Distinct Structures for Ruthenium and Osmium Hydrido Halides: $Os(H)_3X(P^iPr_3)_2$ (X = Cl, Br, I) Are Nonoctahedral Classical Trihydrides with Exchange Coupling

Dmitry G. Gusev,*,† Roger Kuhlman,† Gjergji Sini,‡ Odile Eisenstein,*,‡ and Kenneth G. Caulton*,†

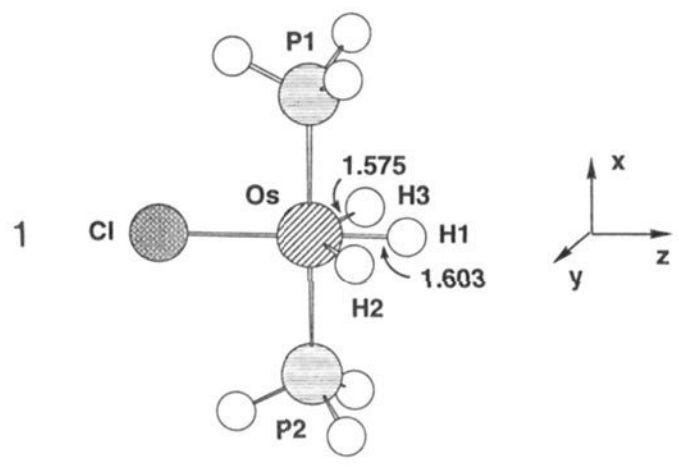
Department of Chemistry, Indiana University Bloomington, Indiana 47405
Laboratoire de Chimie-Théorique, Bâtiment 490 Université de Paris-Sud, 91405 Orsay, France

Received November 15, 1993

There is a qualitative difference between known phosphine (L) polyhydride complexes of Os and Ru. While the former are typically classical (e.g., $Os(H)_6L_2$, $Os(H)_4L_3$, $Os(H)_4(CO)L_2$), the latter generally contain at least one H_2 ligand ($Ru(H)_2(H_2)_2L_2$, $Ru(H)_2(H_2)L_3$, $Ru(H)_2(H_2)(CO)L_2$).[1] The ruthenium compounds $RuH_3X(PCy_3)_2$ (X = Cl, I) have been shown (X-ray diffraction for the iodide example) to be unusual examples of unsaturated (16-electron) *dihydrogen* complexes, $RuH(H_2)X(PCy_3)_2$.[2] Analogous unsaturated osmium compounds were unknown prior to the present report.

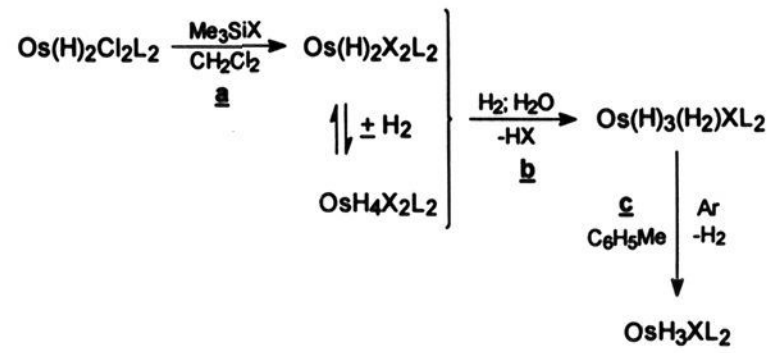
We report here a number of surprising spectroscopic and structural features of the compounds $OsH_3X(P^iPr_3)_2$ (X = Cl, Br, I), which can be prepared according to the high-yield reactions[3] of Scheme 1 (L = P^iPr_3). Step b is a two-phase process and appears to benefit by transport of HX into the aqueous phase. Step c represents verification of a reaction which was proposed earlier[4] to account for the ready exchange of $Os(H)_3(H_2)ClL_2$[5] with free H_2. ^1H NMR spectral data[6] for fluxional OsH_3XL_2 species are consistent with the species being six-coordinate classical trihydrides. The spectra show AB_2 patterns in the hydride region below −80 °C. The T_{1min} values for all three X are 72(2) ms (300 MHz) and permit an estimate of the H_A/H_B distance of 1.64(3) Å.[7] For an Os–H distance of 1.65 Å (the average value in $Os(H)_6(P^iPr_2Ph)_2$ and $Os(H)_4(PMe_2Ph)_3$[1a,b]), this yields a notably small H_A–Os–H_B angle of *ca.* 60°. A search for H–D coupling at various degrees of deuterium incorporation shows that it is less than 2 Hz.

In order to understand these large distortions from an octahedral structure, the model complexes $Os(H)_3X(PH_3)_2$ (X = Cl, Br, I) have been fully optimized by analytical gradient with *ab initio* Hartree–Fock calculations.[8] For these three complexes, the C_{2v} structure **1**, with H1–Os–H2 angles of 58.3° (X = Cl), 58.6° (X = Br), and 58.7° (X = I), was a minimum. Calculations beginning



with a non-C_{2v} structure did not produce an $OsH(H_2)X(PH_3)_2$ minimum but instead minimized at the C_{2v} trihydride structure.[9]

Scheme 1



The PH_3 groups in **1** remain perpendicular to the plane containing the other ligands. In the three complexes, the H1/H2 distance is 1.549 (Cl) and 1.555 Å (Br and I). Since this distance is more than twice that in H_2, we feel that these complexes are best considered as d^4 Os(IV) trihydrides.

The H1–Os–H2 angle value of less than 90° is a consequence of the d^4 electron count at the metal. The octahedral geometry is not favorable for heavy metal d^4 complexes, which prefer to be diamagnetic. These complexes therefore undergo a distortion which destabilizes one orbital from the t_{2g} set and simultaneously stabilizes some occupied orbital(s) (not necessarily part of the t_{2g} set). In contrast to the systems studied by Kubacek and Hoffmann,[10] where deviations from the octahedron were distributed among all interligand angles, only one significant angular change occurs for $Os(H)_3XL_2$. Bending H2 and H3 toward H1 destabilizes primarily d_{yz}, which then becomes hybridized away from H2 and H3 (**2**). This increases the overlap between the hybridized d_{yz} and the p_y halide lone pair, which stabilizes the latter orbital and creates an Os–X π bond (**3**). While an Os–X

† Indiana University.
‡ Université de Paris-Sud.

(1) (a) Howard, J. A. K.; Johnson, O.; Koetzle, T. F.; Spencer, J. L. *Inorg. Chem.* **1987**, *26*, 2930. (b) Hart, D. W.; Bau, R.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 7557. (c) Esteruelas, M. A.; Lahoz, F. J.; López, J. H.; Oro, L. A.; Schlünken, C.; Valero, C.; Werner, H. *Organometallics* **1992**, *11*, 2034. (d) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155.

(2) Chaudret, B.; Chung, G.; Eisenstein, O.; Jackson, A.; Lahoz, F. J.; Lopez, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 2314.

(3) $Os(H)_2Cl_2(P^iPr_3)_2$ was prepared according to: Aracama, M.; Esteruelas, M. A.; Lahoz, F. J.; Lopez, J. A.; Meyer, U.; Oro, L. A.; Werner, H. *Inorg. Chem.* **1991**, *30*, 288. Details of the synthesis of OsH_3XL_2 species are available as supplementary material.

(4) Gusev, D. G.; Kuznetsov, V. F.; Eremenko, I. L.; Berke, H. *J. Am. Chem. Soc.* **1993**, *115*, 5831.

(5) Observation of a 2:1:1:1 upfield ^1H NMR pattern for all of these complexes below −100 °C is consistent with a pentagonal bipyramidal structure containing one H_2 ligand: $Os(H)_3(H_2)XL_2$. Two of the unit intensity resonances of the iodide compound constitute an AB pattern with $J(AB)$ = 605 Hz.[6] We are investigating the possibility of exchange coupling in the chloro and bromo analogs.

(6) NMR data have been reported for $Os(H)_2Cl_2(P^iPr_3)_2$,[3,4] $OsH_4Cl_2(P^iPr_3)_2$,[4] and $Os(H)_3(H_2)Cl(P^iPr_3)_2$.[4] Hydride signals: $Os(H)_3(H_2)Br(P^iPr_3)_2$, ^1H NMR (CD_2Cl_2, toluene-d_8, −110 °C) δ −3.08 (br, 2H, $Os(H_2)$), −4.08 (br, 1H, OsH), −14.68 (br, 1H, OsH), −15.34 (br, 1H, OsH); $Os(H)_3(H_2)I(P^iPr_3)_2$, ^1H NMR (CD_2Cl_2, toluene-d_8, −120 °C) δ ca. −4.6, −5.28 (overlapped, 3H, $Os(H_2)$, OsH), −12.71 (d, J = 605 Hz, 1H, OsH), −16.11 (d, 1H, OsH); $OsH_3Cl(P^iPr_3)_2$, ^1H NMR (toluene-d_8, −100 °C) non-first-order AB_2 pattern, δ_A −14.56, δ_B −21.76, J(H–H) = 920 ± 20 Hz; $OsH_3Br(P^iPr_3)_2$, ^1H NMR (toluene-d_8, −100 °C) non-first-order AB_2 pattern, δ_A −15.15, δ_B −22.08, J(H–H) = 550 ± 20 Hz; $OsH_3I(P^iPr_3)_2$, ^1H NMR (toluene-d_8, −100 °C) δ −15.85 (t, J(H–H) = 280 ± 10 Hz, 1H, OsH), −22.06 (d, 2H, OsH_2).

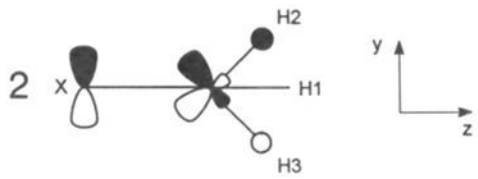
(7) The dipole–dipole interactions between the hydrides and between these ligands and phosphine protons are responsible for the total relaxation rate. The latter contribution is reasonably estimated as 4–6 s^{-1} at 300 MHz (e.g., T_{1min}(OsH) = 200 ms in $Os(H)_2Cl_2(P^iPr_3)_2$ and 260 ms in *trans*-$OsH(H_2)(CO)Cl(P^iPr_3)_2$. The remainder of the rate R (7.9–9.9 s^{-1} or 60–70% of the relaxation) can be used to estimate the distance r(H···H) (Å) from the following equation at 300 MHz: $R(H\cdots H) = 129.18/[r(H\cdots H)]^6$,[1d] where $R(H\cdots H) = 3R/4$ because of the C_{2v} geometry of the $Os(H)_3$ unit.

(8) These systems have been calculated by core potential (ECP) *ab initio* HF calculations using the GAMESS and GAUSSIAN92 sets of programs. (GAMESS: Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, S.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Elbert, S. T. QCPE Bull. 1990, *10*. GAUSSIAN92: 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.; Andres, 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. *Gaussian92, Revision B*; Gaussian, Inc.: Pittsburgh, PA, 1992). The ECP parameters and the basis sets are described in the supplementary material.

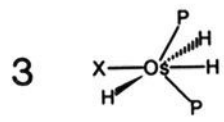
(9) Calculation of the Hessian matrix (X = Cl) confirms that the optimized structure is a minimum.

(10) Kubacek, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4320.

0002-7863/94/1516-2685$04.50/0 © 1994 American Chemical Society

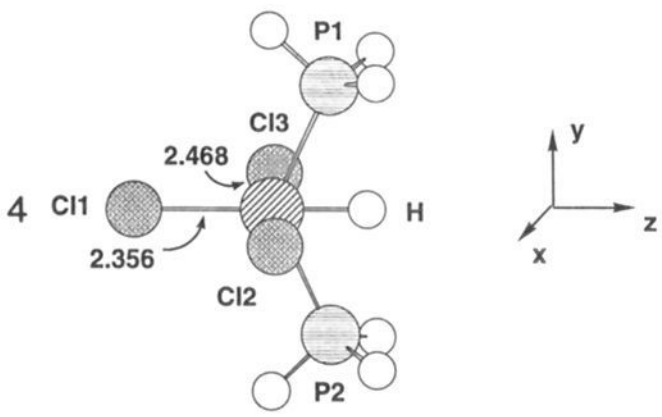


π bond could also have been achieved by bending the phosphines (rather than the hydrides) toward H1, calculations show that this alternate structure (**3**) is not favored.[11a] The reason that **1**



is preferred over **3** is the diminution of the strong *trans* effect between the two hydrides upon bending.

Comparison with the known[12] structure of $OsCl_3H(P^iPr_3)_2$ (**4**) supports our analysis. In this case, the calculations on the PH_3



analog of **4** show that the phosphines bend toward the unique H (P1–Os–P2 = 131.3°), while the transoid chlorides remain essentially perpendicular to the Os–H vector, in agreement with the crystal structure (experimental P1–Os–P2 angle = 126.4°). The alternate structure with Cl atoms bent toward H is considerably higher in energy.[11b] Preferred bending of the phosphines in this case is due to their larger *trans* effect in comparison to Cl. This last calculation also reveals the drastic influence of the distortion upon the Os–Cl bond lengths since the Os–Cl1 bond is significantly shorter (due to the Os–Cl1 π bond, **3**) than the other Os–Cl bonds *despite it being trans to H*. The remarkable analogy between **1** and **4** clearly shows that the angular distortion in $Os(H)_3XL_2$ is not primarily due to any attraction between the hydrides.

The AB_2 patterns of $Os(H)_3XL_2$ are distinguished by the magnitude of the J(AB) values at −100 °C: 920, 550, and 280 Hz for X = Cl, Br, and I, respectively.[13] It is interesting to note that practically the same MH_3 geometry is found for this system (AB_2 spin system with "intermediate" H–H distances) as for other well-documented examples of exchange coupling: $CpIr(PMe_3)(H)_3^+$ and $Cp_2Nb(H)_3$. The osmium compounds are the first non-cyclopentadienyl species[14] and the first unsaturated species to exhibit this phenomenon.

The current model of exchange coupling between two hydrogens requires a relatively short H/H distance and high-amplitude

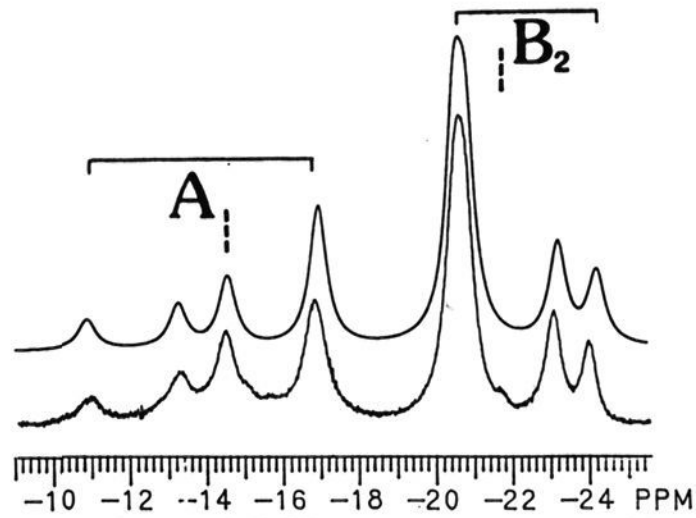


Figure 1. Experimental (300 MHz, toluene-d_8, −100 °C) and simulated (above) ^1H NMR patterns of OsH_3 subspectrum in $OsH_3Cl(P^iPr_3)_2$.

H–M–H bending vibrations.[15] These (especially the latter) are consistent with the presence of a thermally accessible H_2 isomer. Although $Os(H)_3XL_2$ differs from its ruthenium analog in being classical,[16] $OsH(H_2)X(P^iPr_3)_2$ is a realistic intermediate or transition state for the intramolecular hydride site-exchange observed here for $Os(H)_3X(P^iPr_3)_2$ above −80 °C. The rate of site-exchange increases slightly from X = I to X = Cl. For X = I, $\Delta G^{\ddagger}$(205 K) for the hydride site exchange is 8.8 kcal/mol.[17] This establishes the maximum in the energy surface, which appears to govern exchange coupling in $Os(H)_3X(P^iPr_3)_2$.

This study permits a number of conclusions. (1) The occurrence of a quantum exchange contribution to H/H coupling constants is not limited to C_5R_5- and C_6H_6-containing species. (2) This is the first *neutral* 5d metal complex to exhibit exchange coupling (contrast $Cp^*Os(CO)(H)_3$ and $Cp_2Ta(H)_3$). (3) The magnitude of quantum exchange coupling is sensitive to halide identity. (4) The d^4 configuration (without a unified H_3 ligand) discussed here suffers major distortions from octahedral symmetry, and (*cf.* $OsCl_3HP_2$) these are not dependent on high hydride content or on the nature of the halide. Such distortion, involving movement of the most σ-donating ligands, as well as the loss of H_2 from $Os(H)_3X(H_2)L_2$ is aided by the formation of an Os–X π bond.

Since the ground-state structure of $RuH_3I(PCy_3)_2$ shows an H_2 ligand, a full experimental comparison of Ru and Os analogs in this system should enhance our understanding of the influence of the metal on the dihydride/dihydrogen energetics.

Acknowledgment. The Laboratoire de Chimie Théorique is associated with the CNRS (UA 506) and is a member of ICMO and IPCM. This work was supported by the U.S. National Academy of Sciences/AID, by NSF Grant CHE-9103915, and by the NSF/CNRS for an international grant for USA/France collaboration. G.S. thanks the CNRS for a fellowship. R.K. thanks NSF for a NSF Graduate Fellowship. We also thank the referees for useful perspectives into this problem.

Supplementary Material Available: Synthetic details and full spectral data (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(11) (a) Since **4** is not found to be a secondary minimum, no geometry optimization could be performed. A single point calculation, keeping all bond lengths identical to those in **2** and assuming a P–Os–P equal to H2–Os–H3 of **2** and H2–Os–H3 = 180°, gives an energy 76 kcal/mol higher (X = Cl). (b) A similar calculation was conducted for $OsCl_3H(PH_3)_2$. With Cl–Os–Cl taken equal to the P–Os–P angle in **5** and P–Os–P assumed equal to 180°, the energy is raised by 90 kcal.

(12) Gusev, D. G.; Eremenko, I. L.; Berke, H., personal communication.

(13) In $CpIrL(H)_3^+$, the exchange coupling decreases as the donor power of L increases. See ref 15a. Independent studies based on heats of protonation of 18-electron osmium halide compounds and ν_{CO} values of 16-electron ruthenium halide compounds both yield a ranking of halogen electron donor power of Cl > Br > I. See: Rottink, M. K.; Angelici, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 7267. Poulton, J. T.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 3190.

(14) For an η^6-benzene example, $(C_6H_6)OsL(H)_3^+$, showing exchange coupling, see: Heinekey, D. M.; Harper, T. G. P. *Organometallics* **1991**, *10*, 2891.

(15) (a) Heinekey, D. M.; Millar, J. M.; Koetzle, T. F.; Payne, N. G.; Zilm, K. W. *J. Am. Chem. Soc.* **1990**, *112*, 909. (b) Zilm, K. W.; Heinekey, D. M.; Millar, J. M.; Payne, N. G.; Neshyba, S. P.; Duchamp, J. C.; Szczyrba, J. *J. Am. Chem. Soc.* **1990**, *112*, 920. (c) Zilm, K. W.; Millar, J. M. *Adv. Magn. Reson.* **1990**, *15*, 163. (d) Barthelat, J. C.; Chaudret, B.; Daudey, J. P.; DeLoth, P.; Poilblanc, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 9896. (e) Limbach, H. H.; Scherer, G.; Maurer, M.; Chaudret, B. *Angew. Chem., Intl. Ed. Engl.* **1992**, *31*, 1369. (f) Jarid, A.; Moreno, M.; Lledós, A.; Lluch, J. M.; Bertrán, J. *J. Am. Chem. Soc.* **1993**, *115*, 5861 and references cited therein. (g) Riehl, J.-F., Ph.D. Thesis, Université de Paris-Sud, 1991.

(16) We prefer the trihydride formulation to hydride–dihydrogen (as in $RuH(H_2)XL_2$), based not only on calculations but also on its lack of observable $J_{(H-D)}$ and the similarity of the trihydride structure to other exchange-coupled trihydrides. In fact, the low-temperature AB_2 pattern is itself indicative, since decoalescence of signals of a hydride *cis* to dihydrogen is rare.

(17) Simulated with the DNMR5 program (QCMP 059, available from QCPE, Indiana University).