.; Jean, Y. *Organometallics* **1998**, *17*, 190.

(13) (a) Aracama, M.; Esteruelas, M. A.; Lahoz, F. J.; López, J. A.; Meyer, U.; Oro, L. A.; Werner, H. *Inorg. Chem.* **1991**, *30*, 288. (b) Esteruelas, M. A.; Lahoz, F. J.; López, J. A.; Oro, L. A., Schlünken, C.; Valero, C., Werner, H. *Organometallics* **1992**, *11*, 2034. (c) Esteruelas, M. A.; Jean, Y.; Lledós, A.; Oro, L. A.; Ruiz, N.; Volatrón, F. *Inorg. Chem.* **1994**, *33*, 3609. (d) Atencio, A.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A., Ruiz, N. *Inorg. Chem.* **1995**, *34*, 1004. (e) Demachy, I.; Esteruelas, M. A.; Jean, Y.; Lledós, A.; Maseras, F.; Oro, L. A.; Valero, C.; Volatron, F. *J. Am. Chem. Soc.* **1996**, *118*, 8388. (f) Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A.; Ruiz, N.; Sola, E.; Tolosa, J. I. *Inorg. Chem.* **1996**, *35*, 7811. (g) Castillo, A.; Esteruelas, M. A.; Oñate, E.; Ruiz, N. *J. Am. Chem. Soc.* **1997**, *119*, 9691. (h) Castillo, A.; Barea, G.; Esteruelas, M. A.; Lahoz, F. J.; Lledós, A.; Maseras, F.; Modrego, J.; Oñate, E.; Oro, L. A.; Ruiz, N.; Sola, E. *Inorg. Chem.* **1999**, *38*, 1814. (i) Barrio, P.; Castarlenas, R.; Esteruelas, M. A.; Lledós, A.; Maseras, F.; Oñate, E.; Tomás, J. *Organometallics* **2001**, *20*, 442.

(14) Howard, J. A. K.; Johnson, O.; Koetzle, T. F.; Spencer, J. L. *Inorg. Chem.* **1987**, *26*, 2930.



(1)

1 **2**

The presence of a diphenylphosphine ligand in **2** is strongly supported by the IR and $^{31}P\{^1H\}$ and ^1H NMR spectra of the complex. The IR spectrum in KBr shows the ν(P−H) absorption at 2292 cm^{-1}, along with three bands at 2052, 2013, and 1886 cm^{-1}, corresponding to the Os−H vibrations. At room temperature, the $^{31}P\{^1H\}$ NMR spectrum contains at 39.2 ppm a doublet due to the triisopropylphosphine ligands and at −4.6 ppm a triplet corresponding to the triphenylphosphine group. The value of the P−P coupling constant is 17.1 Hz. This spectrum is temperature-invariant between 25 and −80 °C. This, along with the equivalence of the triisopropylphosphine ligands and the value of the P−P coupling constant, suggests a T-shaped OsP_2P' skeleton, which is rigid in solution. This disposition agrees well with that found for the OsP_3 skeleton of the complex $OsH_4(PMe_2Ph)_3$ by neutron and X-ray diffraction studies.[15] The structure of the latter complex is a distorted pentagonal bipyramid, like that shown in eq 1 for **2**, with the four hydride ligands, osmium, and one phosphorus atom being essentially coplanar. A theoretical study of $OsH_4(PH_3)_3$ gave this pentagonal bipyramid as the most stable isomer.[8a] In contrast to **2**, the OsP_3 skeletons of $OsH_4(PMe_2Ph)_3$ and related $OsH_4(PR_3)_3$ complexes appear to be nonrigid in solution.[16] The ^1H NMR spectrum of **2** is temperature-dependent. At 80 °C, it shows in the hydrido region (−10.19 ppm) a single resonance. This observation is consistent with the operation of some thermally activated exchange process, which proceeds at a rate sufficient to lead to the single hydride resonance. Consistent with this, lowering the sample temperature leads to broadening of the resonance, although decoalescence is not observed at −80 °C. At 80 °C, the hydrido resonance is observed as a triplet of doublets of doublets, by spin coupling with the phosphorus atoms of the triisopropylphosphine (J(HP) = 10.5 Hz) and diphenylphosphine (J(HP) = 3.0 Hz) ligands, and the PH hydrogen atom of the diphenylphosphine group (J(HH) = 3.0 Hz). The latter coupling was confirmed by ^1H-COSY and selective heteronuclear $^1H\{^{31}P\}$ NMR spectra. In the low-field region the most noticeable resonance is that due to the PH hydrogen, which appears at 7.45 ppm as a doublet of triplets of doublets with H−P coupling constants of 346.0 and 8.4 Hz. The value of the H−H coupling constant (3.0 Hz) is similar to the values found for the H−H(E) coupling constants (E = P, N) in the ^1H NMR spectra of the complexes $MH_2(PHPh_2)(P^iPr_3)_2$ (M = Ru (4.1 Hz), Os (4.5 Hz))[17] and $[OsH(\eta^5\text{-}C_5H_5)\{NH{=}C(Ph)C_6H_4\}(P^iPr_3)]BF_4$ (4.1 Hz),[18] where, via four-membered rings of the type EH···HM, a weak hydrogen−hydrogen interaction has been proposed to exist.

The T_1 values of the hydrogen nuclei of the OsH_4 of **2** were determined over the temperature range 293−213 K. The T_1(min) value (137 ms) was obtained at 233 K and supports the tetrahydride character of this complex. In contrast to **2**, the carbonyl derivative $OsH_4(CO)(P^iPr_3)_2$[19] has a T_1(min) of 32 ms, which suggests nonclassical interaction between two of the four hydrogens bonded to the osmium atom.[20] DFT calculations on the model compound $OsH_4(CO)(PH_3)_2$ indicate the presence of a dihydrogen ligand *trans* to a hydride, with an H−H separation of 0.87 Å. An $Os{-}H_2$ dissociation energy of 18.9 kcal/mol, similar to that found for **1**, was calculated for $OsH_2(\eta^2\text{-}H_2)(CO)(PH_3)_2$.[20] In agreement with this, the carbonyl derivative and **1** show the same reactivity toward phosphines. The reactions of both compounds afford molecular hydrogen and OsH_{n-2} species.

In contrast to **1** and the carbonyl derivative, the replacement of a hydrogen molecule from **2** by phosphine is a complex process (Scheme 1). The treatment of **2** with 1.0 equiv of diphenylphosphine in toluene at 80 °C does not produce a significant amount of reaction after 1 h. The disappearance of about 50% of **2** is observed after 3 days. However, the expected $OsH_2(PHPh_2)_2(P^iPr_3)_2$ (**3**) complex is not formed, instead $OsH_2(PHPh_2)_3(P^iPr_3)$ (**4**) is obtained in about 50% yield, as a white solid. The formation of **4** suggests that the dissociation energy of a hydrogen molecule from **2** is similar to the energy necessary to break a $Os{-}P^iPr_3$ bond. CCSD(T)//B3LYP calculations on the $OsH_4(PH_3)_3$, $OsH_2(PH_3)_3$, and $OsH_4(PH_3)_2$ model complexes have allowed a good estimation of these dissociation energies. The strong hydridic character of the H ligands in **2**, which agrees with the high energy required for the H_2 elimination, has already been pointed out in a theoretical study.[21] Our results fully agree with this previous result, giving a $D_e(M{-}H_2)$ of 40.9 kcal/mol. The dissociation energy for the PH_3 phosphine is somewhat higher (50.1 kcal/mol). However, with $PHPh_2$ instead of PH_3, one can expect that the formation of $Os(PHPh_2)_3(P^iPr_3)$ might be further prevented by steric congestion around the Os atom. This fact, along with the high dissociation energy for the H_2 moiety, might well explain the reactivity found for complex **2**.

The IR spectrum of **4** in KBr contains three ν(P−H) absorptions at 2374, 2361, and 2348 cm^{-1}, along with two bands at 2000 and 1927 cm^{-1} corresponding to the Os−H vibrations, which indicate a mutually *cis* disposition for the hydrido ligands. The $^{31}P\{^1H\}$ and ^1H NMR spectra are temperature-invariant, suggesting that the complex has a rigid structure in solution. The $^{31}P\{^1H\}$ NMR spectrum shows an XYZ_2 (X = P^iPr_3, Y = $PHPh_2$ *trans* to P^iPr_3, Z = $PHPh_2$ *trans* to hydrides) simplified spin system, which is defined by $\delta_x = 33.1$, $\delta_y = 13.9$, $\delta_z = \delta_{z'} = -8.0$, $J(P_xP_y) = 209.3$ Hz, $J(P_xP_z) = J(P_xP_{z'}) = 18.4$ Hz, and $J(P_yP_z) = J(P_yP_{z'}) = 11.5$ Hz. In the ^1H

---

[15] Hart, D. W.; Bau, R.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 7557.

[16] (a) Douglas, P. G.; Shaw, B. L. *Chem. Commun.* **1969**, 624. (b) Douglas, P. G.; Shaw, B. L. *J. Am. Chem. Soc. A* **1970**, 334. (c) Bell, B.; Chatt, J.; Leigh, J. *J. Chem. Soc., Dalton Trans.* **1973**, 997.

[17] Buil, M. L.; Esteruelas, M. A.; Oñate, E.; Ruiz, N. *Organometallics* **1998**, *17*, 3346.

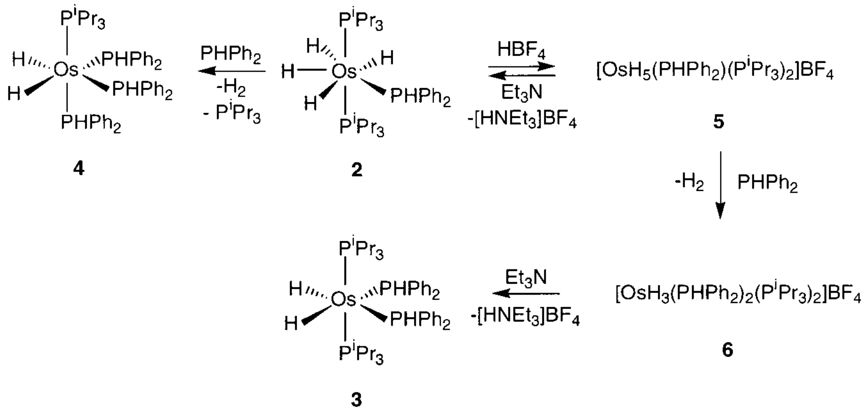
[18] Esteruelas, M. A.; Gutiérrez-Puebla, E.; López, A: M.; Oñate, E.; Tolosa, J. I. *Organometallics* **2000**, *19*, 275.

[19] Werner, H.; Esteruelas, M. A.; Meyer, U.; Wrackmeyer, B. *Chem. Ber.* **1987**, *120*, 11.

[20] Gusev, D. G.; Kuhlman, R. L.; Renkema, K. B.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1996**, *35*, 6775.

[21] Maseras, F.; Lledós, A.; Costas, M.; Poblet, J. M. *Organometallics* **1996**, *15*, 2947.

Scheme 1



NMR spectrum, the most noticeable resonances are those due to hydride ligands and the PH hydrogen atoms of the diphenylphosphine groups, which appear at −10.00, and between 5.91 and 7.00 ppm as the parts CC′ and AA′B, respectively, of an AA′BCC′XYZZ′ (A, A′, and B = P*H*Ph$_2$, C and C′ = H−Os, X = *P*^{i}Pr$_3$, Y = *P*HPh$_2$ *trans* to P^{i}Pr$_3$, Z and Z′ = *P*HPh$_2$ *trans* to hydrides) spin system. The spin coupling between the hydride ligands (CC′) and the PH hydrogen atoms of the diphenylphosphine groups (B and AA′) was confirmed by a ^{1}H-COSY NMR spectrum.

The preparation of **3** requires the protonation of **2**, in agreement with the tendency of the acydolysis to facilitate the elimination of molecular hydrogen from polyhydrides.[22] Treatment of diethyl ether solutions of **2** with 1.0 equiv of HBF$_4$·OEt$_2$ (Scheme 1) leads to the pentahydride derivative [OsH$_5$(PHPh$_2$)(P^{i}Pr$_3$)$_2$]BF$_4$ (**5**), which was isolated as a white solid in 97% yield. The reaction is reversible. Thus, the addition of 1.0 equiv of Et$_3$N to dichloromethane solutions of **5** regenerates **2**. In contrast to the tetrahydride **2**, the addition at room temperature of 1.0 equiv of diphenylphosphine to dichloromethane solutions of **5** produces the elimination of a hydrogen molecule and the formation of the trihydride [OsH$_3$(PHPh$_2$)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ (**6**), which was isolated as a white solid in 86% yield. The deprotonation of **6** with Et$_3$N yields **3**.

Figure 1 shows a view of the skeleton of the cation of **5**. Selected bond distances and angles are listed in Table 1.

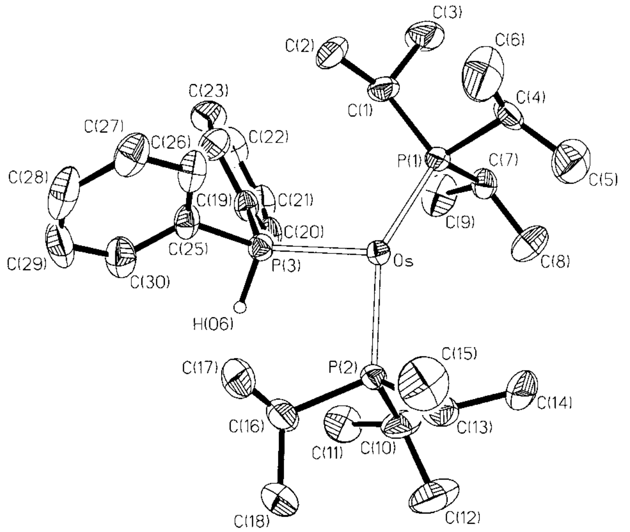


Figure 1. Molecular diagram of the cation of complex [OsH$_5$(PHPh$_2$)(P^{i}Pr$_3$)$_2$]BF$_4$ (**5**).

Table 1. Selected Bond Distances (Å) and Angles (deg) for [OsH$_5$(PHPh$_2$)(P^{i}Pr$_3$)$_2$]BF$_4$ (5)

Os−P(1)	2.3870(16)	P(3)−H(06)	1.27(5)
Os−P(2)	2.3867(16)	P(3)−C(19)	1.818(6)
Os−P(3)	2.3891(16)	P(3)−C(25)	1.820(7)
P(1)−Os−P(2)	149.43(6)	Os−P(3)−C(19)	120.3(2)
P(1)−Os−P(3)	105.72(6)	Os−P(3)−C(25)	117.8(2)
P(2)−Os−P(3)	94.80(6)	Os−P(3)−H(06)	110(2)
		C(19)−P(3)−C(25)	106.6(3)
		C(19)−P(3)−H(06)	101(2)
		C(25)−P(3)−H(06)	98(2)

The configuration is consistent with a Y-shaped OsP$_2$P′ skeleton, with the osmium atom situated in the common vertex. The three Os−P distances are statistically identical, about 2.39 Å, while the three P−Os−P angles are different. The P(1)−Os−P(2) angle that involving both triisopropylphosphine ligands (149.43(6)°) is bigger than the other two, P(1)−Os−P(3) (105.72(6)°) and P(2)−Os−P(3) (94.80(6)°). Despite the asymmetry, at room temperature, the ^{31}P{^{1}H} NMR spectrum of **5** shows only one resonance for the triisopropylphosphine ligands, which appears at 42.2 ppm as a doublet with a P−P coupling constant of 10.1 Hz. The resonance corresponding to the diphenylphosphine ligand is observed at −24.4 ppm, as a triplet. Lowering the sample temperature produces a very light broadening of the resonances. Decoalescence is not observed upon −80 °C. This suggests that in solution the P(1)−Os−P(3) and P(2)−Os−P(3) angles average rapidly and that the Y-shaped OsP$_2$P′ skeleton does not undergo an important distortion.

Unfortunately, from the X-ray diffraction study, it was not possible to locate the hydride ligands. However their presence is strongly supported by the IR and ^{1}H NMR spectrum. The IR spectrum in KBr shows the ν(P−H) absorption at 2362 cm^{-1}, along with three bands at 2096, 2086, and 1984 cm^{-1} corresponding to the Os−H vibrations, and the absorption due to the [BF$_4$]$^-$ anion with T_d symmetry centered at 1058 cm^{-1}. In the ^{1}H NMR spectrum in dichloromethane at room temperature, the most noticeable resonances are a triplet at −8.26 ppm with a H−P coupling constant of 8.2 Hz, corresponding to the hydride ligands, and at 6.97 ppm

---

[22] Bruno, J. W.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 1663, and references therein.

a double triplet with H−P coupling constants of 373.7 and 3.9 Hz, due to the PH hydrogen of the diphenylphosphine group. In this spectrum, spin coupling between the hydride and the PH hydrogen atom is not observed. However the ^{1}H-COSY NMR spectrum shows signals of crossing between the hydride and PH resonances. The two spectra together suggest that the H−H coupling constant between the hydrides and PH hydrogen atom is smaller than 1 Hz. The decrease of the value of this coupling constant in **5** with regard to **2** appears to indicate a decrease of the fortress of the PH−hydride interaction in **5** with regard to **2**, mainly as a result of the increase in the electrophilicity of the hydride ligands. Although the net positive charge on **5** should increase the acidity of the PH group, it should be noted that the deprotonation of **5** occurs at the osmium atom instead of at the diphenylphosphine group. A relationship similar to the above-mentioned for **2** and **5** has been previously found between the complexes $RuH_2(CO)(PHPh_2)(P^iPr_3)_2$ and $[RuH(CO)_2(PHPh_2)(P^iPr_3)_2]^+$.[17]

The T_1 values of the hydrogen nuclei of the OsH_5 unit of **5** were determined over the temperature range 293−213 K. The T_1(min) value (112 ms) was obtained at 233 K and is 44 ms higher than that reported for $[OsH_5(PMe_2Ph)_3]^+$ (68 ms).[9a] At first glance, this suggests that the contribution of nonclassical species to the structure of **5** is smaller than that to the Caulton's pentahydride.

The protonation of **2** with $DBF_4{\cdot}D_2O$ affords $[OsH_4D(PHPh_2)(P^iPr_3)_2]BF_4$, which shows a H−D coupling constant of 1.7 Hz. Exchange between the deuterium and PH positions is not observed.

The IR spectrum of **6** in KBr shows two ν(P−H) absorptions at 2358 and 2326 cm^{-1} along with three bands at 2068, 2058, and 1978 cm^{-1}, corresponding to the Os−H vibrations, and the absorption due to the $[BF_4]^-$ anion with T_d symmetry centered at 1057 cm^{-1}. The $^{31}P\{^1H\}$ and ^{1}H NMR spectra in dichloromethane-d_2 are temperature-dependent. At room temperature the $^{31}P\{^1H\}$ NMR spectrum shows a broad signal at 28.2 ppm corresponding to the diphenylphosphine ligands and at −23.6 ppm a triplet with a P−P coupling constant of 7.3 Hz, due to the triisopropylphosphine groups.

Lowering the sample temperature leads to the broadening of both resonances. At about −40 °C, decoalescence of the diphenylphosphine resonance is observed, to give a triplet at 26 ppm and a multiplet at −26 ppm. Upon −80 °C, decoalescence of the triisopropylphosphine resonance is not observed. In the ^{1}H NMR spectrum at room temperature, the most noticeable resonances are those due to the hydrides and PH hydrogen atoms. The hydride resonance appears at −10.68 ppm as a triplet with a H−P coupling constant of 16.5 Hz, whereas the PH resonance is observed at 6.98 ppm as a broad doublet with a H−P coupling constant of about 350 Hz. The ^{1}H-COSY NMR spectrum shows weak signals of crossing between the hydride and PH resonances, suggesting that in this case, as for **5**, there is a small spin coupling between the hydride and PH nuclei. Lowering the sample temperature leads to the broadening of the hydride and PH resonances, although decoalescence is not observed at −80 °C.

The T_1 values of the hydrogen nuclei of the OsH_3 unit of **6** were determined over the temperature range 293−213 K. A T_1(min) value of 157 ms was found at 233 K. This value suggests a low contribution of nonclassical species to the structure of **6**. In agreement with this, a H−D coupling constant smaller than 1 Hz has been found in the partially deuterated complex $[OsH_2D(PHPh_2)_2(P^iPr_3)_2]BF_4$, which was prepared by addition of 1.0 equiv of $DBF_4{\cdot}D_2O$ to dichloromethane-d_2 solutions of **3**. These values agree well with those previously reported for the complexes $OsH_3(Hbiim)(P^iPr_3)_2$, $(P^iPr_3)_2H_3Os(\mu\text{-biim})M(COD)$ (M = Rh, Ir; H_2biim = 2,2′-biimidazole),[13f] $[OsH_3(\eta^4\text{-diolefin})(P^iPr_3)_2]^+$ (diolefin = tetrafluorobenzobarrelene, 2,5-norbornadiene),[13g] $OsH_3\{\kappa\text{-N},\kappa\text{-S-(2-Spy)}\}(P^iPr_3)_2$, $OsH_3\{\kappa\text{-N},\kappa\text{-O-OC(O)CH-}[CH(CH_3)_2]NH_2\}(P^iPr_3)_2$, $OsH_3\{\kappa\text{-N},\kappa\text{-O-(2-Opy)}\}(P^iPr_3)_2$, and $[(P^iPr_3)_2H_3Os(\mu\text{-biim})M(TFB)]_2$ (M = Rh, Ir).[13h] However, they differ from those found for derivatives of the types $[OsH_3(R_2PCH_2CH_2PR_2)_2]^+$ [23] and $[OsH_3\{P(OR)_3\}_4]^+$,[24] which have been described as hydride-elongated dihydrogen species.

On the basis of the closely related $OsH_3(PPh_3)_4{}^+$, $OsH_3(PMe_3)_4{}^+$, and $OsH_3(PEt_3)_4{}^+$ complexes[25] along with the spectroscopical data, a distorted tetrahedral P_4 coordination environment with three of the four trigonal P_3 faces occupied by the hydride ligand is suggested for this complex **6**. Furthermore, as has been previously reported in similar cases, the exchange process that averages the ^{31}P chemical shifts would be the hydride migration process between the two $P^iPr_3-P^iPr_3-PHPh_2$ faces.[26]

The IR spectrum of **3** in KBr shows a ν(P−H) absorption at 2265 cm^{-1} and, in agreement with the mutually *cis* disposition of the hydride ligands, a Os−H band at 1993 cm^{-1}. The $^{31}P\{^1H\}$ and ^{1}H NMR spectra are temperature-invariant and consistent with the structure shown for this compound in Scheme 1. Thus, the $^{31}P\{^1H\}$ shows the X_2YY' part of a simplified $AA'CC'X_2YY'$ spin system ($X = P^iPr_3$, $Y = Y' = PHPh_2$) defined by the parameters $\delta_X = 25.5$ ppm, $\delta_Y = \delta_{Y'} = -17.8$ ppm, $J(P_XP_Y) = J(P_XP_{Y'}) = 14.0$ Hz, $J(P_YP_{Y'}) = 1.7$ Hz). In the ^{1}H NMR spectrum the PH and hydride resonances appear at 7.88 and −11.24 ppm as the parts AA′ and CC′, respectively, of the $AA'CC'X_2YY'$ spin system. According to selective heteronuclear and homonuclear spin decoupling spectra, the coupling constants of the spin system are $J(H_AH_{A'}) = 0$, $J(H_AH_C) \approx J(H_{A'}H_{C'}) < 2$ Hz, $J(H_{A'}P_{Y'}) = J(H_AP_Y) = 309.2$ Hz, $J(H_{A'}P_Y) = J(H_AP_{Y'}) = 0$, $J(H_AP_X) = J(H_{A'}P_X) = 6.4$ Hz, $J(H_CH_{C'}) = 4.2$ Hz, $J(H_CP_X) = J(H_{C'}P_X) = 26.6$ Hz, $J(H_CP_{Y'}) = J(H_{C'}P_Y) = 55.2$ Hz, and $J(H_CP_Y) = J(H_{C'}P_{Y'}) = -16.4$ Hz. These values were confirmed by simulation of the signal corresponding to the CC′ part of the spin system (Figure 2).

2. Reaction of $[OsH_5(PHPh_2)(P^iPr_3)_2]BF_4$ with Methanol and Water. We have recently shown that the treatment of the cyclopentadienyl complex $Os(\eta^5\text{-}C_5H_5)Cl(PHPh_2)(P^iPr_3)$ with $TlPF_6$ in the presence of methanol or water leads to the complexes $[Os(\eta^5\text{-}C_5H_5)H_2\{P(OR)Ph_2\}(P^iPr_3)]PF_6$ (R = Me, H).[27] The formation

---

(23) Earl, K. A.; Jia, G.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 3027.

(24) Amendola, P.; Antonintti, S.; Albertin, G.; Bordignon, E. *Inorg. Chem.* **1990**, *29*, 318.

(25) (a) Siedle, A. R.; Newmark, R. A.; Pignolet, L. H. *Inorg. Chem.* **1986**, *25*, 3412. (b) Gusev, D. G.; Hübener, R.; Burger, P.; Orama, O.; Berke, H. *J. Am. Chem. Soc.* **1997**, *119*, 3716.

(26) Gusev, D. G.; Berke, H. *Chem. Ber.* **1996**, *129*, 1143.

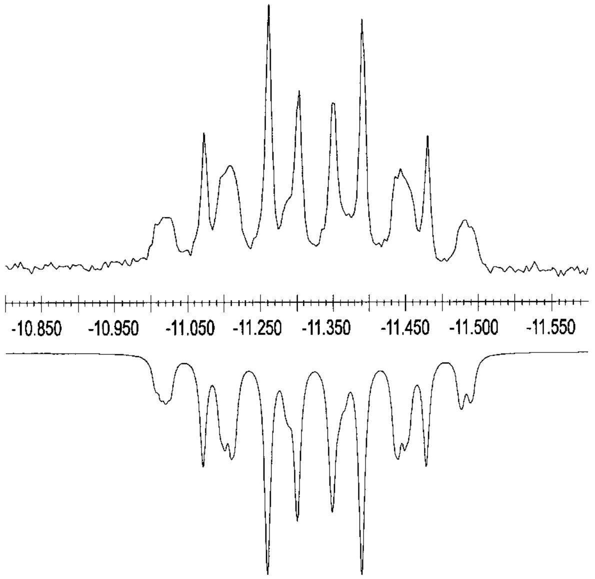


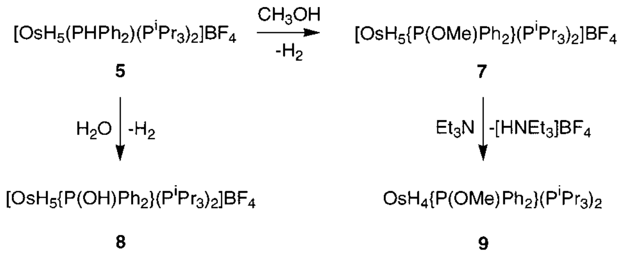
Figure 2. ^{1}H NMR spectra (300 MHz) in C_6D_6 in the high-field region of $OsH_2(PHPh_2)(P^iPr_3)_2$ (**3**) at room temperature: experimental UP and simulated DOWN.

of these species involves the release of the chloro ligand followed by the intramolecular P−H oxidative addition of diphenylphosphine in the unsaturated $[Os(\eta^5\text{-}C_5H_5)(PHPh_2)(P^iPr_3)]^+$ metallic fragment. The oxidative addition of the P−H bond of secondary phosphines to unsaturated transition metal complexes is a well-known process of interest in connection with the catalytic phosphination and hydrophosphination of olefins.[28] Once the hydride-phosphido intermediate $[Os(\eta^5\text{-}C_5H_5)H(PPh_2)(P^iPr_3)]^+$ is formed, the RO−H addition to the Os−phosphino bond affords $[Os(\eta^5\text{-}C_5H_5)H_2\{P(OR)Ph_2\}(P^iPr_3)]^+$. Related additions of methanol and water across W═P bonds have also been reported.[29]

The previously mentioned tendency of **5** to lose a hydrogen molecule prompted us to carry out the reactions of **5** with methanol and water, and as expected, the complexes $[OsH_5\{P(OMe)Ph_2\}(P^iPr_3)_2]BF_4$ (**7**) and $[OsH_5\{P(OH)Ph_2\}(P^iPr_3)_2]BF_4$ (**8**) were formed (Scheme 2). Complex **7** was obtained in 74% yield by stirring **5** in methanol for 6 days at room temperature, whereas complex **8** was obtained in 69% yield by stirring a dichloromethane solution of **5** with water for 5 days, also, at room temperature.

In the IR spectrum of **7** in KBr, the most noticeable feature is the absence of any ν(P−H) absorption and the presence at 1101 cm^{-1} of a P−O vibration. In addition the spectrum contains three bands at 2085, 2012, and

Scheme 2



1917 cm^{-1}, corresponding to the Os−H vibrations, and the absorption due to the $[BF_4]^-$ anion with T_d symmetry centered at 1049 cm^{-1}. At room temperature, the $^{31}P\{^1H\}$ NMR spectrum in dichloromethane-d_2 shows at 102.4 ppm a triplet with a P−P coupling constant of 8.8 Hz and at 43.3 ppm a doublet with the same coupling constant, which were assigned to methoxydiphenylphosphine and triisopropylphosphine, respectively. In the ^{1}H NMR spectrum at room temperature the methoxy group of the methoxydiphenylphosphine ligand gives rise to a doublet with a H−P coupling constant of 12.0 Hz, at 3.23 ppm, whereas the resonance corresponding to the hydride ligands appears at −8.20 ppm as a doublet of triplets with H−P coupling constants of 9.2 and 5.7 Hz. The $^{31}P\{^1H\}$ and ^{1}H NMR spectra are temperature-dependent and show a behavior with the temperature similar to that previously mentioned for **5**.

T_1 measurements for the hydride resonance gave a value of 308 ms at 294 K, which decreases to 90 ms at 178 K. In this temperature range, a T_1(min) value was not found. However, it is clear that the value of this parameter must be lower than that of **5** (112 ms). This suggests that the contribution of nonclassical species to the structure of **7** is higher than the contribution of this type of species to the structure of **5**. In agreement with this, the H−D coupling constant in $[OsH_4D\{P(OMe)Ph_2\}(P^iPr_3)_2]^+$ (2.5 Hz) is higher than that in $[OsH_4D(PHPh_2)(P^iPr_3)_2]^+$ (1.7 Hz). Complex $[OsH_4D\{P(OMe)Ph_2\}(P^iPr_3)_2]^+$ was formed by protonation of $OsH_4\{P(OMe)Ph_2\}(P^iPr_3)_2$ (**9**) with $DBF_4\cdot D_2O$ in dichloromethane-d_2 as solvent. The tetrahydride was obtained by deprotonation of **7** with Et_3N. The higher contribution of nonclassical species in **7** could be related with a higher π-acceptor power of the methoxydiphenylphosphine with regard to the diphenylphosphine.

The presence of a $P(OH)Ph_2$ ligand in **8** is strongly supported by the IR and ^{1}H NMR spectra. The IR spectrum in KBr shows ν(OH) and ν(P−O) bands at 3223 and 1034 cm^{-1}, respectively. In addition, the spectrum contains three ν(Os−H) absorptions at 2132, 2084, and 2015 cm^{-1} and the absorption due to the $[BF_4]^-$ anion with T_d symmetry centered at 1099 cm^{-1}. At room temperature, the ^{1}H NMR spectrum in dichloromethane-d_2 shows at 1.63 ppm a broad singlet corresponding to the OH proton and at −8.27 ppm a doublet of triplets with H−P coupling constants of 9.0 and 4.8 Hz, due to the hydride ligands. At this temperature, the $^{31}P\{^1H\}$ NMR spectrum contains at 86.6 ($P(OH)Ph_2$) ppm a triplet with a P−P coupling constant of 8.9 Hz and at 42.7 (P^iPr_3) ppm a doublet with the same P−P coupling constant. The ^{1}H and $^{31}P\{^1H\}$ NMR spectra are temperature-dependent and show a behavior with the temperature similar to those of **5** and **7**.

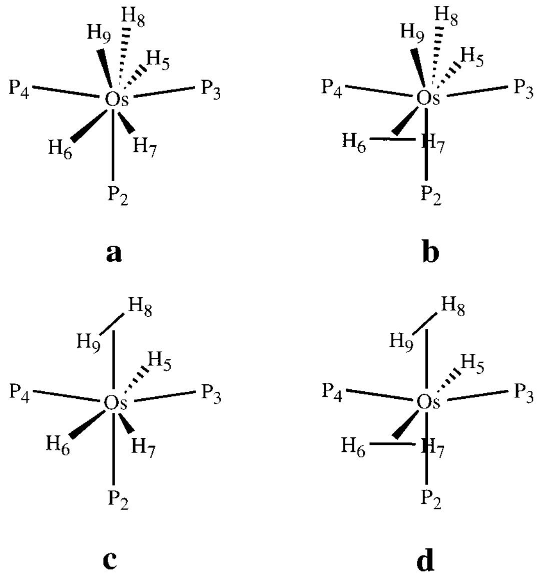
---

(27) Esteruelas, M. A.; López, A. M.; Tolosa, J. I.; Vela, N. *Organometallics* **2000**, *19*, 4650.

(28) See for example: (a) Wicht, D. K.; Kourkine, I. V.; Lew, B. M.; Nthenge, J. M.; Glueck, D. S. *J. Am. Chem. Soc.* **1997**, *119*, 5039. (b) Kourkine, I. V.; Sargent, M. D:; Glueck, D. S. *Organometallics* **1998**, *17*, 125. (c) Wicht, D. K.; Paisner, S. N.; Lew, B. M.; Glueck, D. S.; Yap, G. P. A.; Liable-Sands, L. M.; Rheingold, A. L.; Haar, C. M.; Nolan, S. P. *Organometallics* **1998**, *17*, 652. (d) Wicht, D. K.; Kovacile, I.; Glueck, D. S.; Liable-Sands, L. M.; Incarvito, C. D.; Reingold, A. L. *Organometallics* **1999**, *18*, 5141. (e) Wicht, D. K.; Kourkine, I. V.; Kovacik, I.; Glueck, D. S.; Concolino, T. E.; Glenn, P. A.; Yap, G. P. A.; Incarvito, C. D.; Rheingold, A. L. *Organometallics* **1999**, *18*, 5381.

(29) (a) Jörg, K.; Malisch, W.; Reich, W.; Meyer, A.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 92. (b) Malisch, W.; Hirth, U.-A.; Grün, K.; Schmeusser, M.; Fey, O.; Weis, U. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2500.

Scheme 3. Ligand Numbering for [Os″H_5″$(PF_3)^+$] Complexes



The T_1 values of the hydrogen nuclei of the OsH_5 unit of **8** were determined over the temperature range 293−193 K. In this case, a T_1(min) value of 106 ms was found as 213 K. This value agrees well with that found in **5**.

The tetrahydride complex **9** was obtained as a brown oil in nearly quantitative yield and was characterized by MS and $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. At room temperature, the $^{31}P\{^1H\}$ NMR spectrum shows at 121.2 ($P(OMe)Ph_2$) ppm a triplet with a P−P coupling constant of 11.5 Hz and at 41.6 (P^iPr_3) ppm a doublet with the same coupling constant. At this temperature, the most noticeable resonance in the ^1H NMR spectrum is a doublet of triplets with H−P coupling constants of 15.0 and 7.2 Hz, which appears at −10.05 ppm and corresponds to the four hydride ligands. The $^{31}P\{^1H\}$ and ^1H NMR spectra show a behavior with the temperature similar to that of **2**.

3. Theoretical Study of $[OsH_5P_3]^+$ Complexes. $[OsH_5(PR_3)_3]^+$ complexes have received a lot of attention in the recent past. The possibility of isomerism between a wide array of classical and nonclassical forms, along with the availability of an unambiguous structural characterization of the $OsH_5(PMePh_2)_3{}^+$ complex by neutron diffraction techniques, has made them an appealing target to theoretical chemistry. Thus, we have chosen them within the whole series of reported $OsH_n(PR_3)_m$ ($n = 2, 3, 4, 5$; $m = 2, 3$) complexes in order to get a deeper insight into the structure and dynamic processes involved in such polyhydride systems. In the next section, there follows a high-level ab initio study, supplemented by QM/MM IMOMM calculations.

i. $[OsH_5(PH_3)_3]^+$ Model System. On the basis of a previous theoretical study and the available X-ray and neutron diffraction data, four isomeric forms have been initially considered for the $[OsH_5(PH_3)_3]^+$ model complex **10**: eight-coordinate pentahydride (**10a**), seven-coordinate dihydrogen/trihydride (**10b** and **10c**), and six-coordinate bisdihydrogen/hydride (**10d**) (Scheme 3). **10a** corresponds to the dodecahedral structure with the three phosphine ligands in B sites and one hydride occupying the last B site available (H9 according to our labeling, see Scheme 3), which was found to be the most stable isomer in the previous theoretical study.[10b] It resembles the neutron diffraction structure of $[OsH_5(PMe_2Ph)_3]^+$ (**11**). If two adjacent H atoms approach each other, structures **10b** and **10c** are attained. The simultaneous shortening of two H−H distances leads to the **10d** structure.

Table 2. Main Geometrical Parameters of Pentahydride (10a), Dihydrogen Trihydride (10b and 10c), and Bis-dihydrogen Hydride (10d) $[OsH_5(PH_3)^+]$ Model Complexes (distances in Å, angles in deg)

	10a	**10b**	**10c**	**10d**	expt[a]
Os−P(2)	2.454	2.458	2.392	2.381	2.389(2)
Os−P(3)	2.392	2.384	2.398	2.384	2.387(2)
Os−P(4)	2.392	2.384	2.398	2.384	2.387(2)
Os−H(5)	1.672	1.633	1.676	1.639	
Os−H(6)	1.645	1.800	1.650	1.811	
Os−H(7)	1.645	1.800	1.651	1.811	
Os−H(8)	1.624	1.606	1.706	1.706	
Os−H(9)	1.626	1.633	1.698	1.729	
H(6)−H(7)	1.598	0.863	1.634	0.855	
H(8)−H(9)	1.636	1.605	0.955	0.921	
H(5)−H(8)	1.904	1.626	2.188	2.002	
P(2)−Os−P(3)	96.32	95.25	93.56	92.07	105.72(6)
P(2)−Os−P(4)	95.32	95.24	93.57	92.07	94.80(6)
P(3)−Os−P(4)	154.46	165.32	152.77	165.72	149.43(6)

[a] X-ray diffraction data for the $OsH_5(P^iPr_3)_2(PHPh_2)^+$ complex.

A B3LYP optimization has been performed for the four structures. All of them are actual minima in the B3LYP potential energy surface. Their main geometrical parameters are listed in Table 2. For the ligand numbering, see Scheme 3.

B3LYP distances and angles in the pentahydride are very similar to the MP2-optimized geometry of this species.[10b] The shortening of the H(6)−H(7) distance leads to a dihydrogen heptacoordinate complex (**10b**) which can be described as a distorted pentagonal bipyramid with P(3) and P(4) occupying its axial positions. **10c** is also a pentagonal bipyramid, but with a phosphine (P(2)) and a dihydrogen (H(8)−H(9)) as axial ligands. The bis-dihydrogen (**10d**) adopts a distorted octahedral geometry. The P(3)−Os−P(4) angle is very sensitive to the decrease of the coordination number. It is to be expected that P−Os−P bond angles will be affected considerably by steric effects, but this cannot be accounted for by calculations in the model system **10** with PH_3 ligands. The P(3)−Os−P(4) angle in **10a** (154.5°) is slightly different from that experimentally determined in $[OsH_5(PMe_2Ph)_3]^+$(**11**) (146.6°) and **5** (149.43(6)°). As is to be expected, although C_1 geometry optimizations were carried out, the asymmetry in the phosphine arrangement caused by the pattern of asymmetrical substituents in **5** is not reproduced. Thus, P(2)−Os−P(3) and P(2)−Os−P(4) optimized angles in the model system have nearly the same value. As a consequence, the P(2)−Os−P(3) angle is far away from that experimentally determined, indicating clearly that both the asymmetry and the P(2)−Os−P(3) angle opening in the real system are caused by the substitution pattern of the actual phosphines. Despite all discrepancies between model and experiment, the P(3)−Os−P(4) angle suggests that from a geometrical point of view the pentahydride form is the one that fits the experimental data in a better way. This geometrical comparison will be later recalled with a theoretical discussion on the real systems.

Table 3. Relative Energies at Different Levels of Calculation for Pentahydride (10a), Dihydrogen Trihydride (10b and 10c), and Bis-dihydrogen (10d) Structures of $OsH_5(PH_3)_3^+$ Model Complexes Taken from B3LYP Geometry Optimizations

	B3LYP	HF	MP2	MP4SDQ	CCSD	CCSD(T)
10a	0.0	0.0	0.0	0.0	0.0	0.0
10b	−3.4	−10.2	6.3	1.6	1.0	1.9
10c	1.3	−5.1	9.7	6.3	5.6	6.2
10d	−3.6	−16.2	14.4	15.3	6.0	7.5

Relative energies of the four isomers of the $[OsH_5(PH_3)_3]^+$ system are shown in Table 3. The energetic order at the B3LYP//B3LYP level (both geometry optimization and energy at the B3LYP level of therory) agrees neither with previous calculations for this system[10b] nor with the neutron diffraction assignment of a pentahydride structure to $[OsH_5(PMe_2Ph)_3]^+$ (**11**).[9b] Surprisingly the most stable form is not the pentahydride, but the bis-dihydrogen isomer **10d**, which lies 3.6 kcal/mol below the pentahydride. Even the dihydrogen/trihydride **10b** is 3.4 kcal/mol more stable than the pentahydride. Single-point energy only calculations have been performed at different levels using the B3LYP optimized geometries (Table 3).

Data in Table 3 suggest that B3LYP overestimates the stability of dihydrogen species, whereas MP2 underestimates it. This conclusion has already been pointed out by other authors.[30] The bis-dihydrogen species is the most affected by the methodology chosen. Relative energies at the higher computational levels (MP4SDQ, CCSD, and CCSD(T)) are very similar, indicating that the quantum mechanical description is practically converged. CCSD(T) calculations reverse the B3LYP ordering, giving the pentahydride as the most stable isomer, in better agreement with neutron diffraction data of $[OsH_5(PMe_2Ph)_3]^+$ (**11**). From now on we will present only CCSD(T) energies.

Our CCSD(T)//B3LYP calculations (CCSD(T) single-point energy calculations on B3LYP optimized geometries) give the pentahydride and the dihydrogen **10b** very close in energy. From a structural, *static*, point of view the existence of both is possible. Can their interconversion occur easily? This question is related to the *dynamic* behavior of the system and can be answered looking at the potential energy surface (PES) for the interconversion. A bidimensional potential energy surface has been calculated at the CCSD(T)//B3LYP level in order to estimate the energetic cost of the pentahydride/dihydrogen trihydride/bis-dihydrogenhydride interconversion processes. This bidimensional PES was built by varying the H(6)−H(7) and H(8)−H(9) distances between 0.8 and 1.8 Å. At each fixed value of the H(6)−H(7) and H(8)−H(9) distances all the geometrical parameters were optimized. The obtained potential energy surface is depicted in Figure 3.

At first glance, it should be noted that the less stable isomers (**10c** and **10d**) found as minima in the B3LYP potential energy surface are no longer minima in the CCSD(T) potential energy surface. The most striking finding is the extreme flatness of the surface along the H(6)−H(7) axis, in the direction corresponding to the **10a** → **10b** rearrangement. The very low energy difference between both isomers is kept along the whole interconversion process. The energy of the $[OsH_5(PH_3)_3]^+$ system is practically independent of the H(6)−H(7) separation between 0.8 and 1.8 Å. The pentahydride → dihydrogen/trihydride isomerization takes place with an energy cost of no more than 2 kcal/mol. The energy barrier for the breaking/formation of such a strong bond is lower than or the same order as a rotational barrier. This behavior is very similar to that found in theoretical studies of elongated dihydrogen complexes: two hydrogen atoms moving almost freely in a large region within the coordination sphere of the metal.[6] This result opens the door to a new explanation for the system under study: a certain extent of delocalization concerning the H(6)−H(7) moiety could explain the hybrid behavior between classical and nonclassical forms of this kind of complex. In some way **10** is simultaneously a polyhydride and a dihydrogen hydride.

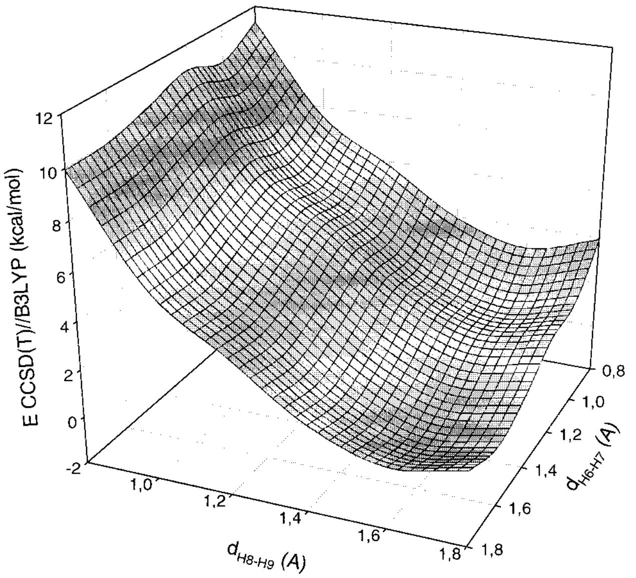


Figure 3. CCSD(T)//B3LYP potential energy surface for H_6-H_7 and H_8-H_9 elongation in $OsH_5(PH_3)^+$ model complex.

In the next section there follows an analysis of the real systems (**5**, **7**, and $[OsH_5(PMe_2Ph)_3]^+$ (**11**)) through IMOMM calculations in order to establish how the inclusion of the real phosphine substituents modifies the structural parameters and affects the relative stabilities of the four studied isomers (**a**−**d**).

ii. $[OsH_5P_3]^+$ Real Systems. Geometry optimizations with the IMOMM (B3LYP:MM3) methodology were carried out on the pentahydride (**a**), dihydrogen trihydride (**b** and **c**), and bis-dihydrogen hydride (**d**) structures of the reported $[OsH_5(PHPh_2)(P^iPr_3)_2]^+$ (**5**) and $[OsH_5\{P(OMe)Ph_2\}(P^iPr_3)_2]^+$ (**7**) complexes, as well as for the neutron-characterized $[OsH_5(PMePh_2)_3]^+$ (**11**). A first and very remarkable fact is that not all of the four minima found in the model system can be found in the real systems: complexes **5c**, **7c**, and **11c** revert to **5b**, **7b**, and **11b**, respectively. Thus the less stable dihydrogen isomer is not a minimum in the real systems. Similarly, the existence of a bis-dihydrogen form, although reliable in energy terms for the model system, depends strongly on the phosphine substituents. When the less bulky phosphines are present, it does exist (**11d**). It could be thought that bulky phospines

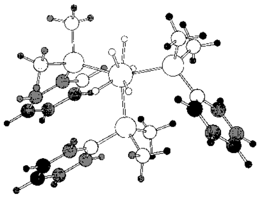
---

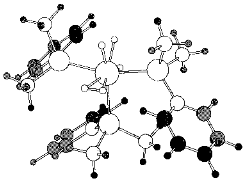
[30] Bytheway, I.; Backsay, G. B.; Hush, N. S. *J. Phys. Chem.* **1996**, *100*, 6023. (b) Clot, E.; Eisenstein, O. *J. Phys. Chem. A* **1998**, *102*, 3592.

Table 4. IMOMM (B3LYP:MM3) Optimized Distances and Angles of $[OsH_5(PMe_2Ph)_3]^+$ (11a, 11b, and 11d), $[OsH_5(P^iPr_3)_2(PHPh_2)]^+$ (5a and 5b), and $[OsH_5(P^iPr_3)_2(P(OMe)Ph_2)]^+$ (7a and 7b) Complexes (distances in Å, angles in deg)

	11a[a]	**11b**	**11d**	**5a**	**5b**	**7a**	**7b**	expt[a]
Os−P(2)	2.475	2.474	2.412	2.479	2.495	2.457	2.478	2.389(2)
Os−P(3)	2.414	2.398	2.399	2.448	2.435	2.460	2.452	2.387(2)
Os−P(4)	2.401	2.396	2.399	2.437	2.429	2.439	2.432	2.387(2)
Os−H(5)	1.667	1.630	1.633	1.664	1.629	1.660	1.627	
Os−H(6)	1.641	1.789	1.806	1.634	1.774	1.635	1.771	
Os−H(7)	1.642	1.790	1.807	1.639	1.777	1.636	1.772	
Os−H(8)	1.622	1.609	1.692	1.617	1.602	1.619	1.602	
Os−H(9)	1.623	1.629	1.713	1.615	1.618	1.617	1.620	
H(6)−H(7)	1.576	0.872	0.859	1.576	0.881	1.605	0.885	
H(8)−H(9)	1.605	1.605	0.943	1.650	1.589	1.684	1.638	
H(5)−H(8)	1.656	1.656	1.986	1.919	1.675	1.903	1.641	
P(2)−Os−P(3)	98.62	97.30	94.33	102.27	101.23	103.86	103.22	105.72(6)
P(2)−Os−P(4)	97.80	95.53	93.98	95.40	93.72	96.78	95.79	94.80(6)
P(3)−Os−P(4)	151.92	163.32	164.82	150.81	160.21	149.84	157.95	149.43(6)

[a] X-ray diffraction data for the $OsH_5(P^iPr_3)_2(PHPh_2)^+$ complex.


11a


11b

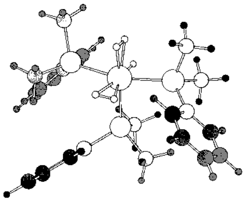

11d

Figure 4. IMOMM(B3LYP:MM3) optimized structures of $OsH_5(PMe_2Ph)_3^+$ complexes **11a**, **11b**, and **11d**.

should favor the presence of two dihydrogen ligands, occupying less space in the coordination sphere than four hydride ligands. But this is not the case due to the octahedral geometry of the bis-dihydrogen isomer. The P−Os−P angles imposed by an octahedral arrangement (around 90° and 180°) are hardly possible when bulky phosphines (as P^iPr_3) are present.

The main geometrical parameters of the minima are listed in Table 4, whereas optimized geometries for systems **11**, **5**, and **7** are depicted in Figures 4, 5, and 6, respectively.

The main structural modifications caused by changing the phosphines are found in the P−Os−P angles. Comparisons with the experimental structures are promising: with the inclusion of real phosphine substituents, calculations nicely take account of the asymmetry in the phosphine backbone of the complexes. The P(3)−Os−P(4) angle fits almost exactly the X-ray-determined angle in **5** if the pentahydride structure **5a** is taken into account. Moreover, the pattern for the P(2)−Os−P(3) and P(2)−Os−P(4) is also reproduced, the optimized value of the former being slightly larger than the latter and thus leading to the distorted T-shape reported in the X-ray diffraction structure. The reliability of our IMOMM geometries is also confirmed by the optimization of $OsH_5(PMe_2Ph)_3^+$ (**11**), as this allows us to consider a different case where there is a symmetric phosphine substituents pattern. For this complex, P(2)−Os−P(3) and P(2)−Os−P(4) angles are rather similar, in agreement with neutron diffraction data available for complex **11**. Moreover, being that these angles concerning the OsP_3 backbone are nearly the same as that found for the $OsH_5(PH_3)^+$ model complex, we should conclude that PMe_2Ph causes a lesser steric hindrance in the system than phosphines used in complexes **5** and **7**, a quite logical result taking into account the smaller cone angle for PMe_2Ph.[31] Another interesting geometrical feature of IMOMM calculations is related to the OsH_5 moiety. Although the trends in Os−H distances are maintained when **5** and **7** are compared to model complex **10**, in general IMOMM

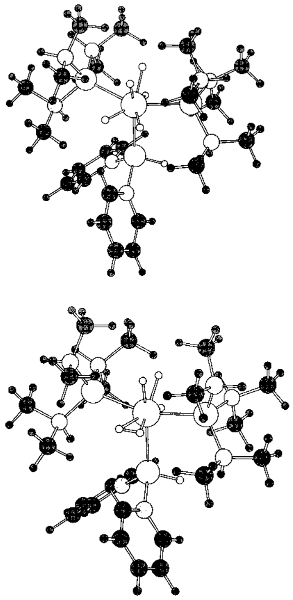


Figure 5. IMOMM(B3LYP:MM3) optimized structures of $OsH_5(P^iPr_3)_2(PHPh_2)^+$ complexes **5a** and **5b**.

---

(31) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

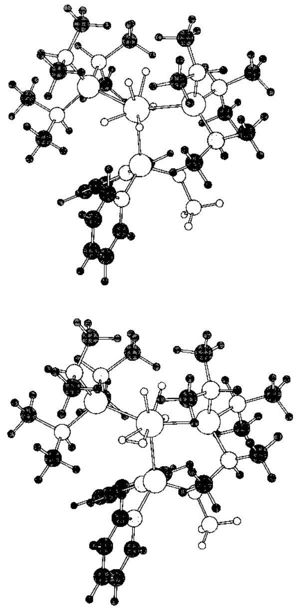


Figure 6. IMOMM(B3LYP:MM3) optimized structures of $OsH_5(P^iPr_3)_2(P(OMe)Ph_2)^+$ complexes **7a** and **7b**.

Table 5. Relative Energies of $[OsH_5(PMe_2Ph)_3]^+$ (11a, 11b, and 11d), $[OsH_5(P^iPr_3)_2(PHPh_2)]^+$ (5a and 5b), and $[OsH_5(PiPr_3)_2(P(OMe)Ph_2)]^+$ (7a and 7b) Complexes (energies in kcal/mol)

	11a	**11b**	**11d**	**5a**	**5b**	**7a**	**7b**
B3YLP	0.0	−3.8	−3.6	0.0	−2.6	0.0	−2.3
CCSD(T)	0.0	1.4	7.2	0.0	2.4	0.0	2.8
MM3	0.0	0.5	1.2	0.0	0.2	0.0	0.2
B3LYP+MM3	0.0	−3.3	−2.4	0.0	−2.4	0.0	−2.1
CCSD(T)+MM3	0.0	1.9	8.4	0.0	2.6	0.0	3.0

distances are slightly shorter. This may not be important, but one has to recall that if a dihydrogen form is accessible, the ease of H_2 elimination is related to Os−H_2 bond strength. Thus, when we compare **5b** and **7b** with their model counterpart **10b**, there is a small but noticeable difference in the Os−H(6)−H(7) dihydrogen unit: as in the real systems Os−H distances are shorter and H−H distances are longer, and we might expect that the actual substitution pattern would render H_2 elimination less favorable. Finally, a word about Os−P distances is probably to the point: if it is true that the calculated distances are in all cases longer than the experimental ones, this seems to be a common feature of the IMOMM method; this fact should not affect the validity of the results, as many prior examples have proved.[32]

Relative energies of the different isomers are shown in Table 5. The inclusion of the real phosphine substituents does not change significantly the patterns found in the ab initio calculations on the model system, since the steric energy differences are small in comparing the pentahydride and dihydrogen trihydride isomers (0.2 kcal/mol in favor of pentahydride for complexes **5** and **7**). For the three compounds the energy of the pentahydride structure is the lowest one, but the dihydrogen forms **b** are very close in energy. However, the presence of bulky phosphines also induces a distortion in the ab initio part of the system. Thus, it remains clear that increasing the size of phosphine substituents plays a role against the stability of dihydrogen forms, because of the higher steric congestion of lower coordination number complexes arising from repulsions between bulky phosphines. This is nicely shown when complexes **5**, **7**, and **11** are considered: for the latter, with the comparatively small $P(Me_2Ph)_3$ phosphines, a lesser distortion of the ab initio part of the system is to be expected. As a consequence, the same relative energy difference than for calculations in the model system $OsH_5(PH_3)_5^+$ is found between **11a** and **11b** (1.9 kcal/mol). For complexes **5** and **7**, this difference is somewhat higher (2.6 and 3.0 kcal/mol, respectively) but still small enough to keep valid the definition of the $[OsH_5(P_3)_3]^+$ systems as having two delocalized hydrogen atoms when the real phosphines are included in the calculations.

Concluding Remarks

The investigations on the reactivity of the hexahydride complex $OsH_6(P^iPr_3)_2$ have been focused on the tendency of this compound to lose molecular hydrogen. However, the dominant point of view has been that the dissociation energy of molecular hydrogen was high. Thus, because of the saturated character of $OsH_6(P^iPr_3)_2$, it has been assumed that this complex had a relative kinetic inertia toward the hydrogen substitution and that its activation should involve the previous acidolysis[33] or alternatively the use of ligands containing relatively acidic hydrogen atoms.[13f,h] Recently we have shown that the complex $OsH_6(P^iPr_3)_2$ also activates C−H and C−F bonds of aromatic ketones. On the basis of a low energy for the dissociation of molecular hydrogen from $OsH_6(P^iPr_3)_2$ we have proposed that the first step of these activation processes involves the loss of molecular hydrogen to give the unsaturated species $OsH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$.[13i] This study reports the first experimental observation of the low energy necessary to dissociate molecular hydrogen from $OsH_6(P^iPr_3)_2$.

The dissociation energy of a hydrogen molecule from $OsH_6(P^iPr_3)_2$ is similar to that reported for the dihydride−dihydrogen $OsH_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$,[20] and as the former compound, $OsH_6(P^iPr_3)_2$ reacts with diphenylphosphine to give molecular hydrogen and the tetrahydride $OsH_4(PHPh_2)(P^iPr_3)_2$. In contrast to the hexahydride, this tetrahydride has a high dissociation energy of molecular hydrogen, which is lower than or of the same order as the energy necessary to break an Os−P bond. The reaction of $OsH_4(PHPh_2)(P^iPr_3)_2$ with diphenylphosphine requires drastic conditions and does not give rise to the selective substitution of molecular hydrogen, but the replacement of this small molecule is accompanied with the substitution of a triisopropylphosphine ligand. The selective replacement of molecular hydrogen in $OsH_4(PHPh_2)(P^iPr_3)_2$ requires its previous acidolysis, which leads to $[OsH_5(PHPh_2)(P^iPr_3)]^+$.

This compound, containing five hydrogen atoms bonded to the osmium atom, shows a behavior similar to that of the hexahydride. The reaction with diphenylphosphine produces the selective loss of molecular hydrogen and the formation of $[OsH_3(PHPh_2)_2(P^iPr_3)_2]^+$. Moreover, the treatment of $[OsH_5(PHPh_2)(P^iPr_3)_2]^+$ with methanol and water yields $[OsH_5\{P(OR)Ph_2\}(P^iPr_3)_2]^+$ ($R = CH_3$, H). According to a recent study carried out by our

---

[32] (a) Maseras, F. *Top. Organomet. Chem.* **1999**, *4*, 165. (b) Maseras, F. *Chem. Commun.* **2000**, 1821.

[33] Smith, K. T.; Tilset, M.; Kuhlman, R.; Caulton, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 9473.

group,[27] the formation of the latter compounds involves not only the loss of molecular hydrogen but also the intramolecular P−H oxidative addition in unsaturated $[OsH_3(PHPh_2)(P^iPr_3)_2]^+$ intermediates.

Geometry optimizations with the IMOMM(B3LYP:MM3) methodology on the species $[OsH_5(PHPh_2)(P^iPr_3)_2]^+$ and $[OsH_5\{P(OMe)Ph_2\}(P^iPr_3)_2]^+$ and that previously reported by Caulton, $[OsH_5(PMe_2Ph)_3]^+$,[9] indicate, in the three cases, that a dodecahedral pentahydride structure, similar to that found by neutron diffraction for $[OsH_5(PMe_2Ph)_3]^+$, and a pentagonal bipyramid trihydride-dihydrogen structure, with the triisopropylphosphine ligands (or dimethylphenylphosphine, in the case of the Caulton's complex) in the axial positions are minima in the potential energy surface. Not only are these structures very close in energy, but furthermore the energy of the systems is practically independent of the separation between the hydrogen atoms involved in the nonclassical interaction, in the range 0.8−1.8 Å. The energy barrier for the breaking/formation of the hydrogen bond is lower than or the same order as a rotation barrier. In this context, the description of these OsH_5 species as pentahydride or trihydride-dihydrogen compounds loses significance; it appears to be more appropriate to describe them as species containing two hydrogen atoms moving freely in a wide region of the coordination sphere of the osmium atom.

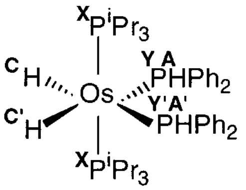
Experimental Section

Physical Measurements. ^1H, $^1H\{^{31}P\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on either a Varian Gemini 2000, a Varian Unity 300, or a Bruker 300 ARX spectrometer. The probe temperature of the NMR spectrometers was calibrated at each temperature against a methanol standard. For the T_1 measurements the 180° pulses were calibrated at each temperature. The conventional inversion−recovery method (180−τ−90) was used to determine T_1. Chemical shifts are expressed in ppm upfield from Me_4Si (^1H) or 85% H_3PO_4 (^{31}P). Coupling constants (J and N ($N = J(HP) + J(HP')$)) are given in hertz. IR data were recorded on a Perkin-Elmer 883 or Nicolet 550 spectrophotometer. Elemental analyses were carried out with a Perkin-Elmer 2400 CHNS/O microanalyzer. Mass spectra analyses were performed with a VG Autospec instrument. In FAB$^+$ mode, ions were produced with the standard C$^+$ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as the matrix. The simulation of the hydride signal of **3** was carried out with the gNMR v 3.6 for Macintosh program.[34]

Synthesis. All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were dried using appropriate drying agents and freshly distilled under argon before use. The starting complex $OsH_6(P^iPr_3)_2$ was prepared by the published method.[13a]

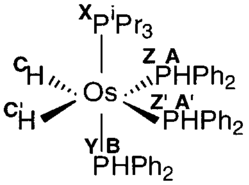
Preparation of $OsH_4(PHPh_2)(P^iPr_3)_2$ (2). A colorless solution of $OsH_6(P^iPr_3)_2$ (**1**) (892.0 mg, 1.73 mmol) in 10 mL of toluene was treated with diphenylphosphine (296 μL, 1.73 mmol) and heated at 80 °C for 1 h to obtain a yellow solution. The solvent was removed in vacuo. The residue was washed with methanol to afford a white solid. Yield: 859 mg (71%). Anal. Calcd for $C_{30}H_{57}OsP_3$: C, 51.41; H, 8.20. Found: C, 51.05; H, 7.76. IR (KBr, cm^{-1}): ν(PH) 2292(m); ν(OsH) 2052(m), 2013(m), 1886(s); $\nu(C{=}C)_{aromatic}$ 1587(w), 1575(w). ^1H NMR (300 MHz, toluene-d_8, 353 K): δ 7.75 (m, 4H; $H_{ortho-Ph}$), 7.45 (dtd, 1H, J(HP) = 346.0 Hz, J(HP) = 8.4 Hz, J(HH) = 3.0 Hz; P*H*Ph$_2$), 7.06 (m, 4H; $H_{meta-Ph}$), 6.98 (m, 2H; $H_{para-Ph}$), 1.67 (m, 6H; PC*H*$(CH_3)_2$), 1.08 (dvt, 36 H, N = 12.6 Hz, J(HH) = 5.9 Hz; PCH$(CH_3)_2$), −10.19 (tdd, 4H, J(HP) = 15.0 Hz, J(HP) = 3.0 Hz, J(HH) = 3.0 Hz; OsH). $^{31}P\{^1H\}$ NMR (121.4 MHz, toluene-d_8, 293 K): δ 39.2 (d, J(PP) = 17.1 Hz; P^iPr_3), −4.6 (t, J(PP) = 17.1 Hz; $PHPh_2$). T_1 (ms, "OsH_4", 300 MHz, toluene-d_8): 383 (293 K), 249 (273 K), 168 (253 K), 137 (223 K), 183 (213 K).

Preparation of $OsH_2(PHPh_2)_2(P^iPr_3)_2$ (3). A solution of $[OsH_3(P^iPr_3)_2(PHPh_2)_2]BF_4$ (**6**) (391.0 mg, 0.40 mmol) in 10 mL of dichloromethane was treated with triethylamine (56 μL, 0.40 mmol) and stirred for 1 day to give a dark brown solution. The solvent was removed in vacuo. Toluene (10 mL) was added, and the suspension was filtered to eliminate $[HNEt_3]BF_4$. Solvent was evaporated, and the residue was washed with methanol to afford a white solid. Yield: 132 mg (37%). Anal. Calcd for $C_{42}H_{66}OsP_4$: C, 57.00; H, 7.52. Found: C, 56.73; H, 7.98. IR (KBr, cm^{-1}): ν(PH) 2265(m); ν(OsH) 1993(m); $\nu(C{=}C)_{aromatic}$ 1587(w), 1574(w).



^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.88 (AA′ part of an AA′CC′X$_2$YY′ spin system, 2H, $J(H_AH_C) \approx J(H_{A'}H_{C'}) < 2$ Hz, $J(H_{A'}P_{Y'}) = J(H_AP_Y) = 309.0$ Hz, $J(H_AP_X) = J(H_{A'}P_X) = 6.4$ Hz; P*H*Ph$_2$), 7.73 (m, 8H; $H_{ortho-Ph}$), 7.10 (m, 8H; $H_{meta-Ph}$), 7.00 (m, 4H, $H_{para-Ph}$), 1.91 (m, 6H; PC*H*$(CH_3)_2$), 1.10 (dvt, 36H, N = 12.2 Hz, J(HH) = 5.3 Hz; PCH$(CH_3)_2$), −11.24 (CC′ part of an AA′CC′X$_2$YY′ spin system, 2H, $J(H_AH_C) \approx J(H_{A'}H_{C'}) < 2$ Hz, $J(H_CH_{C'}) = 4.2$ Hz, $J(H_CP_X) = J(H_{C'}P_X) = 26.6$ Hz, $J(H_CP_{Y'}) = J(H_{C'}P_Y) = 55.2$ Hz, $J(H_CP_Y) = J(H_{C'}P_{Y'}) = -16.4$ Hz; OsH). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 25.5 (X part of a simplified AA′CC′X$_2$YY′ spin system, 2P, $J(P_XP_Y) = J(P_XP_{Y'}) = 14.0$ Hz; P^iPr_3), −17.8 (YY′ part of a simplified AA′CC′X$_2$YY′ spin system, 2P, $J(P_XP_Y) = J(P_XP_{Y'}) = 14.0$ Hz, $J(P_YP_{Y'}) = 1.7$ Hz; $PHPh_2$).

Preparation of $OsH_2(PHPh_2)_3(P^iPr_3)$ (4). A solution of **2** (208.0 mg, 0.30 mmol) in 13 mL of toluene was treated with diphenylphosphine (50 μL, 0.30 mmol) and heated at 80 °C. After 3 days, the solvent was removed in vacuo. The residue was washed with methanol to afford a white solid. Yield: 127 mg (47%). Anal. Calcd for $C_{45}H_{56}OsP_4$: C, 59.30; H, 6.20. Found: C, 59.00; H, 6.51. IR (KBr, cm^{-1}): ν(PH) 2374(m), 2361(m), 2348(m); ν(OsH) 2000(m), 1927(m); $\nu(C{=}C)_{aromatic}$ 1586(w), 1573(w).



^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.80−6.90 (m, 30H; Ph), 7.00−5.91 (AA′B part of an AA′BCC′XYZZ′ spin system, 3H; P*H*Ph$_2$), 1.95 (m, 3H; PC*H*$(CH_3)_2$), 1.12 (dd, 18H, J(HP) = 12.3 Hz, J(HH) = 6.9 Hz; PCH$(CH_3)_2$), −10.00 (CC′ part of an AA′BCC′XYZZ′ spin system, 2H; OsH). $^{31}P\{^1H\}$ (121.4 MHz, C_6D_6, 293 K): δ 33.1 (X part of a simplified AA′BCC′XYZZ′ spin system, 1P, $J(P_XP_Y) = 209.3$ Hz, $J(P_XP_Z) = J(P_XP_{Z'}) = 18.4$ Hz; P^iPr_3), 13.9 (Y part of a simplified AA′BCC′XYZZ′ spin system, 1P, $J(P_YP_X) = 209.3$ Hz, $J(P_YP_Z) = J(P_YP_{Z'}) = 11.5$ Hz; $PHPh_2$), −8.0 (ZZ′ part of a simplified AA′BCC′XYZZ′ spin system, 2P, $J(P_ZP_Y) = J(P_{Z'}P_Y) = 18.4$ Hz, $J(P_ZP_Y) = J(P_{Z'}P_Y)$

---

(34) *gNMR* v. 3.6; Cherwell Scientific Publishing Limited: The Magdalen Center Oxford Science Park, Oxford OX446A, U.K., 1992−1995.

= 11.5 Hz; PHPh$_2$). MS(FAB$^+$): *m/z* 910 (M$^+$ − 1H), 722 (M$^+$ − 2H − PHPh$_2$).

Preparation of [OsH$_5$(PHPh$_2$)(P^{i}Pr$_3$)$_2$]BF$_4$ (5). A solution of **2** (342.0 mg, 0.49 mmol) in 10 mL of diethyl ether was treated with HBF$_4$·OEt$_2$ (68 μL, 0.49 mmol), and a white solid was formed. After 40 min, the solid was filtered off, washed with diethyl ether, and dried in vacuo. Yield: 373 mg (97%). Anal. Calcd for C$_{30}$H$_{58}$OsP$_3$BF$_4$: C, 45.68; H, 7.41. Found: C, 45.69; H, 7.02. IR (KBr, cm^{-1}): ν(PH) 2362(m); ν(OsH) 2096(m), 2086(m), 1984(m); ν(C=C)$_{\text{aromatic}}$ 1576(m); ν(BF$_4^-$) 1058(vs). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 293 K): δ 7.60−7.50 (m, 10 H; Ph), 6.97 (dt, 1H, *J*(HP) = 373.7 Hz, *J*(HP) = 3.9 Hz; P*H*Ph$_2$), 1.92 (m, 6H; PC*H*(CH$_3$)$_2$), 1.10 (dvt, 36H, *N* = 15.0 Hz, *J*(HH) = 8.1 Hz; PCH(*CH$_3$*)$_2$), −8.26 (t, 5H, *J*(HP) = 8,2 Hz; OsH). ^{31}P{^{1}H} NMR (121.4 MHz, CD$_2$Cl$_2$, 293 K): δ 42.2 (d, *J*(PP) = 10.1 Hz; P^{i}Pr$_3$), −24.4 (t, *J*(PP) = 10.1 Hz; PHPh$_2$). MS(FAB$^+$): *m/z* 695 (M$^+$ − 6H). *T*$_1$ (ms, “OsH$_5$”, 300 MHz, CD$_2$Cl$_2$): 383 (293 K), 260 (273 K), 175 (253 K), 112 (233 K), 124 (213 K).

Preparation of [OsH$_3$(PHPh$_2$)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ (6). A solution of **5** (294.0 mg, 0.37 mmol) in 7 mL of dichloromethane was treated with diphenylphosphine (63 mL, 0.37 mmol). After 1 day at room temperature, the solvent was removed in vacuo. The residue was washed with diethyl ether to afford a white solid. Yield: 310 mg (86%). Anal. Calcd for C$_{42}$H$_{67}$OsP$_4$BF$_4$: C, 51.85; H, 6.94. Found: C, 51.44; H, 6.71. IR (KBr, cm^{-1}): ν(PH) 2358(m), 2326(m); ν(OsH) 2068(m), 2058(m), 1978(m); ν(C=C)$_{\text{aromatic}}$ 1588(m), 1576(m); ν(BF$_4^-$) 1057(vs). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 293 K): δ 7.50−7.40 (m, 20H; Ph), 6.98 (brd, 2H, *J*(HP) ≈ 350 Hz; P*H*Ph$_2$), 2.03 (m, 6H; PC*H*(CH$_3$)$_2$), 1.05 (dvt, 36H, *N* = 14.4 Hz, *J*(HH) = 7.2 Hz; PCH(*CH$_3$*)$_2$), −10.68 (t, 3H, *J*(HP) = 16.5 Hz; OsH). ^{31}P{^{1}H} NMR (121.4 MHz, CD$_2$Cl$_2$, 293 K): δ 28.2 (br, PHPh$_2$), −23.6 (t, *J*(PP) = 7.3 Hz; P^{i}Pr$_3$). MS(FAB$^+$): *m/z* 886 (M$^+$), 722 (M$^+$ − 4H − P^{i}Pr$_3$), 696 (M$^+$ − 4H − PHPh$_2$). *T*$_1$ (ms, “OsH$_3$”, 300 MHz, CD$_2$Cl$_2$): 425 (293 K), 294 (273 K), 204 (253 K), 167 (233 K), 157 (213 K), 184 (193 K).

Preparation of [OsH$_5${P(OMe)Ph$_2$}(P^{i}Pr$_3$)$_2$]BF$_4$ (7). Complex **5** (111.0 mg, 0.14 mmol) was stirred in 6 mL of methanol. After 6 days at room temperature, the solvent was removed in vacuo. The residue was washed with diethyl ether to afford an ivory solid. Yield: 85 mg (74%). Anal. Calcd for C$_{31}$H$_{60}$OOsP$_3$BF$_4$: C, 45.48; H, 7.39. Found: C, 45.11; H, 7.25. IR (KBr, cm^{-1}): ν(OsH) 2085(m), 2012(m), 1917(w); ν(C=C)$_{\text{aromatic}}$ 1589(w), 1579(w); ν(PO) 1101(s); ν(BF$_4^-$) 1049(vs). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 293 K): δ 7.80−7.50 (m, 10H; Ph), 3.23 (d, 3H, *J*(PH) = 12.0 Hz; OCH$_3$), 2.02 (m, 6H; PC*H*(CH$_3$)$_2$), 1.07 (dvt, 36H, *N* = 15.0 Hz, *J*(HH) = 8.1 Hz; PCH(*CH$_3$*)$_2$), −8.20 (td, 5H, *J*(HP) = 9.2 Hz, *J*(HP) = 5.7 Hz; OsH). ^{31}P{^{1}H} NMR (121.4 MHz, CD$_2$Cl$_2$, 293 K): δ 102.4 (t, *J*(PP) = 8.8 Hz; P(OMe)Ph$_2$), 43.3 (d, *J*(PP) = 8.8 Hz; P^{i}Pr$_3$). MS(FAB+): *m/z* 727 (M$^+$ − 5H). *T*$_1$ (ms, OsH$_5$, 300 MHz, CD$_2$Cl$_2$): 308 (294 K), 251 (273 K), 188 (253 K), 134 (233 K), 105 (213 K), 98 (193 K), 90 (178 K).

Preparation of [OsH$_5${P(OH)Ph$_2$}(P^{i}Pr$_3$)$_2$]BF$_4$ (8). A solution of **5** (165.0 mg, 0.21 mmol) in 4 mL of dichloromethane was treated with water (15 mL, 0.84 mmol). After 5 days at room temperature, the solvent was removed in vacuo. The residue was washed with diethyl ether to afford an ivory solid. Yield: 117 mg (69%). Anal. Calcd for C$_{30}$H$_{58}$OOsP$_3$BF$_4$: C, 44.78; H, 7.27. Found: C, 44.73; H, 7.38. IR (KBr, cm^{-1}): ν(OH) 3223(s), ν(OsH) 2132(m), 2084(m), 2015(m); ν(C=C)$_{\text{aromatic}}$ 1580(vw); ν(BF$_4^-$) 1099(vs); ν(PO) 1034(s). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 293 K): δ 7.80−7.40 (m, 10H; Ph), 1.96 (m, 6H; PC*H*(CH$_3$)$_2$), 1.63 (br, 1H; OH), 1.09 (dvt, 36H, *N* = 15.0 Hz, *J*(HH) = 7.2 Hz; PCH(*CH$_3$*)$_2$), −8.27 (td, 5H, *J*(HP) = 4.8 Hz, *J*(HP) = 9.0 Hz; OsH). ^{31}P{^{1}H} (121.4 MHz, CD$_2$Cl$_2$, 293 K): δ 86.6 (t, *J*(PP) = 8.9 Hz; P(OH)Ph$_2$), 42.7 (d, *J*(PP) = 8.9 Hz; P^{i}Pr$_3$). MS (FAB$^+$): *m/z* 713 (M$^+$ − 5H). *T*$_1$ (ms, “OsH$_5$”, 300 MHz, CD$_2$Cl$_2$): 268 (293 K), 198 (273 K), 146 (253 K), 114 (233 K), 106 (213 K), 118 (193 K).

Table 6. Crystal Data and Data Collection and Refinement for [OsH$_5$(PHPh$_2$)(P^{i}Pr$_3$)$_2$]BF$_4$ (5)

formula	C$_{30}$H$_{58}$BF$_4$OsP$_3$
mol wt	788.68
color, habit	yellow, prismatic
space group	monoclinic, *P*2$_1$/*n*
a, Å	8.463(1)
b, Å	25.996(2)
c, Å	16.114(2)
β, deg	98.072(8)
V, Å^3	3509.2(7)
Z	4
D(calcd), g cm^{-3}	1.493
μ, mm^{-1}	3.81
scan type	ω scans
θ range, deg	$2 < \theta < 26$
temp, K	173.0(2)
no. of data collected	8425
no. of unique data	6842 ($R_{\text{int}} = 0.0345$)
no. of params refined	369
$R_1{}^a$ ($F^2 > 2\sigma(F^2)$ (4766 ref)	0.0383
$wR_2{}^b$ (all data)	0.0832
S^c (all data)	0.952 ($a = 0.0377$, $b = 0$)

^{a} $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR_2(F^2) = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2}$; $w^{-1} = [\sigma^2(F_o{}^2) + (aP)^2 + bP]$, where $P = [\max(F_o{}^2,0) + 2F_c{}^2)]/3$. ^{c} $S = [\sum[w(F_o{}^2 - F_c{}^2)^2/(n-p)]^{1/2}$, where *n* is the number of reflections and *p* the number of refined parameters.

Preparation of OsH$_4${P(OMe)Ph$_2$}(P^{i}Pr$_3$)$_2$ (9). A solution of **7** (85.0 mg, 0.10 mmol) in 6 mL of dichloromethane was treated with triethylamine (15 μL, 0.10 mmol). After 1 day at room temperature, the solvent was removed in vacuo. Toluene (10 mL) was added, and the suspension was filtered to eliminate [HNEt$_3$]BF$_4$. Solvent was evaporated, and the residue was washed with methanol to afford a brown oil. ^{1}H NMR (300 MHz, C$_6$H$_6$, 293 K): δ 8.03 (m, 4H; H$_{\text{ortho-Ph}}$), 7.17 (m, 4H; H$_{\text{meta-Ph}}$), 7.04 (m, 2H; H$_{\text{para-Ph}}$), 2.94 (d, 3H, *J*(PH) = 11.1 Hz; OCH$_3$), 1.79 (m, 6H; PC*H*(CH$_3$)$_2$), 1.10 (dvt, 36H, *N* = 12.9 Hz, *J*(HH) = 6.0 Hz; PCH(*CH$_3$*)$_2$), −10.05 (dt, 4H; *J*(HP) = 15.0 Hz, *J*(HP) = 7.2 Hz; OsH). ^{31}P{^{1}H} NMR (121.4 MHz, C$_6$D$_6$, 293 K): δ 121.2 (t, *J*(PP) = 11.5 Hz; P(OMe)Ph$_2$), 41.6 (d, *J*(PP) = 11.5 Hz; P^{i}Pr$_3$). MS(FAB$^+$): *m/z* 727 (M$^+$ − 4H).

Crystal Data for 5. Crystals suitable for X-ray diffraction analysis were mounted onto a glass fiber and transferred to a Bruker-Siemens P4 (*T* = 173.0(2) K) automatic diffratometer (Mo Kα radiation, graphite monochromator, λ = 0.71073 Å). Accurate unit cell parameters were determined by least-squares fitting from the setting of high-angle reflections. Data were collected by the ω scan method. Lorentz and polarization corrections were applied. Decay was monitored by measuring three standard reflections throughout data collection. Corrections for decay and absorption (semiempirical ψ scan method) were also applied.

The structures were solved by the Patterson method and refined by full-matrix least-squares on F^2.[35] Non-hydrogen atoms were anisotropically refined, and the hydrogen atoms were observed or included at idealized positions. Although peaks with adequate geometry to be assigned to the hydrido ligands were observed in the difference Fourier maps, the presence of residuals close to the Os atom prevented their proper refinement. Crystal data and details of the data collection and refinement are given in Table 6.

Computational Details. DFT optimizations on model complexes were carried out with the Gaussian94[36] series of programs using the B3LYP functional.[37] Furthermore, CCSD(T)[38] single-point calculations on the DFT optimized

---

[35] Sheldrick, G. M. *SHELX-97*; University of Göttingen: Göttingen, Germany, 1997.

[36] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala,

structures were performed in order to obtain more reliable energies. A quasi-relativistic effective core potential operator was used to represent the 60 innermost electrons of the osmium atom.[39] The basis set for the osmium atom was that associated with the pseudopotential with a standard valence double-ζ LANL2DZ contraction.[36] The 6-31G(d) basis set was used for the phosphorus atoms.[40] Hydrogens directly attached to the metal were described using a 6-311G(p) basis set,[40] while a 6-31G basis set was used for the rest of hydrogens.[40] Calculations on the real systems were performed using the IMOMM method,[41] with a program built from modified versions of two standard programs: Gaussian 92/DFT [42] for the quantum mechanics part and mm3 (92)[43] for the molecular mechanics part. The OsH_5P_3 backbone has been described at the QM level. In the $OsH_5(P^iPr_3)_2(PHPh_2)^+$ complex, the hydrogen atom of the $PHPh_2$ phosphine has also been included in the QM part of the calculations, while in the $OsH_5(P^iPr_3)_2(P(OMe)Ph_2)^+$ complex, the whole OMe group has also been treated with QM methods. The QM part of the calculations was done at the B3LYP[37] level for the optimizations and CCSD(T)[38] level for single-point energy calculations. The same basis sets were used for complexes **7** and **11**, while for complex **5** the hydrogen of $PHPh_2$ was treated with a 6-311G(p) basis set.[36,40] The MM part of the calculations used the mm3(92) force field.[44] Van der Waals parameters for the osmium atom were taken from the UFF force field.[45] Torsional contributions involving dihedral angles with the metal were set to zero. All geometrical parameters were optimized, except the bond distances between the QM and the MM regions of the molecule. The frozen values were 1.41 Å for the P−H bonds in the QM part and the crystallographic values for P−C bonds in the MM part.

Acknowledgment. Financial support from the DGES of Spain (Projects PB98-0916-02-01 and PB98-1591) is acknowledged. J.T. acknowledges the “Direcció General de Recerca de la Generalitat de Catalunya” for a grant. The use of computational facilities of the Centre de Supercomputació i Comunicacions de Catalunya is gratefully appreciated as well. We also acknowledge Dr. Dmitri G. Gusev for the careful reading of the manuscript and his useful advice.

Supporting Information Available: Tables of atomic coordinates for the non-hydrogen atoms, anisotropic displacement coefficients, atomic coordinates for hydrogen atoms, full experimental details for the X-ray analysis, and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010173C

P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*; Gaussian Inc.: Pittsburgh, PA, 1995.

(37) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (c) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(38) (a) Bartlett, R. J. *J. Phys. Chem.* **1989**, *93*, 1697. (b) Bartlett, R. J.; Watts, J. D.; Kucharski, S. A.; Noga, J. *Chem. Phys. Lett.* **1990**, *165*, 513.

(39) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(40) (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (c) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(41) Maseras, F.; Morokuma, K. *J. Comput. Chem.* **1995**, *16*, 1170.

(42) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andrés, J. L.; Raghavachari, K.; Binkley, J. S.; González, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92/DFT*; Gaussian Inc.: Pittsburgh, PA, 1993.

(43) Allinger, N. L. *mm3(92)*; QCPE: Bloomington, IN, 1992.

(44) Allinger, N. L.; Yuh, Y. H.; Lii, J. H. *J. Am. Chem. Soc,* **1989**, *111*, 8551.

(45) Rappé, A. K.; Casewit, C. J.; Cowell, K. S.; Goddard, W. A., III; Skiff, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 10024.