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An Unusual Example of H_2 Coordination by a d^4 Metal Center: Reactions between $OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2$ and H_2

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Addition of hydrogen to 16-e complexes of transition metals often leads to formation of 18-e classical and nonclassical hydrides.[1] Several recent studies have focused on reactions between H_2 and 16-e complexes containing both H and Cl ligands[2] where dehydrohalogenation makes possible more profound transformations to produce polyhydrides.[2d–f] Unusual[3] reversible coordination of H_2 to a d^4 osmium complex ($OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2$) is reported in this communication. The adduct formed, nonclassical $OsH_4Cl_2(P\text{-}i\text{-}Pr_3)_2$, readily eliminates HCl upon further reaction with H_2 to form a new d^4 dihydrogen complex ($Os(H_2)(H)_3Cl(P\text{-}i\text{-}Pr_3)_2$) or, under basic conditions, $OsH_6(P\text{-}i\text{-}Pr_3)_2$ and $[OsH_5(P\text{-}i\text{-}Pr_3)_2]^-$.

The ^1H and $^{31}P\{^1H\}$ NMR spectra of $OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2$ (**1**)[4] in CD_2Cl_2 under 1 atm of H_2 show well-resolved resonances of **1**[5] together with an additional set of resonances[6] due to the new complex **2** in the ratio [**2**]:[**1**] = 1:2. In the hydride-coupled ^{31}P NMR spectrum of the mixture, a triplet and quintet are observed for **1** and **2**, respectively. These observations demonstrate that 16-e $OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2$ reversibly binds H_2 to produce $OsH_4Cl_2(P\text{-}i\text{-}Pr_3)_2$ (**2**)[7] (eq 1). The ratio [**2**]:[**1**] increases on decreasing

$$\underset{\mathbf{1}}{OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2} + H_2 \rightleftarrows \underset{\mathbf{2}}{OsH_4Cl_2(P\text{-}i\text{-}Pr_3)_2} \qquad (1)$$

the temperature, but equilibrium 1 is rather slow[8] and makes measurement of the equilibrium constants difficult.

Complex **2** was isolated,[9] and its molecular structure was determined by a single-crystal X-ray diffraction study at −40 °C.[10] The structure of **2** (Figure 1) dramatically differs from that of the parent dihydride characterized as a distorted square antiprism with two vacant coordination sites where the P_1–Os–P_2 angle is 112.15(3)°.[4b] The apparent arrangement of the Cl and P atoms in **2** seems to be a part of an octahedron. The Os–P distances are practically equal (2.415(2) and 2.411(2) Å) and similar to the 2.43-Å sum of Pauling's covalent radii[11] of the atoms but longer than the Os–P distances in $OsH_6(P\text{-}i\text{-}Pr_2Ph)_2$ (2.338(2) and 2.347(2) Å).[12] The Os–Cl distances in **2** (2.445(3) and 2.441(3) Å) are appreciably, ca. 0.12 and 0.07 Å, longer than the Os–Cl distances in $OsCl_4(PMePh_2)_2$[13] and $OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2$,[4b] respectively.

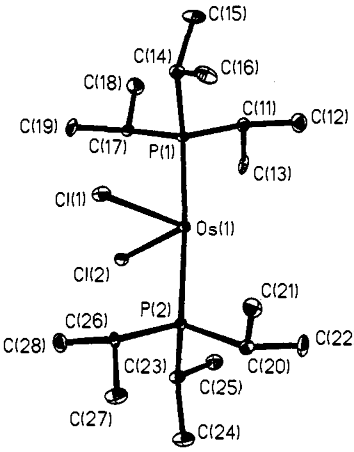

Figure 1. ORTEP projection of the nonhydrogen atoms of $OsH_4Cl_2(P\text{-}i\text{-}Pr_3)_2$. Selected bond lengths (Å): Os–Cl(1) = 2.445(3), Os–Cl(2) = 2.441(3), Os–P(1) = 2.415(2), Os–P(2) = 2.411(2). Selected bond angles (deg): Cl(1)–Os–Cl(2) = 88.7(1), Cl(1)–Os–P(1) = 87.2(1), Cl(1)–Os–P(2) = 92.0(1), Cl(2)–Os–P(1) = 90.2(1), Cl(2)–Os–P(2) = 86.8(1), P(1)–Os–P(2) = 176.9(1).

An independent X-ray analysis attempted at −80 °C gave the same positions of the $OsCl_2(P\text{-}i\text{-}Pr_3)_2$ framework. By the results of the two experiments, hydride ligands could not be reliably located.

In solution, the detailed structure of **2** also remains unclear because of fast intramolecular exchange between the metal-bound protons. The $T_{1\min}$ value of 39 ms (300 MHz) measured for the averaged OsH_4 resonance of **2**[14] and the observation of an AM_2X_3 ($M = {}^{31}P$, $X = {}^2H$; $^2J(H\text{–}P) = 10.2$ Hz, $J(H\text{–}D) = 4.4$ Hz) pattern in the hydride region of the ^1H NMR spectrum of **2**-d_3[7] are evidence for bonding interactions between H-ligands in **2**.

Complex **2** can be formulated as $Os(H_2)_2Cl_2(P\text{-}i\text{-}Pr_3)_2$ (**2a**) or $Os(H_2)(H)_2Cl_2(P\text{-}i\text{-}Pr_3)_2$ (**2b**). Using the experimental $T_{1\min}$ and $J(H\text{–}D)$ values, these being exchange-averaged data, the expected $r(H\text{–}H)$ and $^1J(H\text{–}D)$ for structures **2a** and **2b** can be calculated:[15] for **2a**, $r(H\text{–}H) = 1.06$ Å (assuming fast intramolecular spinning of the dihydrogen ligands) or 1.33 Å (slow spinning), $^1J(H\text{–}D) = 13.2$ Hz; for **2b**, $r(H\text{–}H) = 0.95$ Å (fast spinning) or 1.20 Å (slow spinning), $^1J(H\text{–}D) = 26.4$ Hz. Thus, both structures seem to be plausible.

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[2] (a) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Meyer, U.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1563. (b) Andriollo, A.; Esteruelas, M. A.; Meyer, U.; Oro, L. A.; Sanchez-Delgado, K. A.; Sola, E.; Valero, S.; Werner, H. *J. Am. Chem. Soc.* **1989**, *111*, 7431. (c) Gusev, D. G.; Bakhmutov, V. I.; Grushin, V. V.; Vol'pin, M. E. *Inorg. Chim. Acta* **1990**, *175*, 19. (d) Gusev, D. G.; Bakhmutov, V. I.; Grushin, V. V.; Vol'pin, M. E. *Inorg. Chim. Acta* **1990**, *177*, 115. (e) Grushin, V. V.; Vymenits, A. B.; Vol'pin, M. E. *J. Organomet. Chem.* **1990**, *382*, 185. (f) Gusev, D. G.; Vymenits, A. B.; Bakhmutov, V. I. *Inorg. Chem.* **1992**, *31*, 1. (g) Mediati, M.; Tachibana, G. N.; Jensen, C. M. *Inorg. Chem.* **1992**, *31*, 1827.

[3] The other known d^4 dihydrogen complexes, $CpM(H_2)(CO)_3$ (M = V, Nb) and $[Re(H_2)(H)_2(CO)(PMe_2Ph)_3]^+$, were prepared by UV photolysis of $CpM(CO)_4$ in liquid xenon under H_2[3a] and protonation of $Re(H)_3(CO)(PMe_2Ph)_3$,[3b] respectively. (a) Howard, M. T.; George, M. W.; Hamley, P.; Poliakoff, M. *J. Chem. Soc., Chem. Commun.* **1991**, 1101. (b) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 6912.

[4] (a) The dihydride $OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2$ was prepared according to the reported procedure.[4b] (b) Aracama, M.; Esteruelas, M. A.; Lahoz, F. J.; Lopez, J. A.; Meyer, U.; Oro, L. A.; Werner, H. *Inorg. Chem.* **1991**, *30*, 288.

[5] ^1H NMR (CD_2Cl_2, 20 °C): δ −16.16 (t, $^2J(H\text{–}P) = 35$ Hz, 2H, OsH_2), 1.32 (dd, $^3J(H\text{–}H) = 7.2$ Hz, $^3J(H\text{–}P) = 14.5$ Hz, 36H, CH_3), 2.31 (m, 6H, CH). $^{31}P\{^1H\}$ (CD_2Cl_2, 20 °C): δ 45.3.

[6] ^1H NMR (CD_2Cl_2, 20 °C): δ −10.55 (t, $^2J(H\text{–}P) = 10.1$ Hz, 4H, OsH_4), 1.25 (app q, $J = 6.7$ Hz, 36H, CH_3), 2.76 (m, 6H, CH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 23.8.

[7] A mixture of **1**-d_2 and **2**-d_4 formed in a CD_2Cl_2 solution of **1** sealed under an atmosphere of D_2. Residual (ca. 2% H) resonances of $OsHDCl_2(P\text{-}i\text{-}Pr_3)_2$ and $OsHD_3Cl_2(P\text{-}i\text{-}Pr_3)_2$ were detectable in the ^1H NMR spectra.

[8] More than 10 h was necessary to reestablish the equilibrium at −25 °C.

[9] A 5-mm NMR tube containing a suspension of $OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2$ (50 mg) in 0.5 mL of CF_2Cl_2:CD_2Cl_2 (4:1) sealed under ca. 1 atm of H_2 was allowed to stand at −25 °C for 48 h. Formation of colorless crystals of **2** accompanied by disappearance of the red-brown **1** was observed, and finally the crystals were isolated under nitrogen. In the solid state, **2** is moderately stable under N_2.

[10] Crystallographic data: space group $P2_1$, $Z = 2$; $a = 8.735(4)$ Å, $b = 15.029(5)$ Å, $c = 9.685(4)$ Å, $\beta = 105.71(3)°$, $V = 1223.9(9)$ Å^3, $\rho_{\text{calcd}} = 1.592$ g/cm^3, $\mu = 56.66$ cm^{-1}; Siemens R5 m/v diffractometer, Mo Kα radiation ($\lambda = 0.710\,73$ Å); 3080 independent reflections with $5° < 2\theta < 58°$ collected, 3017 reflections used in refinement with $I > 4\sigma(I)$; $R = 0.029$, $R_w = 0.038$.

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[12] Howard, J. A. K.; Johnson, O.; Koetzle, T. F.; Spencer, J. L. *Inorg. Chem.* **1987**, *26*, 2930.

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[14] For $OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2$, $T_{1\min}(OsH_2) = 200$ ms (300 MHz).

[15] For details, see ref 1 and (a) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 3027. (b) Earl, K. A.; Jia, C.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 3027.

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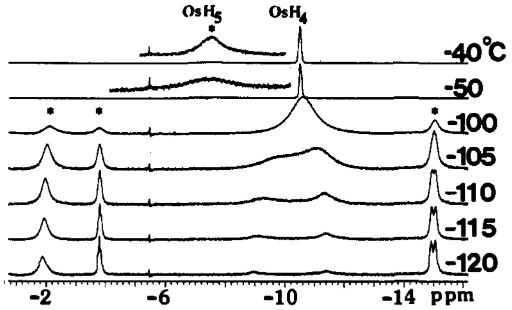

Figure 2. Variable-temperature ^1H NMR spectra of $OsH_4Cl_2(P\text{-}i\text{-}Pr_3)_2$ (**2**) and $Os(H_2)(H)_3(P\text{-}i\text{-}Pr_3)_2$ (**3**) in a mixture CF_2Cl_2:CD_2Cl_2 (3:1). Below −100 °C, the resonances between δ −8 and −10 decrease because of precipitation of **2**.

On the basis of recent theoretical and experimental data,[16] one would probably consider the d^6 octahedral structure **2a** to be preferable. Our low-temperature experiments with solutions of **2** in mixtures of CF_2Cl_2 and CD_2Cl_2 revealed decoalescence of the averaged OsH_4 resonance into two (1:2) broad lines (δ −9.0, −11.4) below −105 °C.[17] The ratio indicates that **2** probably exists in solution as a mixture of isomers and that intramolecular fluxionality within each isomer has not yet been halted.

Besides formation of **2**, the appearance and slow increase of amounts of the new hydride complex **3** was detected by ^1H and ^{31}P NMR[18] in the solutions of **1** in CF_2Cl_2:CD_2Cl_2 under H_2. The molar percentage of **3** of 10% was achieved 2 days after preparation but remained unchanged during subsequent observation. In the ^1H NMR spectra, the line width of the hydride resonance of **3** (δ −7.54) is the smallest (50–60 Hz) between −20 and −30 °C. The resonance broadens on raising the temperature because of exchange with dissolved H_2 (δ 4.5). This was clearly revealed by a saturation-transfer experiment at −10 °C. At temperatures below −50 °C, broadening becomes significant again (Figure 2), and below −90 °C three new resonances are observed for **3** at δ −1.91 (br s), −3.81 (t, $^2J(H\text{–}P) = 16$ Hz), and −15.0 (apparent doublet with splitting of 42 Hz or two closely separated resonances) in the ratio 2:1:2, respectively.[19] T_1 times are very short (20 ms) for all hydride signals at −100 °C. On further cooling to −120 °C, T_1 shortens for the broad line at δ −1.91 (10.6 ms) but becomes longer for the others (91 and 60 ms) because of slowing of the exchange on the T_1 time scale.

The amount of **3** formed in the CF_2Cl_2:CD_2Cl_2 mixtures was substantially higher than in neat CD_2Cl_2, probably because of higher solubility of H_2 in fluorinated solvents. However, a mixture containing 10% of **3** was prepared in CD_2Cl_2 in the presence of solid KOH by stirring the solution at 24 °C for 45 min. Thus, formation of **3** seems to be an equilibrium process of HCl/H_2 substitution in **2** (eq 2), similar to that known for related iridium

$$\underset{\mathbf{2}}{OsH_4Cl_2(P\text{-}i\text{-}Pr_3)_2} + H_2 \rightleftarrows \underset{\mathbf{3}}{OsH_5Cl(P\text{-}i\text{-}Pr_3)_2} + HCl \qquad (2)$$

complexes $IrHCl_2(PR_3)_2$ (R = *i*-Pr, Cy) where $Ir(H_2)(H)_2Cl(PR_3)_2$ forms in solution under H_2.[2d]

3 can be formulated as a dihydrogen complex ($Os(H_2)(H)_3Cl(P\text{-}i\text{-}Pr_3)_2$) ($\delta(H_2)$ −1.91) on the basis of the spectroscopic data and the exchange with H_2 in solution. The latter process probably goes via formation of a 16-e complex ($OsH_3Cl(P\text{-}i\text{-}Pr_3)_2$). Related ruthenium complex, $RuH_3Cl(PCy_3)_2$, has been recently prepared.[20]

At 20 °C under 1 atm of H_2 and strong basic conditions (18-crown-6, KOH, THF-d_8), dihydride **1** undergoes fast (ca. 15 min) and complete dehydrohalogenation with clean formation of known[4b,12] $OsH_6(P\text{-}i\text{-}Pr_3)_2$ (**4**).[21] Subsequent slow (>10 h) deprotonation of **4** occurs in the reaction mixture to give anionic $[OsH_5(P\text{-}i\text{-}Pr_3)_2]^-$ (**5**)[22] as the sole product of the reaction.

The data presented in this work for the osmium polyhydrides and those available in the literature for the analogous iridium complexes IrH_5P_2,[23] $Ir(H_2)(H)_2ClP_2$,[2g] and $Ir(H_2)HCl_2P_2$[2d] show a clear trend for the polyhydride complexes to avoid the highest possible oxidation states by adopting nonclassical structures in the presence of strongly electronegative Cl ligands.

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Supplementary Material Available: Tables of positional and thermal parameters and bond distances and angles (5 pages). Ordering information is given on any masthead page.

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(16) Lin, Z.; Hall, M. B. *Inorg. Chem.* **1992**, *31*, 4262 and references therein.

(17) The $^{31}P\{^1H\}$ NMR spectrum of the solution shows broadened but single resonance at −120 °C.

(18) ^1H NMR (CF_2Cl_2:CD_2Cl_2 (3:1), 20 °C): δ −7.54 (br s, 5H, OsH_5), 1.38 (app q, $J = 8$ Hz, 36H, CH_3), 2.37 (m, 6H, CH). $^{31}P\{^1H\}$ NMR (CF_2Cl_2:CD_2Cl_2 (3:1), 20 °C): δ 38.7.

(19) Note that the exchange-averaged δ (OsH_5) value, −7.54 ppm, is in agreement with the result of averaging of the slow-exchange data: $(-1.91 \times 0.4) + (-3.81 \times 0.2) + (-15.0 \times 0.4) = -7.53$ ppm.

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(21) Our ^1H and $^{31}P\{^1H\}$ NMR data are in agreement with those published for **4** previously.[4b] $T_{1min}(OsH_6) = 120$ ms (300 MHz).

(22) ^1H NMR (THF-d_8, 20 °C): δ −12.41 (t, $^2J(H\text{–}P) = 14.8$ Hz, 5H, OsH_5), 1.09 (app q, $J = 7$ Hz, 36H, CH_3), 1.51 (m, 6H, CH). $T_{1min}(OsH_5) = 500$ ms (300 MHz). $^{31}P\{^1H\}$ NMR (THF-d_8, 20 °C): δ 65.7 (sextet in the hydride-coupled ^{31}P NMR spectra).

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