J. Am. Chem. Soc. **1996,** *118,* 8388−8394

Hydride Exchange Processes in the Coordination Sphere of Transition Metal Complexes: The $OsH_3(BH_4)(PR_3)_2$ System

Isabelle Demachy,[§] Miguel A. Esteruelas,[‡] Yves Jean,[§] Agustí Lledós,*,[†] Feliu Maseras,[†] Luis A. Oro,[‡] Cristina Valero,[‡] and François Volatron[§]

Contribution from the Unitat de Química Física, Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain, Departamento de Química Inorgánica, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain, and Laboratoire de Chimie Théorique (CNRS URA 506, ICMO), Bat. 490, Université de Paris-Sud, 91405 Orsay Cedex, France

Received August 3, 1995. Revised Manuscript Received June 10, 1996[⊗]

Abstract: The problem of intramolecular hydrogen atom exchange in the $OsH_3(BH_4)(PR_3)_2$ system is examined from both theoretical and experimental points of view, through ab initio MO calculations on the $OsH_3(BH_4)(PH_3)_2$ system at the MP2, MP4, and CCSD(T) computational levels and variable-temperature ^1H NMR studies on the $OsH_3(BH_4)(P^iPr_3)_2$ complex. Three different exchange processes are fully characterized from a theoretical point of view through location of intermediates and transition states. Experimental results supporting the existence of these three different exchange processes and providing definitely its intramolecular nature are also presented.

Introduction

Interest in transition metal complexes containing hydride ligands has been rising steadily for a number of years.[1−6] Part of this growing interest in the field surely can be traced back to new discoveries, like the existence of a brand new coordination mode in dihydrogen complexes,[2−6] or the presence of novel quantum exchange coupling effects in ^1H NMR spectra.[7] But part of the interest is also related to dynamic processes involving hydrogen atoms coordinated to transition metal complexes, a set of phenomena that, despite having been known for years, keep providing new and surprising results. A number of different processes are found to be operative in different systems, and their unequivocal assignment from experimental measurements, usually variable-temperature ^1H NMR, is difficult.

The main problem for the characterization of these dynamic phenomena is precisely their great diversity.[8,9] There are the formally simplest examples where two nonequivalent hydride ligands exchange their positions, like $[OsH_2(CO)(NO)(PR_3)_2]^+$,[10] $Re(CO)H_2(PR_3)_2(NO)$,[11] and $MH_2(PR_3)_4$ (M = Fe, Ru).[12,13] There are cases where the hydride ligand exchanges with another hydrogen atom not originally attached to the metal, being it from a thiol group of another ligand in $[IrH_2(HS(CH_2)_3SH)(PCy_3)_2]^+$,[14] or an acidic proton present in the solvent in $[HM(CO)_4L]^-$ (M = Cr, Mo, W; L = CO, PR_3)[15] and $Re(CO)H_2(NO)L_2$,[16] these latter processes going very likely through weakly bound complex−solvent species. There is finally the wealth of exchange processes associated with bridging hydrogen atoms, especially with BH_4 and derivatives[17] ($(C_5H_5)_2V(BH_4)$,[18a] $(C_5H_5)_2Ta(PMe_3)(H_3BSi(^tBu)_2H)$,[18b] $[Mo(CO)_4(BH_4)]^-$,[18c] $(C_5H_5)ZrH(BH_4)$,[19] $OsH_3(BH_4)(P(c\text{-}C_5H_9)_3)_2$[20]), but not limited to them ($RhH((\mu H)SnR_3)_2(PPh_3)_2$[21]). The problem is further complicated by the existence of different mechanistical possibilities, with the eventual involvement of dihydrogen-like intermediate and transition states, changes in the coordination mode of polydentate ligands, changes in the oxidation state of the metal atom, ...

This paper intends to contribute to a better understanding of the topic through a systematic theoretical and experimental study of a complex where different exchange processes are in principle possible. It is $OsH_3(BH_4)(PR_3)_2$. Recently, we reported the preparation of $OsH_3(BH_4)(P^iPr_3)_2$ and its characterization through a combined use of spectroscopic techniques and ab initio theoretical calculations on the model complex $OsH_3(BH_4)(PH_3)_2$ (**1**), its pentagonal bipyramidal structure being shown in Chart 1. The simultaneous presence of two nonequivalent classes of hydride ligand (H_A and H_B) and a bidentate BH_4 ligand with two more different classes of hydrogen atoms (bridging, H_b,

---

[†] Universitat Autònoma de Barcelona.

[‡] Universidad de Zaragoza-CSIC.

[§] Université de Paris-Sud.

[⊗] Abstract published in *Advance ACS Abstracts*, August 1, 1996.

(1) Dedieu, A., Ed. *Transition Metal Hydrides*; VCH: Weinheim, Germany, 1991, and references cited therein.

(2) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120.

(3) (a) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95. (b) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789.

(4) Morris, R. H.; Jessop, P. G. *Coord. Chem. Rev.* **1992**, *121*, 155, and references cited therein.

(5) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913.

(6) Lin, Z.; Hall, M. B. *Coord. Chem. Rev.* **1994**, *135/136*, 845.

(7) (a) Heinekey, D. M.; Millar, J. M.; Koetzle, T. F.; Payne, N. G.; Zilm, K. W. *J. Am. Chem. Soc.* **1990**, *112*, 909. (b) Antiñolo, A.; Chaudret, B.; Commenges, G.; Fajardo, M.; Jalón, F.; Morris, R. H.; Otero, A.; Schweitzer, C. T. *J. Chem. Soc., Chem. Commun.* **1988**, 1210. (c) Gusev, D. G.; Kuhlman, R.; Sini, G.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 2685.

(8) Moore, D. S.; Robinson, S. D. *Chem. Soc. Rev.* **1983**, *12*, 415.

(9) Hlatky, H.; Crabtree, R. H. *Coord. Chem. Rev.* **1985**, *65*, 1.

(10) Johnson, B. F.; Segal, J. A. *J. Chem. Soc., Dalton Trans.* **1974**, 981.

(11) Bakhmutov, V.; Bürgi, T.; Burger, P.; Ruppli, U.; Berke, H. *Organometallics* **1994**, *13*, 4203.

(12) Meakin, P.; Guggenberger, L. J.; Peet, W. G.; Muetterties, E. L.; Jesson, P. J. *J. Am. Chem. Soc.* **1973**, *95*, 1467.

(13) (a) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748. (b) Jesson, P. J.; Muetterties, E. L. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; pp 253−316.

(14) Jessop, P. G.; Morris, R. H. *Inorg. Chem.* **1993**, *32*, 2236.

(15) Gaus, P. L.; Kao, S. C.; Darensbourg, M. Y.; Arndt, L. W. *J. Am. Chem. Soc.* **1984**, *106*, 4752.

(16) Feracin, S.; Bürgi, T.; Bakhmutov, V. I.; Eremenko, I.; Vorontsov, E. V.; Vimenits, A. B.; Berke, H. *Organometallics* **1994**, *13*, 4194.

(17) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263 and references cited therein.

(18) (a) Marks, T. J.; Kennelly, W. J. *J. Am. Chem. Soc.* **1975**, *97*, 1439. (b) Jiang, Q.; Carroll, P. J.; Berry, D. H. *Organometallics* **1993**, *12*, 177. (c) Kirtley, S. W.; Andrews, M. A.; Bau, R.; Grynkewich, G. W.; Marks, T. J.; Tipton, D. L.; Whittlesey, B. R. *J. Am. Chem. Soc.* **1977**, *99*, 7154.

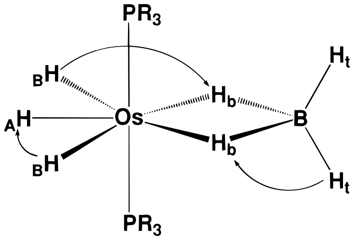
(19) Marks, T. J.; Kolb, J. R. *J. Am. Chem. Soc.* **1975**, *97*, 3397.

(20) Frost, P. W.; Howard, J. A. K.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1984**, 1362.

(21) Carlton, L.; Weber, R. *Inorg. Chem.* **1993**, *32*, 4169.

S0002-7863(95)02617-5 CCC: $12.00

Chart 1



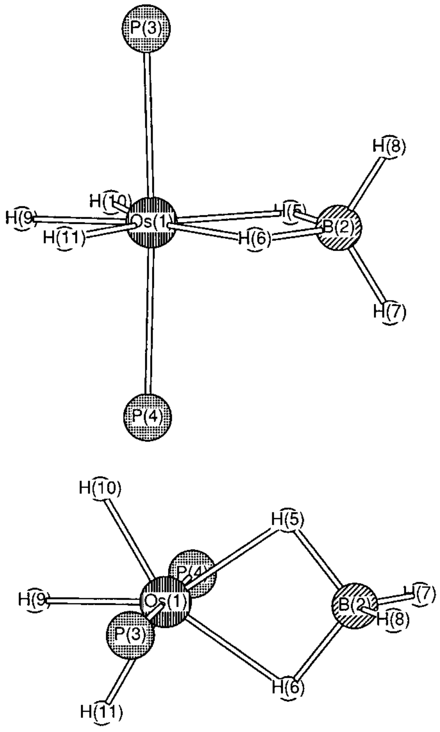
and terminal, H_t) makes this system an excellent probe for different exchange processes. Certainly, the three different H/H rearrangements presented in Chart 1 are possible for complex **1**, namely, H(hydride)/H(hydride), $H_{bridging}$(tetrahydroborate)/$H_{terminal}$(tetrahydroborate), and H(hydride)/H(tetrahydroborate). To our knowledge, this constitutes the first attempt of ab initio characterization of the H(hydride)/H(tetrahydroborate) exchange process. The three kinds of rearrangement are investigated in this paper at the ab initio level, and the validity of the results is checked against variable-temperature NMR experiments.

Results and Discussion

This section is divided into four subsections. The first three deal with the theoretical study of each of the possible exchange processes in complex $OsH_3(BH_4)(PH_3)_2$. Tables 1 and 2 collect geometrical and energetical results concerning all stationary points discussed in these subsections. Finally, the fourth subsection presents the experimental results obtained in the variable-temperature ^1H NMR study of $OsH_3(BH_4)(P^iPr_3)_2$.

(1) H(hydride)/H(hydride) Exchange. As mentioned above, complex **1** had been previously characterized as a d^4 heptacoordinate complex.[22] Its main geometrical features are recalled here for the sake of completeness of this paper. **1** has an almost regular pentagonal bipyramidal structure with the three hydride ligands and two boron-bridging hydrogen atoms in the equatorial plane. The two phosphine ligands occupy the axial positions. No bonding interactions exist between the hydride ligands, the shortest H−H distances being 1.58 Å. This structure is shown in Figure 1, and its main bond distances and angles are collected in the first column of Table 1.

The problem of the exchange of two cis hydride ligands has been studied theoretically before at the ab initio MP2 level for the $[(C_5H_5)IrLH_3]^{+}$ [7a] and $OsH_3X(PR_3)_2$[7c] systems. In both cases, the exchange was found to take place via an out-of-plane twist of the adjacent hydrogen atoms. Consequently, we started our search for the transition state of the H(hydride)/H(hydride) exchange in this region of the potential energy hypersurface. The search was successful, and we could locate a stationary point, which we label as **2** (Figure 2, second column of Table 1). Structure **2** is a true transition state, as shown by its single negative eigenvalue in the estimated hessian. The main component of the transition vector happens to be the H_9−H_{11} rotation around the Os−X (X = midpoint of H_9−H_{11}) axis. Therefore, we conclude that structure **2** is the transition state for the exchange between the two adjacent hydride ligands H_9 and H_{11}.



1

Figure 1. MP2 optimized geometry of **1**, the absolute minimum for the $OsH_3(BH_4)(PH_3)_2$ system. Hydrogen atoms of the phosphine ligands are omitted for clarity.

Table 1. Selected Geometrical Parameters (angstroms and degrees) of the MP2 Optimized Stationary Points Related to the Hydride Exchange Processes in the $OsH_3(BH_4)(PH_3)_2$ System

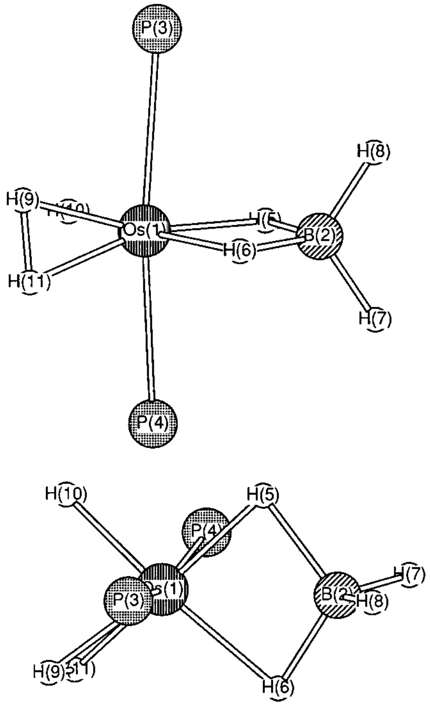
	1	2	3	4	5
Os−B	2.305	2.120	2.407	2.118	2.131
Os−P_3	2.391	2.404	2.400	2.414	2.416
Os−P_4	2.391	2.400	2.400	2.414	2.408
Os−H_5	1.817	1.687	1.850	1.744	1.761
Os−H_6	1.813	1.811	2.532	1.588	1.581
Os−H_9	1.590	1.661	1.576	1.621	1.616
Os−H_{10}	1.578	1.600	1.552	1.676	1.671
Os−H_{11}	1.578	1.655	1.579	1.588	1.584
B−H_5	1.311	1.475	1.312	1.370	1.375
B−H_6	1.307	1.351	1.211	2.300	2.054
B−H_7	1.195	1.200	1.193	1.200	1.211
B−H_8	1.195	1.200	1.203	1.200	1.192
P_3−Os−P_4	177.1	166.3	176.6	153.8	154.1
H_5−Os−H_9	146.0	162.9	144.9	170.6	167.6
H_9−Os−H_{10}	60.6	81.4	56.1	82.9	78.8
H_9−Os−H_{11}	59.8	34.3	61.9	78.0	67.1
H_{10}−Os−H_{11}	120.4	87.1	117.9	145.4	142.7
Os−H_5−B	93.5	83.9	97.7	84.8	84.6

Transition state **2** has an η^2 H_2 complex-like nature. This observation comes directly from the values of the H_9−H_{11} distance (0.978 Å) and the H_9−Os−H_{11} angle (34.3°). If one considered H_9−H_{11} as a dihydrogen ligand occupying one single coordination site, structure **2** could be very well described as an octahedral d^6 Os(II) complex. In view of this, we checked for the eventual existence of a local minimum of a dihydrogen nature in the potential hypersurface. We did not find any, not even with the dihydrogen ligand in the equatorial plane. Another characteristic feature of structure **2** is the coordination of the tetrahydroborate ligand. In **2**, tetrahydroborate is a bidentate ligand, with two bridging hydrogens, as in **1**, even though the bridging hydrogen trans to the dihydrogen ligand has a stronger bond to the metal (Os−H_5 = 1.687 Å).

The energy of transition state **2** is *ca.* 10 kcal/mol above that of the equilibrium structure **1** at all the computational levels (Table 2). The good agreement between the barrier computed at the MP2 level and those of the higher computational levels MP4 and CCSD(T) is important from the methodological point of view, since it proves the accuracy of the geometry optimization at the MP2 level that is being carried out. From a more chemical point of view, the relatively low barrier predicts that the H(hydride)/H(hydride) exchange process will occur even at low temperatures for $OsH_3(BH_4)(PR_3)_2$ systems. Our com-

---

(22) Esteruelas, M. A.; Jean, Y.; Lledós, A.; Oro, L. A.; Ruiz, N.; Volatron, F. *Inorg. Chem.* **1994**, *33*, 3609.



2

Figure 2. MP2 optimized geometry of **2**, the transition state for the H(hydride)/H(hydride) exchange process. Hydrogen atoms of the phosphine ligands are omitted for clarity.

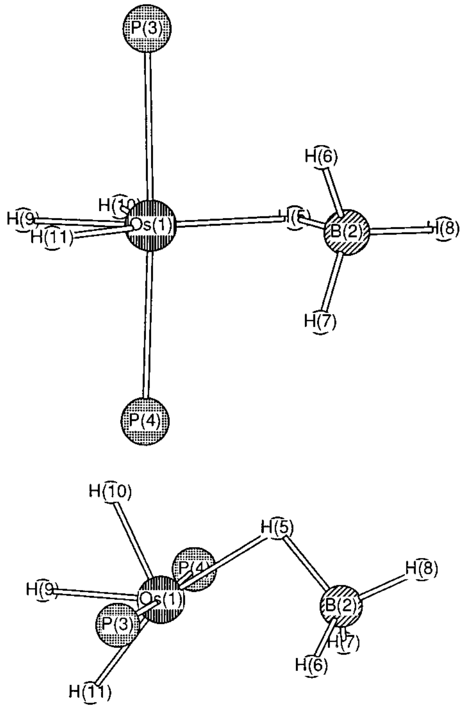
Table 2. Relative Energies (kcal/mol) of the MP2 Optimized Stationary Points Related to the Hydride Exchange Processes in the $OsH_3(BH_4)(PH_3)_2$ System, at the Different Levels of Calculations[a]

	MP2/MP2	MP4(SDTQ)/MP2	CCSD(T)/MP2
1	0	0	0
2	10.9	10.2	9.5
3	22.4	21.3	20.8
4	14.8	15.9	18.5
5	15.4	16.7	19.0

[a] The total energy in hartrees of reference **1** is −135.50504 at the MP2 Level, −135.58293 at the MP4 level, and −135.52290 at the CCSD(T) level.

putational results for this particular process agree with previous theoretical studies of H/H exchange in trihydride complexes,[23,24] and give support to the intramolecular H/H exchange mechanism recently proposed for $Re(CO)H_2(PR_3)_2(NO)$ complexes.[11]

(2) $H_{bridging}$(tetrahydroborate)/$H_{terminal}$(tetrahydroborate) Exchange. The exchange process between terminal and bridging hydrogen atoms of a tetrahydroborate ligand coordinated in a bidentate mode is generally considered to involve a change in the coordination mode of the ligand.[17,25] That is, there are in principle two possible mechanisms: via a monodentate[26] BH_4 ligand (dissociative mechanism)[27] and via a tridentate BH_4 ligand (associative mechanism). We started our search for the transition state of the exchange process with the optimization of two different complexes containing “ideal” monodentate and tridentate BH_4 ligands that were obtained by forcing a local C_{3v} symmetry on the Os−BH_4 fragment. These optimized structures, neither of them corresponding to a stationary point, and both of them quite high in energy (more than 30 kcal/mol above the minimum), were used as starting points for the direct search of the transition state in the full potential energy hypersurface. Both calculations led to the same stationary point, which we label as structure **3** (Figure 3, third column of Table 1). It has a single negative eigenvalue in the estimated hessian, as corresponds to a transition state. The transition vector corresponds essentially to a rotation of the tetrahydroborate ligand around the B−H_5 axis. This process leads to the exchange between the positions of H_6 and H_7, and therefore structure **3** is the transition state for the $H_{bridging}$(tetrahydroborate)/$H_{terminal}$(tetrahydroborate) exchange.



3

Figure 3. MP2 optimized geometry of **3**, the transition state for the $H_{bridging}$(tetrahydroborate)/$H_{terminal}$(tetrahydroborate) exchange process. Hydrogen atoms of the phosphine ligands are omitted for clarity.

Transition state **3** can be described as a monodentate BH_4 complex-like structure. There is certainly only one bridging hydrogen atom (Os−H_5 = 1.850 Å, Os−H_6 = Os−H_7 = 2.532 Å). Therefore, it must be concluded that the exchange mechanism follows a dissociative pathway. This result can actually be explained with the electron counting concepts previously applied to the rationalization of BH_4 coordination.[28,29] The basic idea is that BH_4 behaves as a 2-, 4-, or 6-electron donor, depending on whether its coordination mode is monodentate, bidentate, or tridentate, respectively. Applying this criterion, the equilibrium structure **1** happens to be an 18-electron complex, while the dissociative pathway transition state **3** is a

---

(23) (a) Jarid, A.; Moreno, M.; Lledós, A.; Lluch, J. M.; Bertrán, J. *J. Am. Chem. Soc.* **1993**, *115*, 5861. (b) Jarid, A.; Moreno, M.; Lledós, A.; Lluch, J. M.; Bertrán, J. *J. Am. Chem. Soc.* **1995**, *117*, 1069.

(24) Clot, E.; Leforestier, C.; Eisenstein, O.; Pélissier, M. *J. Am. Chem. Soc.* **1995**, *117*, 1797.

(25) Green, M. L. H.; Wong, L.-L. *J. Chem. Soc., Dalton Trans.* **1989**, 2133.

(26) (a) Tagusagawa, F.; Fumagalli, A.; Koetzle, T. F.; Shore, S. G.; Schmitkons, T.; Fratini, A. V.; Morse, K. W.; Wei, C.-Y.; Bau, R. *J. Am. Chem. Soc.* **1981**, *103*, 5165. (b) Ghilardi, C. A.; Midollini, S.; Orlandini, A. *Inorg. Chem.* **1982**, *21*, 4096. (c) Bau, R.; Yuan, H. S.; Baker, M. V.; Field, L. V. *Inorg. Chim. Acta* **1986**, *114*, L27. (d) Jensen, J. A.; Girolami, G. S. *Inorg. Chem.* **1989**, *28*, 2107.

(27) (a) Williams, R. E. *Inorg. Nucl. Chem.* **1961**, *20*, 198. (b) James, B. D.; Nanda, R. K.; Wallbridge, M. G. H. *J. Chem. Soc. A* **1966**, 182. (c) Letts, J. B.; Mazanec, T. J.; Meek, D. W. *J. Am. Chem. Soc.* **1982**, *104*, 3898.

(28) Mancini, M.; Bougeard, P.; Burns, R. C.; Mlekuz, M.; Sayer, B. G.; Thompson, J. I. A.; McGlinchey, M. J. *Inorg. Chem.* **1984**, *23*, 1072.

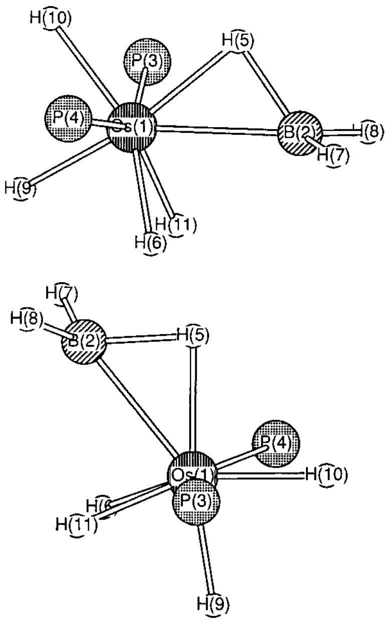
(29) (a) Lledós, A.; Duran, M.; Jean, Y.; Volatron, F. *Inorg. Chem.* **1991**, *23*, 4440. (b) Lledós, A.; Duran, M.; Jean, Y.; Volatron, F. *Bull. Soc. Chim. Fr.* **1992**, *129*, 216. (c) Volatron, F.; Duran, M.; Lledós, A.; Jean, Y. *Inorg. Chem.* **1993**, *32*, 951. (d) Jarid, A.; Lledós, A.; Jean, Y.; Volatron, F. *Inorg. Chem.* **1993**, *32*, 4695. (e) Jarid, A.; Lledós, A.; Jean, Y.; Volatron, F. *Chem. Eur. J.* **1995**, *1*, 436.

16-electron species, an electron count that is by no means uncommon, especially for transition states. A hypothetical associative pathway transition state would be however a 20-electron species, a certainly uncommon electron count, the associative pathway being therefore quite unlikely. Both our result and the qualitative reasoning just presented support strongly the feasibility of the dissociative pathway for the exchange mechanism between bridging and terminal hydrogen atoms of the BH_4 ligand in the $OsH_3(BH_4)(PR_3)_2$ system. Contradiction between this result and those proposing an associative pathway for the $(BH_4)Mn(CO)_4$ and $(BH_4)Cu(PH_3)_2$ systems[30] is only an illusion, since we feel that the differences can be traced back to the diverse electron counting of the complexes. Apart from the change in the coordination mode of tetrahydroborate, the structure of **3** is quite similar to that of **1**. In particular, the three hydride ligands keep their character as such unchanged ($H_9-H_{10} = 1.484$ Å, $H_9-H_{11} = 1.607$ Å).

The energy of transition state **3** is *ca.* 21 kcal/mol above that of equilibrium structure **1** (Table 2). Again, relative energies are similar at the three computational levels, with a difference of only 1.6 kcal/mol between the different methods. Our computed value is substantially higher than reported values of 7.6 kcal/mol for $(C_5H_5)_2V(BH_4)$,[18a] 8.3 kcal/mol for $(C_5H_5)_2Ta(PMe_3)(H_3BSi(^tBu)_2)H$,[18b] and 10 kcal/mol for $[Mo(CO)_4(BH_4)]^-$.[18c] However, this does not necessarily mean that our theoretical result is incorrect. A wide range of energy barriers can be deduced from available experimental data: the complexes just mentioned, such as $OsH(\eta^2BH_4)(CO)(PMe(^tBu)_2)_2$,[31] show $H_{bridging}/H_{terminal}$ exchange at room temperature, while $IrH_2(\eta^2\text{-}BH_4)L_2$ (L = bulky tertiary phosphine)[32] and $OsH_3(\eta^2BH_4)(P(c\text{-}C_5H_9)_3)_2$[20] do not. We interpret our computational result only as an indication that the barrier for the $H_b(BH_4)/H_t(BH_4)$ in complex $OsH_3(BH_4)(PR_3)_2$ lies near the upper limit of the wide range of possible energy barriers for this type of process.

(3) H(hydride)/H(tetrahydroborate) Exchange. Although the existence of an intramolecular exchange process between a hydride ligand and the bridging hydrogen atoms of a BH_4 ligand has been postulated before for the $(C_5H_5)_2ZrH(\eta^2BH_4)$[19] and $OsH_3(\eta^2BH_4)(P(c\text{-}C_5H_9)_3)_2$ complexes,[20] as far as we know no detailed mechanistical proposals have been made for this reaction. This poses a particularly complicated problem for the theoretical study, since the absence of any previous information on the nature of the transition state forces the use of a trial-and-error strategy with different regions of the potential energy hypersurface. We will not go into the lengthy details of this search, but we want to mention that we tried geometries containing BH_3 and BH_5 ligands,[33] and that dihydrogen coordination was not discarded a priori. This search for zero-gradient stationary points in different areas of the potential hypersurface was only successful in one particular region, where two stationary points were located. A discussion of the particular features of these two stationary points is presented in the following paragraphs.

The first of the stationary points we located, labeled as structure **4** (Figure 4, fourth column of Table 1), happens to be a local minimum in the MP2 potential hypersurface: all the eigenvalues of its estimated hessian are positive. The most remarkable geometrical feature of structure **4** is the existence of a BH_3 ligand. The boron atom is bound to only three hydrogen atoms, H_5, H_7, and H_8, the eventual bonds with H_6 and H_{11} being completely broken (B−H distances of 2.300 Å). Apart from this, the $Os-H_6$, $Os-H_{11}$, and H_6-H_{11} distances (1.588, 1.588, and 1.507 Å, respectively), as well as the H_6-Os-H_{11} bond angle (56.7°), indicate no bonding interaction between H_6 and H_{11}. Therefore, **4** must be formulated as a $OsH_4(BH_3)(PH_3)_2$ complex. To our knowledge, complexes containing the BH_3 ligand have not been characterized yet as stable species, but their existence as intermediates has received recent support from both theoretical[34a] and experimental[34b] grounds.



4

Figure 4. MP2 optimized geometry of **4**, the intermediate in the H(hydride)/H(tetrahydroborate) exchange process. Hydrogen atoms of the phosphine ligands are omitted for clarity.

The sheer novelty of BH_3 coordination calls for some discussion on the bonding features of this ligand in complex **4**. Coordination seems to be of an η^2 B−H type, with Os−B and $Os-H_5$ distances of 2.118 and 1.744 Å, respectively. The existence of such a σ bond complex can be easily placed in the context of the growing number of characterized σ bond complexes.[3b] Moreover, the usual molecular orbital reasonings can be applied to justify its stability in terms of donation to the metal atom from the B−H σ orbital and back-donation from the metal atom to the ligand. However, we find in this particular ligand the peculiarity that back-donation from the metal is not to the B−H σ^* orbital, but rather to a p_π orbital of the boron atom that is actually nonbonding with the hydrogen atom. Therefore, one should not expect the breaking of B−H bond, *i.e.*, the oxidative addition reaction, even if there were strong back-bonding.

The second stationary point we located in this region of the potential hypersurface, labeled as structure **5** (Figure 5, fifth column of Table 1), is a transition state, with one negative eigenvalue in the approximate hessian matrix. The main component of the transition vector corresponds to rotation of H_6 and H_{11} around the Os−X axis (with X being now the midpoint between H_6 and H_{11}). Structure **5** is quite similar to **4**, and the main difference between them, mostly the position of H_6, is in the direction of making it more similar to **1**, which is precisely the direction of the transition vector. Therefore, it seems safe to say that transition state **5** connects the local

---

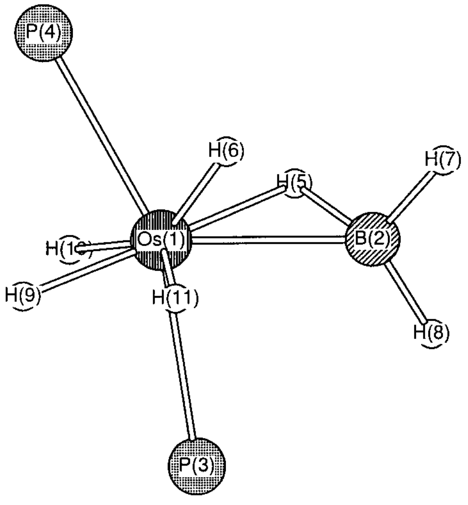
(30) Oishi, Y.; Albright, T. A.; Fujimoto, H. *Polyhedron* **1995**, *14*, 2603.

(31) Werner, H.; Esteruelas, M. A.; Meyer, U.; Wrackmeyer, B. *Chem. Ber.* **1987**, *120*, 11.

(32) Empsall, H. D.; Mentzer, E.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1975**, 861.

(33) (a) Kreevoy, M. M.; Hutchins, J. E. C. *J. Am. Chem. Soc.* **1972**, *94*, 6371. (b) Olah, G. A.; Westerman, P. W.; Mo, Y. K.; Klopman *J. Am. Chem. Soc.* **1972**, *94*, 7859.

(34) (a) Dorigo, A. E.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 115. (b) Hartwig, J. F.; De Gala, S. R. *J. Am. Chem. Soc.* **1994**, *116*, 3661.



5

Figure 5. MP2 optimized geometry of **5**, the transition state for the H(hydride)/H(tetrahydroborate) exchange process. Hydrogen atoms of the phosphine ligands are omitted for clarity.

minima **1** and **4**. We can envisage an exchange process for the hydrogen atoms labeled as H_6 and H_{11} starting from structure **1**, where H_6 is in a bridging position, going through transition state **5** to structure **4**, where H_6 and H_{11} are in equivalent positions, and then continuing through a transition state **5′** to a species **1′**, where the positions of H_6 and H_{11} would be exchanged. In other words, intermediate **4** and transition state **5** completely define a reaction mechanism for the H(hydride)/H(tetrahydroborate) exchange process, a mechanism that has never before been characterized. There is little to be said about the nature of structure **5** apart from its nature as transition state. The $B-H_6$ bond is already broken (2.054 Å), and the H_6-H_{11} distance (1.616 Å) is much closer to its value in **4** (1.507 Å) than to that in **1** (2.301 Å). In summary, it is very similar to **4**.

Relative energies of **4** and **5** with respect to **1** are included in Table 2. The first remarkable detail of the energies of these two complexes is how close they are at all the computational levels, with differences in relative energies between 0.5 and 0.8 kcal/mol. On one hand, this is just a reflection of the similarity in their geometrical features that has been mentioned above. On the other hand, this has the important chemical consequence that complex **4** must be at best an intermediate of short lifetime, since it is quite high above the absolute minimum, and separated from it by a very small energy barrier. In truth, these results do not even provide a definite proof of the existence of **4** as a local minimum, since we feel that the methodological precision for this type of system is below 0.5 kcal/mol. A second detail we want to mention from Table 2 is that the relative energies of **4** and **5** are far more dependent on the method than those of **2** and **3**, with a difference above 3.5 kcal/mol when going from MP2 to CCSD(T). We attribute this to the flatness of the potential energy hypersurface associated with the close placement of an intermediate and a transition state. In other words, we consider the error associated with the use of MP2 geometries to be larger in **4** and **5** than in **1**, **2**, and **3**, and therefore expect the real barrier (that should be obtained with CCSD(T) calculations on computationally unaffordable CCSD(T) geometries) to be closer to 15 than to 19 kcal/mol. The final comment on the energies of **4** and, especially, **5** concerns the energy barrier they suggest for this particular exchange process. The absolute number is reasonably close to the measured value of 20.9 kcal/mol for $(C_5H_5)_2ZrH(\eta^2BH_4)$, although this agreement is probably accidental, since the systems are quite different.[19] More significant is the fact that in our particular system the energy barrier for the H(hydride)/H(tetrahydroborate) exchange appears well separated from those for the H(hydride)/H(hydride) and H_b(tetrahydroborate)/H_t(tetrahydroborate) computed in the previous sections. One should therefore expect significantly different temperatures of coalescence for the eventual processes of fluxionality.

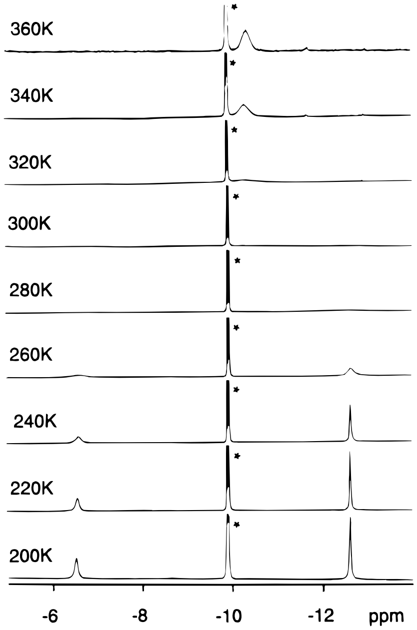


Figure 6. Variable-temperature ^1H NMR spectra of $OsH_3(BH_4)(P^iPr_3)_2$ in toluene-d^8. The signal marked with an asterisk, remaining unchanged in all temperatures, corresponds to $OsH_6(P^iPr_3)_2$, which is present as an impurity in a 25% yield.

(4) Variable−Temperature ^{1}H NMR Spectrum of $OsH_3(BH_4)(P^iPr_3)_2$. According to the structure shows in Chart 1, four different ^1H NMR signals should be expected in the hydride region for complex $OsH_3(BH_4)(P^iPr_3)_2$, corresponding to H_A, H_B, H_b, and H_t, respectively. Measurements in toluene-d_8 solvent at 200 K yield a spectrum containing, apart from the triisopropylphosphine signals, three broad resonances with an intensity ratio of 2:2:3, at 8.84, −6.51 and −12.61 ppm. We assign these three signals to the terminal hydrogen atoms on boron H_t, the bridging hydrogen atoms on boron H_b, and the terminal hydride ligands on osmium H_A and H_B, respectively.

The presence of only one resonance for the nonequivalent H_A and H_B atoms indicates the existence a fast (on the NMR time scale) exchange process between these hydrogen atoms. This process is rapid even at 153 K (measured in a 1:5 mixture of dichloromethane-d_2 and toluene-d_8), the lowest temperature we can reach. Therefore, we conclude that the energy barrier for this H(hydride)/H(hydride) exchange process is quite low, definitely lower than that of any of the other hydrogen exchange processes possible for this system. The theoretically computed activation barrier for this process of *ca.* 10 kcal/mol presented above is consistent with this experimental result.

On raising the temperature, the resonances due to the bridging hydrogen atoms on boron H_b and the terminal hydrogen atoms on osmium H_A and H_B coalesce at 300 K to give finally a broad resonance, as shown in Figure 6. We were able to measure the activation parameters for this H(hydride)/H(tetrahydroborate) exchange process from the variable-temperature ^1H NMR experiments. The free energy barrier of the process at coalescence was calculated using the temperature of coalescence (300 K) of the resonances and the chemical shift differences of these resonances projected from the slow exchange limit ($\delta\nu = 1830$ Hz). We obtained a value of 13 ± 2 kcal/mol for $\Delta G^\ddagger$. Linear least-squares analysis of the Eyring plot for the kinetic data provided values of $\Delta H^{\ddagger} = 12 \pm 1$ kcal/mol and $\Delta S^{\ddagger} = -4.5 \pm 2.7$ eu. These measured values for $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ can be compared with the computed values for $\Delta E^{\ddagger}$ for this H(hydride)/H(tetrahydroborate) process, which range from 15.4 kcal/mol at the MP2 level to 19.0 kcal/mol at the CCSD(T) level. Although the experimental results are somehow smaller than the computed values, we consider the agreement satisfactory. Moreover, the qualitative features of the experimental system are properly reproduced, with the H(hydride)/H(tetrahydroborate) exchange process being the second fastest after H(hydride)/H(hydride).

Coalescence with the signal at 8.84 ppm, corresponding to the terminal hydrogen atoms attached to boron H_t, could not be observed in the range of temperatures studied. However, we want to mention the broadening of this resonance on raising the temperature. Certainly, at 360 K, the highest temperature we used, the spectrum shows two broad resonances centered at 8.79 and −10.34 ppm, along with those of the triisopropylphosphine ligands. This behavior of the spectrum suggests that a very slow (on the NMR time scale) H_b/H_t may be taking place, but that its effects on the ^{1}H NMR spectrum would only be apparent at higher temperatures. Again, there is no contradiction with the theoretical results presented above. The computed barrier for the $H_{bridging}$(tetrahydroborate)/$H_{terminal}$(tetrahydroborate) exchange was above 20 kcal/mol at all the computational levels, and this is by no means a warranty of NMR equivalence in the range of temperatures being considered.

A last bit of information that can be extracted from the experiment is the confirmation of the intramolecular nature of all these processes. In principle, a bimolecular mechanism involving dissociation of molecular hydrogen could also lead to hydrogen exchange. Such a mechanism, which already looked unlikely from the close to zero value of $\Delta S^{\ddagger}$ presented above, could be ruled out by additional experiments. In the first place, the same variable-temperature ^{1}H NMR experiments were repeated under hydrogen atmosphere, and the resulting spectra were very similar to those discussed above. Finally, H/D exchange between molecular deuterium and $OsH_3(BH_4)(P^iPr_3)_2$ could not be observed between 153 and 360 K. Therefore, the intramolecular nature of all hydrogen exchange processes in $OsH_3(BH_4)(P^iPr_3)_2$ is definitely confirmed.

Results of the experimental ^{1}H NMR study are in full agreement with the existence of the three exchange mechanisms predicted by theoretical calculations, and with the precise ordering of their activation barriers found by the calculations. The validity of this part of the theoretical results is therefore fully confirmed. Moreover, this agreement provides strong support for the reliability of all the calculations presented in the previous sections, including the aspects that cannot be determined by these ^{1}H NMR experiments, notably the detailed mechanisms of the exchange processes.

Conclusions

The ab initio theoretical study of the hydride exchange processes in the $OsH_3(BH_4)(PH_3)_2$ system has allowed the characterization of three different intramolecular rearrangements, with the determination of their mechanisms and activation barriers. The lowest energy barrier is associated with the H(hydride)/H(hydride) exchange. This process, consisting of an out-of-plane twist of two adjacent hydride ligands, goes through an η^2 H_2 complex-like transition state. The second lowest energy barrier corresponds to the H(hydride)/H(tetrahydroborate) exchange. In this case, the process goes through a 7-coordinate intermediate containing a BH_3 ligand coordinated in an η^2 H−B fashion. This constitutes the first theoretical characterization at the ab initio level of an H(hydride)/H(tetrahydroborate) rearrangement process. Finally, the highest energy barrier is associated with the exchange process between the bridging and terminal hydrogens of the tetrahydroborate ligand. This rearrangement goes via a dissociative mechanism, the transition state containing a monodentate BH_4 ligand.

The variable-temperature ^{1}H NMR spectra of $OsH_3(BH_4)(P^iPr_3)_2$, recorded from 153 to 360 K, are fully consistent with the results of the theoretical calculations. There is only one signal for the terminal hydrogen atoms attached to osmium in the temperature range explored. This indicates the existence of a fast H(hydride)/H(hydride) exchange process. The signals corresponding to H(hydride) and $H_{bridging}$(tetrahydroborate), separated at low temperature, coalesce in a single resonance at high temperature. The barrier for the H(hydride)/$H_{bridging}$(tetrahydroborate) exchange is therefore higher than that of the H(hydride)/H(hydride) exchange process. Experimentally measured activation parameters for this second exchange process are in reasonable agreement with the computed energy barrier. The third exchange process predicted theoretically, $H_{bridging}/H_{terminal}$, is not directly observed in the NMR spectra. Again, this is consistent with its higher barrier, which should make it observable only at higher temperatures. A last significant result obtained from the experiment is the confirmation of the intramolecular nature of all these processes.

The results presented in this paper for the $OsH_3(BH_4)(PR_3)_2$ system constitute just an example of the wealth of dynamic phenomena associated with the intramolecular rearrangement of hydrogen atoms in the coordination sphere of transition metal complexes, and of the intricate relationship between them. We can still expect new phenomena to be discovered in this exciting field.

Experimental Section

Ab Initio Calculations. All calculations were performed with molecular orbital ab initio methods as implemented in the Gaussian 92 system of programs.[35] Correlation energy through the Møller−Plesset (MP) perturbation approach[36] up to the second (MP2) and fourth (MP4(SDTQ)) levels was applied in most of the cases. Some calculations were also carried out with the coupled-clustered method (CC).[37] In this case, simple and double excitations, as well as a perturbative estimation of the triple excitations, were used (CCSD(T)). In all cases, excitations concerning the lowest energy electrons were neglected (frozen core approach).

Effective core potentials were used to represent the 60 innermost electrons (up to the 4d shell) of the osmium atom,[38] as well as the 10-electron core of the phosphorus atoms.[39] The basis set for the metal atom was that associated to the pseudopotential,[38] with a (541/41/111) contraction,[40] which is triple-ζ for the 5d shell. For the phosphorus atoms, a valence double-ζ basis set[39] was used. The 6-31G(d,p) basis set[41] was used for the boron and most of the hydrogen atoms, with the only exception being the hydrogens atoms of the triphosphine ligands, which were described with the 3-21G basis set.[42]

All geometry optimizations were carried out at the MP2 level. All geometrical parameters were optimized except the dihedral angle of

---

(35) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andrés, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*; Gaussian Inc.: Pittsburgh, PA, 1992.

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

(37) (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.

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

(39) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.

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

(41) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (c) Dill, J. D.; Pople, J. A. *J. Chem. Phys.* **1975**, *26*, 2921.

(42) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

one of the hydrogen atoms of each phosphine ligand, which was fixed in order to avoid chemically meaningless rotations around the M−P axis. First derivatives (gradient) of the energy with respect to the geometrical parameters were computed analytically by the program, the characterization of zero-gradient stationary points being therefore definite. Second derivatives (hessian) of the energy with respect to the geometrical parameters cannot be computed analytically by the program. Instead, they are computed numerically for some selected geometrical variables at certain steps of the geometry optimization process. Therefore, the hessians, and the assignment of stationary points as minima or transition states based on its number of negative eigenvalues, are always approximate. However, we are quite confident of the qualitative accuracy of these hessians, because common experience shows that transition states are almost impossible to locate without a proper value of the hessian. Single-point energy-only calculations were carried out on the MP2 optimized geometries at the more sophisticated MP4(SDTQ) and CCSD(T) computational levels.

Acknowledgment. We acknowledge financial support from the Spanish “Dirección General de Investigación Científica y Técnica” (DGICYT) under project Nos. PB-920092 and PB-920621 and from the European Union under the project “Selective Processes and Catalysis Involving Small Molecules”. Use of the computational facilities of the “Centre de Supercomputació de Catalunya” (CESCA) is also acknowledged.

JA9526170