J. Am. Chem. Soc. **1994,** *116,* 7409–7410

Characterization of $PtH_3(P^tBu_3)_2^+$ as the First Dihydrogen Complex of d^8, Pt(II)

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Received May 23, 1994

The vast majority of H_2 complexes identified at present involve a d^6 configuration of the transition metal, so it is probable that other configurations will better define the limits of existence of molecular H_2 as a ligand. We describe here the case where a platinum dihydrogen complex will have a d^8 configuration, while the product of oxidative addition involves a d^6 configuration (eq 1).[1] To accomplish this, it was necessary to find conditions in

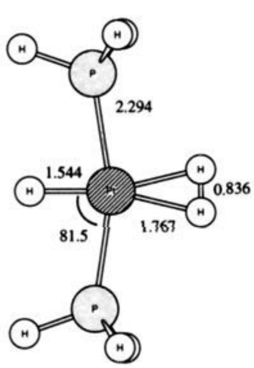
$$L_nPt^{IV}(H)_2 \overset{?}{\rightleftharpoons} L_nPt^{II}(H_2) \qquad (1)$$

which H_2 *loss* is disfavored, since certain compounds formulated as Pt^{IV} hydrides (e.g., $L_2PtH_2Cl_2$, L_2PtH_3Cl) were reported to readily lose H_2.[2] We felt that this might be accomplished by H_2 coordination to L_2PtH^+,[3] where the cation would be particularly electrophilic. We report here the characterization (from each direction) of the equilibrium in eq 2.

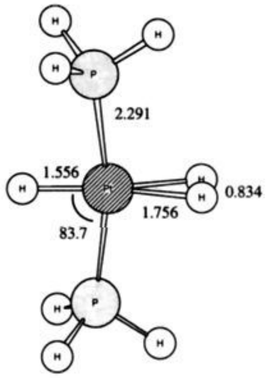
$$L_2PtH_2 + HZ \rightarrow \underset{\mathbf{1}}{L_2PtH_3} + Z^- \underset{k_1}{\rightleftharpoons} \underset{\mathbf{2}}{L_2PtH^+} + Z^- + H_2 \qquad (2)$$

$$L = P^tBu_3 \qquad Z = F_3CSO_3$$

We discuss first the results of calculations of $PtH_3(PH_3)_2^+$, in part since they preceded the experiments chronologically. We have investigated the possible structures of the model ion $PtH_3(PH_3)_2^+$ using core potential *ab initio* calculations with the Gaussian92 set of programs.[4] Geometry optimization[4,5] at the RHF/MP2 level, using a gradient method and without any symmetry constraint, yields a complex (**I**) with H_2 lying in the $HPtP_2$ plane and *trans* to the hydride. The calculated H–H distance, 0.836 Å, is indicative of coordinated dihydrogen. Optimization of the structure with the H–H bond perpendicular to the $HPtP_2$ plane (**II**) yields an energy virtually identical (i.e., within 0.1 kcal/mol) to that of **I**, with no significantly altered bond lengths or angles.[6] $PtH(PH_3)_2^+$ [7] and H_2 were also optimized at the RHF/MP2 level in order to calculate at Pt/H_2 bond dissociation energy for **I** and **II**. After correction (5.2 kcal/mol) for basis set superposition error,[8] a dissociation energy of 16 kcal/mol is determined. No trihydride minimum was obtained on the potential energy surface. C_s constrained optimization of a structure having a T-shaped, mirror-symmetric arrangement of the three hydrides yielded and energy 18 kcal/mol above the minimum. This large energy difference suggests that redox cleavage of the H–H bond in $PtH(H_2)(PH_3)_2^+$ will not lead to *fast* H/H_2 exchange.



I



II

In Figure 1, the ^2H and $^2H\{^1H\}$ NMR spectra (−80 °C) are presented for the isotopomers of $Pt(H,D)_3(P^tBu_3)_2^+$ (**1**), formed by reaction between $Pt(H)_2(P^tBu_3)_2$ and CF_3SO_3D. These deuterium spectra, which are free from overlap with resonances of the phosphines (as in the case of ^1H NMR), reveal PtD and Pt(DH) resonances of **1**.[9] The multiplet of coordinated DH, which appears at unusually low field (δ 1.12), is distinguished by one of the largest known D–H coupling constants (34.7 Hz) and by a ^1J(D–Pt) of 44 Hz; this is the first observation of a metal–H_2 spin–spin interaction. These couplings provide unambiguous evidence for the presence of both H–D and Pt–(HD) bonds, i.e., for formulation of **1** as a dihydrogen complex and uncomplicated by dissociative exchange dynamics at −80 °C.

A ^1J(H–Pt) of 286 Hz can be calculated from ^1J(D–Pt) = 44 Hz according to the difference in the H/D gyromagnetic ratios. Unfortunately, ^1J(H–Pt) couplings are quite sensitive to the nature of the *trans* ligands, which makes a comparison difficult. For example, for the hydride *trans* to H_2 in **1**, ^1J(H–Pt) = 1360 Hz, which is comparable to that (1470 Hz) in $PtH(acetone)(P^tBu_3)_2^+$.[3] In $PtH(P^tBu_3)_2^+$ and *trans*-$Pt(H)_2(P^tBu_3)_2$, the couplings are 2600 and 780 Hz, respectively. The 286-Hz coupling is the least of these, which, perhaps, has some connection with the Pt–H distances in the $Pt(H_2)$ fragment being expected to be quite long.

In the low-temperature ^1H NMR spectra, the H_2 resonance of **1** is overlapped by the very intense methyl resonance and severely broadened by strong H–H dipole–dipole interaction (the latter is more than 10 times weaker in H–D). The hydride signal is a well-resolved triplet at δ −10.4 and has a long T_1 (400 ms at −80

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(1) This is the reverse of the usual situation, where an H_2 form is *favored* by those factors which favor a d^6 octahedral structure. Moreover, Pt(IV) hydrides are little studied, and there is currently no H_2 complex of a divalent platinum group metal.

(2) (a) Anderson, D. W. W.; Ebsworth, E. A. V.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1973**, 854. (b) Ebsworth, E. A. V.; Marganian, V. M.; Reed, F. J. S. *J. Chem. Soc., Dalton Trans.* **1978**, 1167.

(3) $[PtH(P^tBu_3)_2]CF_3SO_3$ was prepared by metathesis of $PtHCl(P^tBu_3)_2$ with $AgCF_3SO_3$: Goel, R. G.; Srivastava, R. C. *Can. J. Chem.* **1983**, *61*, 1352.

(4) Pt and P atoms were both calculated using an ECP, including the 5s and 5p shells for Pt. A triple-ζ basis set was used for the 5d shell of Pt and the 1s shells of the hydrogen atoms bound to the metal center, a double-ζ basis set was used for the valence shell of P, and a single-ζ basis set was used for the 1s shells of the phosphine H atoms. The basis sets of all atoms bound to the Pt also included polarization functions. Additional details are available in the supplementary material. 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.; Reploge, 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. *Gaussian 92*, Revision B; Gaussian, Inc.: Pittsburgh, PA, 1992.

(5) PH_3 rotation was not permitted. Full Cartesian optimization gives structures identical to **I** and **II**. Hessian calculations indicate that **I** and **II** are minima.

(6) The bulky phosphines in the experimental complex will thus determine the structure.

(7) The optimized structure of $PtH(PH_3)_2^+$ is very similar to that calculated for the isoelectronic $RhH(PH_3)_2$. Daniel, C.; Koga, N.; Han, J.; Fu, X. Y.; Morokuma, K. *J. Am. Chem. Soc.* **1988**, *110*, 3773.

(8) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(9) NMR spectroscopic data for **1**: ^2H NMR (CH_2Cl_2, −80 °C) δ −10.3 (^1J(D–Pt) = 202 Hz, PtD), 1.12 (^1J(D–H) = 34.7 Hz, ^1J(D–Pt) = 44 Hz, Pt(DH)); ^1H NMR (CD_2Cl_2, −80 °C) δ −10.42 (t, ^2J(H–P) = 8.3 Hz, ^1J(H–Pt) = 1360 Hz, 1H, PtH), 1.34 (app t, J = 7.3 Hz, 36 Hz, CH_3), 1.58 (unresolved app t, 18 H, CH_3); ^{31}P NMR (CD_2Cl_2, −80 °C) δ 87.2 (^1J(P–Pt) = 2515 Hz) (doublet in the hydride-coupled spectrum).

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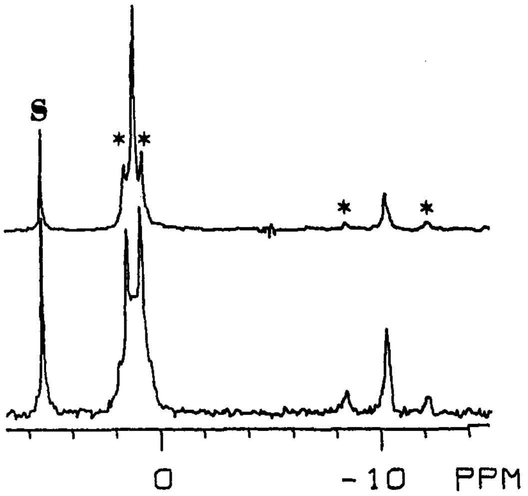

Figure 1. $^2H\{^1H\}$ (upper) and ^2H (lower) NMR spectra of isotopomers of **1** prepared with CF_3SO_3D at -80 °C in CH_2Cl_2(S). ^{195}Pt satellites are indicated by asterisks.

°C) (300 MHz), indicating no H/H_2 exchange on the NMR time scale at -80 °C. Slow exchange is consistent with the hydride and H_2 ligands being mutually *trans*.

The ^1H NMR data for solutions of $PtH(P^tBu_3)_2^+$ (**2**) in the presence of H_2 show that H_2 coordination in **1** is reversible, and the position of the equilibrium (eq 2) is strongly temperature-dependent. Above -20 °C, the ^1H NMR spectra are characterized by the presence of *two* exchange-averaged resonances: one of the temperature-dependent chemical shifts lies between free (δ 4.55) and coordinated (δ 1.12) H_2, and the other is between PtH in **1** (δ -10.4) and PtH in **2** (δ -36.0). Both of the averaged resonances are broadened at 20 °C, but remarkably there is no saturation transfer between them. The exchange-averaged signal in the hydride region is flanked by platinum satellites, while the spin–spin coupling is completely destroyed for the exchange-averaged signal for H_2. These observations clearly indicate that there is no intramolecular H/H_2 scrambling in **1** (on the NMR time scale), even at room temperature.

Eleven ^1H NMR spectra were collected between -10 and 20 °C for three samples with different concentrations of **2** under H_2. Using the experimentally determined line widths, chemical shifts, and T_1 relaxation times, the H_2 exchange was simulated with the DNMR5 program[10] to yield rate constants k_1 for the H_2 loss from **1**. $\Delta H^{\ddagger}$ of 11.0 ± 0.4 kcal/mol and $\Delta S^{\ddagger}$ of 1.8 ± 1.5 eu were derived from the Eyring plot of $\ln(k/T)$ *vs* $1/T$. The bulk of P^tBu_3 is apparently responsible for diminishing the experimental value from that calculated (16 kcal/mol) in the PH_3 model complex. A significantly larger activation enthalpy, $\Delta H^{\ddagger} = 20.0 \pm 0.5$ kcal/mol ($\Delta S^{\ddagger} = -1 \pm 2$ eu), is known for reductive elimination of H_2 from $Pt(H)_2(PMe_3)_2$.[11]

It is probable that the detection of this first dihydrogen complex of Pt(II) relies in part on steric protection (by P^tBu_3) against H_2 displacement by the available (very weak) nucleophiles (triflate and CH_2Cl_2).[12] The very small $\Delta S^{\ddagger}$ for H_2 dissociation has been discussed earlier[10] as due to the nature of the metal overlap with the σ(H–H) orbital, which should decrease faster with distance than σ bonds to more conventional Lewis bases. The large ^1J(H–D) for coordinated HD is consistent with very little back-donation. Thus, $PtH(P^tBu_3)_2^+$ is a sufficiently strong Lewis acid to bind H_2 but has very little reducing ability (not much H–H bond weakening and no evidence for $Pt^{IV}(H)_3(P^tBu_3)_2^+$ and consequent fast scrambling of the H and H_2 nuclei).[13] While $Ir(H)_3(PH_3)_2$ is calculated to have a trihydride ground state,[14] isoelectronic $PtH_3(PH_3)_2^+$ has the metal oxidation state sufficiently high that the d^6 $(H)_3Pt^{IV}$ formulation is no longer favored. This noticeable difference in structure may also be related to the rarity of the Pt(IV) oxidation state when the coordination number is only five.[15] With a different type and number of ligands, Pt^{IV} hydrides have been authenticated.[2,16] Thus, both the Pt^{II}/H_2 complex reported here and Pt^{IV} hydrides are relevant to the catalysis (by Pt^0 and by Pt^{II}) of H_2/D_2 scrambling, since this process requires three or more H at the metal simultaneously.

Acknowledgment. The Laboratoire de Chimie Théorique is associated with the CNRS (URA 506) and is a member of ICMO and IPCM. We would like to thank Eric Clot for very useful discussion and technical assistance. Support for this work was provided by an international NSF/CNRS grant for USA–France scientific collaboration between Indiana University and the Laboratoire de Chimie Théorique. J.U.N. acknowledges support of a Deutsche Akademischer Austauschdienst Fellowship. J.R.R. thanks the Ministere des Affaires Etrangeres for a postdoctoral fellowship.

Supplementary Material Available: Basis sets, Cartesian coordinates, and energies for the RHF/MP2 optimized structures of $PtH(H_2)(PH_3)_2^+$ (3 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.

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(10) A similar kinetic analysis was recently published for $Ir(H_2)(H)_2X(P^tBu_2Me)_2$. For details, see: Hauger, B. E.; Gusev, D.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 208 and references therein.

(11) Packett, D. L.; Trogler, W. C. *Inorg. Chem.* **1988**, *27*, 1768.

(12) This is supported by the fact that the corresponding protonation of $Pt(H)_2(P^iPr_3)_2$ consumes all of this reagent but gives no detectable dihydrogen complex. Even at -90 °C, H_2 is evolved, and this reaction results in a single product, presumably $PtH(CF_3SO_3)(P^iPr_3)_2$ (^1H NMR (CD_2Cl_2, 20 °C) δ 2.44 (m, 6H, CH), 1.28 (app q, $J = 7.5$ Hz, 36H, CH_3), -27.53 (t, ^2J(H–Pt) = 1616 Hz, 1H PtH). The reactivity of PtL_2 differs significantly for L = P^iPr_3 and P^tBu_3, see: Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 2134.

(13) $Pt(H)_3(P^tBu_3)_2^+$ can be present as a transient species in solution. This would explain formation of $PtD(D_2)(P^tBu_3)_2^+$ from $PtH(P^tBu_3)_2^+$ and D_2 (detected by ^2H NMR). The calculated energy difference between $Pt(H)_3(PH_3)_2^+$ and $PtH(H_2)(PH_3)_2^+$ predicts a barrier for oxidative addition $\Delta G^{\ddagger} \geq 18$ kcal/mol (assuming small $\Delta S^{\ddagger}$). The rate constant for this process is less than 0.2 s^{-1} (293 K), which is in agreement with the absence of H/H_2 scrambling on the NMR time scale (~1 s^{-1}).

(14) (a) Riehl, J.-F.; Jean, Y.; Eisenstein, O.; Pélissier, M. *Organometallics* **1992**, *11*, 729. (b) RhH_3L_2 complexes are known[14c] but not characterized structurally. (c) Yoshida, T.; Okano, T.; Thorn, D. L.; Tulip, T. H.; Otsuka, S.; Ibers, J. A. *J. Organomet. Chem.* **1979**, *181*, 183.

(15) Jain, V. K.; Rao, G. S.; Jain, L. *Adv. Organomet. Chem.* **1987**, *27*, 113.

(16) (a) Packett, D. L.; Syed, A.; Trogler, W. C. *Organometallics* **1988**, *7*, 159. (b) Blacklaws, I. M.; Ebsworth, E. A. V.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Dalton Trans.* **1978**, 753. (c) Blacklaws, I. M.; Brown, L. C.; Ebsworth, E. A. V.; Reed, F. J. S. *J. Chem. Soc., Dalton Trans.* **1978**, 877.