Inorg. Chem. **1994**, *33*, 3609-3611

Preparation and Spectroscopic and Theoretical Characterization of the Tetrahydroborate Complex $OsH_3(\eta^2\text{-}H_2BH_2)(P\text{-}i\text{-}Pr_3)_2$

Miguel A. Esteruelas,*,† Yves Jean,§ Agustí Lledós,*,‡ Luis A. Oro,† Natividad Ruiz,† and François Volatron§

Departamento de Química Inorgánica, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain, Departament de Quimica, Universitat Autonoma de Barcelona, 08193 Bellaterra, Barcelona, Spain, and Laboratoire de Chimie Théorique (CNRS URA 506, ICMO), Bât. 490, Université de Paris-Sud, 91405 Orsay Cedex, France

Received December 10, 1993

There is considerable experimental evidence indicative of the action of tetrahydroborate compounds as effective catalyst precursors for isomerization, oligomerization and hydrogenation of olefins.[1] In this line, we have previously reported that the complex $OsHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ in the presence of $NaBH_4$ serves as a catalyst for hydrogen transfer reactions from 2-propanol to cyclohexanone, acetophenone,[2] benzylideneacetone, and benzylideneacetophenone.[3] Under catalytic conditions, the compound $OsHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ reacts with $NaBH_4$ to give initially the tetrahydridoborate complex $OsH(\eta^2\text{-}H_2BH_2)(CO)(P\text{-}i\text{-}Pr_3)_2$, which in the presence of 2-propanol descomposes to the tetrahydride $OsH_4(CO)(P\text{-}i\text{-}Pr_3)_2$.[2-4]

The complex $OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2$ is also an active catalyst for the hydrogen transfer reactions from 2-propanol to ketones in the presence of $NaBH_4$.[5] Under catalytic conditions, in this case, the hexahydride $OsH_6(P\text{-}i\text{-}Pr_3)_2$ can be detected. We have now observed that the formation of $OsH_6(P\text{-}i\text{-}Pr_3)_2$ from $OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2$ and $NaBH_4$ goes by an $OsH_3(BH_4)(P\text{-}i\text{-}Pr_3)_2$ intermediate. In the present Note, we describe the preparation and the spectroscopic and theoretical characterization of this intermediate.

Treatment of a toluene suspension of $OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2$ with $NaBH_4$, in a 1:10 molar ratio, and methanol (ca. 0.6 mL), at −78 °C, leads to a yellow solution from which is separated a yellow solid. The IR and ^1H and ^{31}P NMR spectra of this solid indicate that it is a mixture of the complexes $OsH_3(BH_4)(P\text{-}i\text{-}Pr_3)_2$ and $OsH_6(P\text{-}i\text{-}Pr_3)_2$ in a 3:1 molar ratio. At room temperature, the mixture is quantitatively converted into $OsH_6(P\text{-}i\text{-}Pr_3)_2$ by stirring in methanol.

Different structures are possible for an $OsH_3(BH_4)(P\text{-}i\text{-}Pr_3)_2$ formulation, depending on the way the $[BH_4]^-$ ligand and the H_3 fragment are bound to the metal. The $[BH_4]^-$ ligand can bind the transition metal with one (η^1), two (η^2), or three (η^3) bridging hydrogens. The H_3 fragment can present a trihydride or hydride–molecular hydrogen nature.

The IR spectrum of the yellow solid in Nujol shows absorptions at 2447 and 2351 cm^{-1} suggesting that the tetrahydroborate anion coordinates to the osmium atom as an $\eta^2\text{-}H_2BH_2$ ligand.[6] This is in agreement with the 18-electron rule, which predicts for the tetrahydroborate anion of $OsH_3(BH_4)(P\text{-}i\text{-}Pr_3)_2$ a η^2-coordination mode.[7] In order to confirm this prediction we perform ab initio calculations in the model adduct $OsH_3(BH_4)(PH_3)_2$. In a preliminary study, the geometries of the three structures which differ by the coordination mode of the $[BH_4]^-$ anion (η^1, η^2, and η^3) were optimized at the SCF level. At this level, the structure containing the $\eta^2\text{-}H_2BH_2$ ligand is 23.9 kcal/mol more stable than that containing the $[BH_4]^-$ anion coordinated as η^1-ligand, and 28.2 kcal/mol more stable than the structure corresponding to an $\eta^3\text{-}H_3BH$ group. Moreover, the η^1 and η^3 structures are not stable and collapse to the η^2 one. However, the SCF calculations can not solve the question of the H_3 fragment coordination. The $\eta^2\text{-}H_2BH_2$ structures with a trihydride disposition of the three hydrogen atoms and with a hydride–molecular hydrogen arrangement are both minima in the SCF potencial energy surface and have the same energy.

The $^{31}P\{^1H\}$ NMR spectrum of the mixture in toluene-d_6 shows two singlets at 56.78 and 41.67 ppm, which were assigned to the complexes $OsH_6(P\text{-}i\text{-}Pr_3)_2$ and $OsH_3(BH_4)(P\text{-}i\text{-}Pr_3)_2$ respectively. This spectrum is temperature invariant down to −80 °C. However, the ^1H NMR spectrum is temperature dependent (Figure 1). These spectra suggest that in solution there is an intramolecular exchange process involving to the $Os(\mu\text{-}H)B$ and OsH_3 hydrogen atoms.

The most noticeable signals of the spectrum at −60 °C are three broad resonances of the tetrahydroborate complex with an intensity ratio 2:2:3, at 8.78, −6.78, and −12.89 ppm, which were assigned to hydrogen atoms terminal on boron, bridging and terminal on osmium. Interestingly T_1(min) values at 300 MHz of 74 and 82 ms were found for the resonances at −6.78 and −12.89 ppm. At first glance, these data could suggest the existence of nonclassical interaction between the hydrogen atoms bonded to the metallic center.[8] We note that the structure of the related complex $OsH_3(\eta^2\text{-}H_2BH_2)(P(c\text{-}C_5H_9)_3)_2$ has been previously determined by a single-crystal X-ray diffraction study.[9] However, unfortunately, the terminal hydrogen atoms on the osmium were not located. As a result from this, the trihydrido or hydrido–dihydrogen nature of these compounds can not be determined. In order to cast light on this problem, the geometries of the two minima (trihydride and hydride–dihydrogen) found at the SCF level were reoptimized at the MP2 level. At this level, the molecular hydrogen complex is not stable and its optimization leads to the trihydride. Only the trihydride structure remains as a minimum in the MP2 potential energy surface. Therefore, the ab initio MP2 calculations indicate that the only stable structure corresponds to a trihydride with a $\eta^2\text{-}H_2BH_2$ coordination.

Figure 2 shows the molecular structure of $OsH_3(BH_4)(PH_3)_2$ optimized at the MP2 level. The most conspicuous features of the theoretical calculations are, first that the structural parameters agree well with that found for the complex $OsH_3(\eta^2\text{-}H_2BH_2)(P(c\text{-}C_5H_9)_3)_2$ by X-ray diffraction analysis[9] and, second, the hydrogen–hydrogen separations between the hydrogen atoms of the OsH_3 unit (1.579, 1.598), are about 0.05 Å shorter than that determined by neutron diffraction investigation in the hexahydride $OsH_6(PC_{12}H_{19})_2$, where an H···H interaction has been proposed.[10]

---

† Universidad de Zaragoza-CSIC.
‡ Universitat Autonoma de Barcelona.
§ Université de Paris-Sud.

(1) (a) Green, M. L. H.; Munakata, H. *J. Chem. Soc. A.*, **1974**, *269*. (b) Miller, R. G.; Pinke, P. A.; Stanfer, R. D.; Golden, H. J.; Baker, D. J. *J. Am. Chem. Soc.* **1974**, *96*, 4211. (c) Holah, D. G.; Hughes, A. N.; Hui, B. C.; Kan, C. T. *J. Catal.* **1977**, *48*, 340. (d) Letts, J. B.; Mazanec, T. J.; Meek, D. W. *J. Am. Chem. Soc.* **1982**, *104*, 3898.

(2) (a) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Werner H.; Meyer, U. *J. Mol. Catal.* **1988**, *45*, 1. (b) Esteruelas, M. A.; Valero, C.; Oro, L. A.; Meyer, U.; Werner H. *Inorg. Chem.* **1991**, *30*, 1159.

(3) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Werner H.; Meyer, U. *J. Mol. Catal.* **1989**, *53*, 43.

(4) (a) Werner, H.; Esteruelas, M. A.; Meyer, U.; Wrackmeyer, B. *Chem. Ber.* **1987**, *120*, 11. (b) Esteruelas, M. A.; Lahoz, F. J.; López, J. A.; Oro, L. A.; Schlünken, C.; Valero, C.; Werner, H. *Organometallics*, **1992**, *11*, 2034.

(5) Aracama, M.; Esteruelas, M. A.; Lahoz, F. J.; López, J. A.; Meyer, U.; Oro, L. A.; Werner, H. *Inorg. Chem.* **1991**, *30*, 288.

(6) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263.

(7) (a) Mancini, M.; Bougeard, P.; Burns, R. C.; Mlekuz, U.; Sayer, B. G.; Thompson, J. I. A.; Mc Glinchey, M. J. *Inorg. Chem.* **1984**, *23*, 1072. (b) Lledós, A.; Duran, M.; Jean, Y.; Volatron, F. *Inorg. Chem.* **1991**, *23*, 4440. (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.

(8) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155.

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

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

0020-1669/94/1333-3609$04.50/0

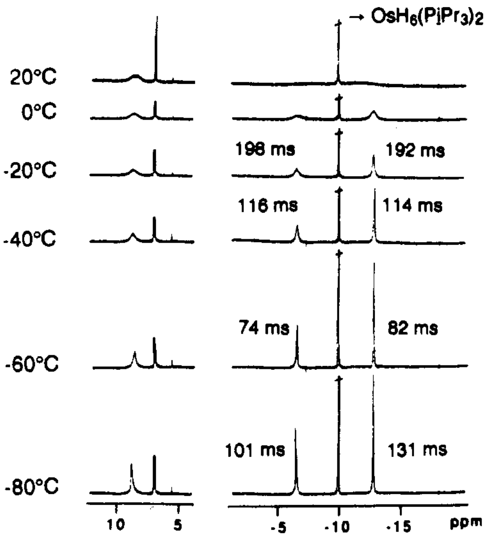

Figure 1. ^1H NMR spectra (300 MHz, C_7D_8) at variable temperature for the complex $OsH_3(BH_4)(P\text{-}i\text{-}Pr_3)_2$. The observed T_1 values are written on the peaks.

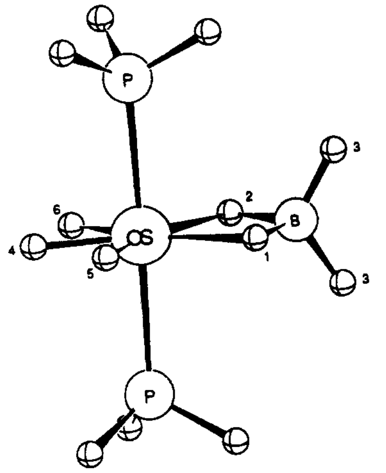

Figure 2. Molecular structure of the model compound $OsH_3(BH_4)(PH_3)_2$ optimized at the MP2 level. Selected bond distances (Å): Os–B = 2.305, Os–P = 2.391, Os–H(1) = 1.817, Os–H(2) = 1.813, Os–H(4) = 1.59, Os–H(5) = 1.579, Os–H(6) = 1.579, B–H(1) = 1.311, B–H(2) = 1.307, B–H(3) = 1.195, H(1)–H(5) = 2.309, H(2)–H(6) = 2.301, H(4)–H(6) = 1.579, H(4)–H(5) = 1.598.

From the analysis of the electron density contour map generated by the ab initio MO calculations, we have not found evidences for any electronic interaction between the hydrogen atoms of the OsH_3 unit of $OsH_3(BH_4)(PH_3)_2$.

It has been recently shown that for polyhydrido complexes, T_1(min) can be calculated by using internuclear distances obtained from neutron or X-ray diffraction studies.[11] In order to test the results obtained from the theoretical studies, we have determined the T_1(min) values for the hydrogen bonded to the metallic center of the model complex $OsH_3(BH_4)(PH_3)_2$,[12] on the basis of the calculated structural parameters. Because at the T_1(min) temperature the ^1H NMR spectrum of $OsH_3(BH_4)(P\text{-}i\text{-}Pr_3)_2$ contains two signals assigned to the hydrogen atoms of the $Os(\mu\text{-}H)_2B$ and OsH_3 units, we have calculated a T_1(min) for H_1 and H_2, and other for H_4, H_5, and H_6.[13] The obtained values converted to the 300-MHz scale (57 ms for for H_1 and H_2, and 85 ms for H_4, H_5, and H_6) agree sufficiently well with those determined experimentally for the related protons of $OsH_3(BH_4)(P\text{-}i\text{-}Pr_3)_2$.

In addition, it should be mentioned that the T_1(min) value of the $Os(\mu\text{-}H)B$ protons is shorter than the T_1(min) value of the OsH_3 protons. This clearly indicates that the boron atoms have a bigger influence in the relaxation of the $Os(\mu\text{-}H)B$ protons than the other atoms of the molecule.

In summary, the reaction of $OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2$ with $NaBH_4$ leads to $OsH_3(\eta^2\text{-}H_2BH_2)(P\text{-}i\text{-}Pr_3)_2$, which decomposes to $OsH_6(P\text{-}i\text{-}Pr_3)_2$ in methanol at room temperature. Spectroscopic and theoretical studies suggest that the tetrahydroborate compound contains three hydrido ligands with a hydrogen–hydrogen separation of about 1.6 Å. Evidences for any electronic interaction between them have not been found.

Experimental Section

NMR spectra were recorded on a Varian UNITY 300 spectrophotometer. Chemical shifts are expressed in ppm upfield from Me_4Si (^1H) and 85% H_3PO_4 (^{31}P). The conventional inversion-recovery method (180–τ–90) was used to determine T_1. Infrared spectra were recorded with a Perkin-Elmer 783 spectrophotometer.

Preparation of $OsH_3(\eta^2\text{-}H_2BH_2)(P\text{-}i\text{-}Pr_3)_2$. Under an atmosphere of argon at −78 °C, a suspension of $OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2$ (200 mg, 0.35 mmol) in toluene was treated with $NaBH_4$ (133 mg, 0.35 mmol) and then dropwise with 0.6 mL of methanol. After the reaction mixture was stirred for 30 min, the suspension was filtered. The filtrate was concentrated to dryness in vacuo at room temperature, addition of hexane caused the precipitation of a yellow solid after storing at −78 °C for 2 h. The solvent was decanted, and the solid, was washed with small quantities of cold hexane, and dried in vacuo. A yellow solid was isolated, which according to the IR, ^1H, and $^{31}P\{^1H\}$ spectra turned out to be a mixture of $OsH_3(\eta^2\text{-}H_2BH_2)(P\text{-}i\text{-}Pr_3)_2$ and $OsH_6(P\text{-}i\text{-}Pr_3)_2$ in a 3:1 molar ratio. Spectroscopic data for $OsH_3(\eta^2\text{-}H_2BH_2)(P\text{-}i\text{-}Pr_3)_2$ are as follows. IR (Nujol): ν(BH) 2447, 2351, ν(OsH) 2141, 2115 cm^{-1}. ^1H NMR (20 °C, 300 MHz, C_7D_8): δ 8.78 (br, 2 H, $Os(\eta^2\text{-}H_2BH_2)$), 2.04 (m, 6 H, $PCHCH_3$), 1.12 (dvt, N = 13.7, J(HH) = 7.0 Hz, 36 H, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (20 °C, 80.98 MHz, C_7D_8): δ 41.67 (s). ^1H NMR spectra at variable temperature are shown in Figure 1.

Details of the ab Initio Calculations. The ab initio calculations are performed with the GAUSSIAN 92 system of programs.[14] A noncorrelated RHF–SCF description is used for preliminary studies, while the more accurate geometry optimizations are performed at the correlated MP2 level,[15] which seems to be the current state of the art for this kind of systems.[16] The geometries are optimized with the Schlegel method,[17] using analytically computed gradients.

The 60 innermost electrons of the osmium atom are represented by an effective core potential (ECP) including relativistic contributions.[18] The basis set for the metal atom is of triple-ζ quality.[18] The 6-31G**

---

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

(12) Since relaxation rates are additive, the total relaxation rate of a given hydride nucleus may be obtained by summing the contributions from the separate dipole–dipole interactions of this nucleus with all other nuclei according to the equation

$$R_{TOT} = \sum_i R_{H(m)Hi} + \sum_i R_{H(l)Hi} + \sum_i R_{HMi} + \sum_i R_{HPi} + \sum_i R_{HBi}$$

$$R_{HX} = K_X\,Å^6\,s^{-1}/r^6$$

where K_X = constant for the nuclei X and r = internuclear distance in Å. The values of K_X for the nuclei of H, Os and P were taken from ref 11. The constants for ^{10}B and ^{11}B were evaluated using Halpern's method.[11] Solving for these nuclei leads to a values of K_X = 14.52 for ^{10}B (abundance, 18.83%) and 38.14 for ^{11}B (abundance, 81.17%)

(13) For fluxional polyhydrides where inequivalent hydrides are rapidly exchanging, the relaxation rate is the weighted average of the relaxation rate for each type of hydride.[11]

(14) GAUSSIAN 92, Revision C, 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, G.; Martin, R. L.; Fox, D. J.; Defreus, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian Inc. Pittsburgh PA, 1992.

(15) Möller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(16) (a) Lin, Z.; Hall, M. B. *Inorg. Chem.* **1991**, *30*, 2569. (b) Lin, Z.; Hall, M. B. *J. Am. Chem. Soc.* **1992**, *114*, 2928. (c) Maseras, F.; Li, X. K.; Koga, N.; Morokuma, K. *J. Am. Chem. Soc.*, in press.

(17) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.

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

basis set[19] is used for the B and H atoms, excepting the H atoms of triphosphine ligands which are described by the 3-21 G basis set.[20] For the P atoms an ECP complement with a valence double-ζ basis set are used.[21]

Acknowledgment. We thank the DGICYT (Projects PB 92-0092 and PB 92-0621, Programa de Promoción General del Conocimiento) and the EU (Project: *Selective Processes and Catalysis involving Small Molecules*) for financial support. This work greatly benefited from an Acción Integrada Hispano-Francesa (1993/186 B). We thank the European Center for Parallelism of Barcelona, CEPBA, for providing computational time in a CONVEX C-3480 computer.

---

(19) (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**, *62*, 2921.

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

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