

A Molecular Rotor Possessing an H–M–H “Spoke” on a P–M–P “Axle”: A Platinum(II) *trans*-Dihydride Spins Rapidly Even at 75 K

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Supporting Information

ABSTRACT: A new class of low-barrier molecular rotors, metal *trans*-dihydrides, is suggested here. To test whether rapid rotation can be achieved, the known complex *trans*-H₂Pt(P^tBu₃)₂ was experimentally studied by ²H and ¹⁹⁵Pt solid-state NMR spectroscopy (powder pattern changes with temperature) and computationally modeled as a ‘Bu₃P–Pt–P^tBu₃ stator with a spinning H–Pt–H rotor. Whereas the related chloro-hydride complex, *trans*-H(Cl)-Pt(P^tBu₃)₂, does not show rotational behavior at room temperature, the dihydride *trans*-H₂Pt(P^tBu₃)₂ rotates fast on the NMR time scale, even at low temperatures down to at least 75 K. The highest barrier to rotation is estimated to be ~3 kcal mol⁻¹, for the roughly 3 Å long rotor in *trans*-H₂Pt(P^tBu₃)₂.

Inspired in part by nature’s molecular machinery, current research is developing functional parts for future human-made molecular machines.¹ Among the key “machine parts” are molecular rotors, devices that possess a functional axis of rotation, which allows the mobile part, the *rotator*, to rotate independently of a static part, the *stator*.² Research toward the design of functional rotors can be broadly divided into either developing rotors that move randomly in both directions powered by thermal energy in equilibrium or devising unidirectional rotors that require a ratchet mechanism and a source of free energy.^{2–4} Our focus is on hindered random rotors, where lowering the barrier(s) to rotation is the key challenge. While such devices will initially not be unidirectional, uses as gyroscopes,^{5–7} for example, can be envisioned, and unidirectional movement may conceivably be added later, perhaps by making the rotor polar and exploiting its dipole moment.⁸

Mislow’s solution-state triptycene rotors were among the first (1980s) intensely studied rotors.⁹ Later, the groups of Gladysz, Garcia-Garibay, and others have explored factors that enable molecular rotation in the solid state as well.^{5,6,8,10} The size, shape, and symmetry of the rotor and its parts all influence its mobility. The synthesis of rotors with high mobility in a solid-state structure (relevant for future devices) is difficult to accomplish¹¹ and requires careful design of a protective stator. Nearly all current examples of molecular rotors involve large

organic stators.^{2,5,6,8,10} Often, the rotator is also organic; however, inorganic rotators are very promising as well. In 1994, Gray’s group reported a *trans*-spanning diphosphine molybdenum(0) tetracarbonyl complex capable of low-barrier random rotations at temperatures as low as 253 K.¹² In 2000, Gladysz’ group reported a singly *trans*-spanning diphosphine platinum(II) perfluorophenyl chloride complex where the perfluorophenyl and chloride could potentially rotate.⁵ No rotation was observed even at 368 K,^{13a} but partial rotation in the solid-state was later seen for a derivative.^{13b} Other rotor-like transition-metal complexes followed which employed halides, nitriles, and carbonyl ligands as the rotors.⁶ The multistep syntheses of the large stator ligands have pushed the boundaries of organic synthesis; however, many of the most impressive random rotors have high barriers to rotation (≥10 kcal mol⁻¹) and become fixed in place (“jammed”) in the solid state.^{6b,d}

The question arises: are there overlooked classes of low-barrier rotors? Rapidly spinning “molecular machine parts” that are easily synthesized? We think there are and would like to draw attention to transition-metal *trans*-dihydrides. Such rotors would be rather large in one direction (~3 Å for the H–H separation),¹⁴ but the small van der Waals radius of hydrogen gives hope for a low barrier to rotation. The H–M–H geometry in *trans*-dihydrides is linear for *d*⁸ metals. Here, we provide the first demonstration that a *trans*-dihydride can act as a molecular rotor with a low rotational energy barrier. The known complex *trans*-H₂Pt(P^tBu₃)₂ is shown here to exhibit rapid rotations of the Pt-bound hydrogen positions, down to temperatures of around 75 K.

The *trans*-H₂Pt(P^tBu₃)₂ (**1**) was specifically chosen to give a H–Pt–H rotator steric protection through a bulky phosphine stator. Compound **1** was synthesized by a modified literature procedure in one step from [(COD)PtCl₂], in 83% yield (see SI).¹⁵ Recrystallization from toluene/hexanes at –30 °C gave crystals suitable for X-ray crystallography. The structure (at 147 K)¹⁶ is shown in Figure 1 (left). For comparison, the formally similar chloro-hydride complex *trans*-H(Cl)Pt(P^tBu₃)₂ (**2**), which turns out not to be a rotor, was also synthesized. Its deuterated version, *trans*-D(Cl)Pt(P^tBu₃)₂ (**2-D**), was also crystallographically characterized (Figure 1, right).

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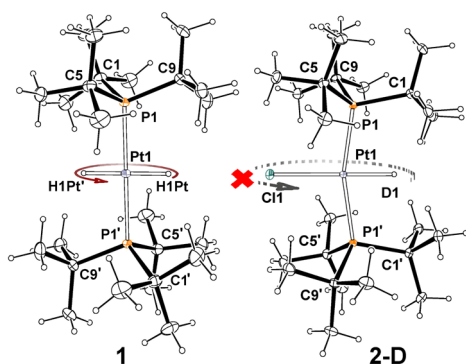


Figure 1. Structures of rotor **1** (*trans*-H₂Pt(P^tBu₃)₂) and “jammed rotor” **2-D** (*trans*-(D)ClPt(P^tBu₃)₂). Bond distances (Å) and angles (deg): for **1**: Pt1–H1Pt, 1.35(4); Pt1–P1, 2.2783(5); P1–Pt1–P1’, 180.0; P1–Pt1–H1Pt, 91.0(16); P1’–Pt1–H1Pt, 89.0(16); for **2-D**: Pt1–D1, 1.68(3); Pt1–P1, 2.3260(5); Pt1–Cl1, 2.4344(7); P1–Pt1–P1’, 164.01(2); P1–Pt1–D1, 82.004(12); P1–Pt1–Cl1, 97.996(11); Cl1–Pt1–D1, 180.

Close examination of the X-ray crystal structure of **1** suggested that the hydrides may be mobile. The apparent Pt–H bond length in **1**, from refinement, is 1.35(4) Å, which is very short. Apparent Pt–H bond lengths, from X-ray crystallography, are commonly in the range of 1.5–1.8 Å,^{17,18} and a neutron diffraction study has yielded 1.55(3) Å in one example of a terminal hydride coordinated to a Pt(II) *trans*-diphosphine complex.¹⁹ The Pt–D bond distance in **2-D** (1.68 Å) fits into the typical range of bond lengths. The short Pt–H bond distance seen for **1** is likely an artifact from mobility due to “smearing” of the electron density around a section of a circular path. Given the limitations of X-ray crystallography in determining H positions, a disorder model was also tested: three disordered positions (6 partial hydrides, each with 1/3 occupancy) resulted in no change to the (excellent) *R*-factor (1.36%). Hence, X-ray data are consistent with mobility of the platinum-bound hydrides, but do not provide strong evidence.

A similar conclusion (pointing toward mobility) may be obtained from ¹⁹⁵Pt solid-state NMR (SSNMR) data (Figure 2). The ¹⁹⁵Pt isotropic chemical shift, δ_{iso} , is extremely sensitive

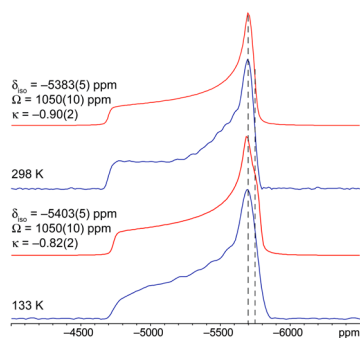


Figure 2. WURST-CPMG ¹⁹⁵Pt SSNMR spectra and simulations of **1** at 298 and 133 K. Dashed lines show relative positions of δ_{22} and δ_{33} .

to both the oxidation state of Pt and the local structure.²⁰ ¹⁹⁵Pt SSNMR powder patterns are typically dominated by the effects of chemical shift anisotropy, which is described by the span (Ω) and the skew (κ) (see SI for definitions).²¹ Using the WURST-CPMG pulse sequence,²¹ ¹⁹⁵Pt SSNMR spectra for complex **1** were obtained at room temperature and 133 K (Figure 2). The spectra collected at both low and high temperatures have

similar values of δ_{iso} and almost identical values of Ω . However, skew values are different enough ($\kappa = -0.82(2)$ at 133 K and $\kappa = -0.90(2)$ at 298 K) to suggest that the motion in **1** at 298 K results in a partial averaging of the δ_{22} and δ_{33} components of the ¹⁹⁵Pt CS tensor, resulting in a more axially symmetric spectrum (i.e., κ approaches -1 , see Table S3). The orientation of the ¹⁹⁵Pt CS tensor in the molecular frame was determined using DFT calculations (Figure S14): the δ_{11} component is along the P–Pt–P axis, δ_{22} is parallel to the H–Pt–H vector, and δ_{33} is perpendicular to the P–Pt–H plane. This is consistent with the partial averaging of the δ_{22} and δ_{33} components due to rapid rotation of the hydrides. However, the small differences between the low- and high-temperature ¹⁹⁵Pt SSNMR spectra elucidate neither the exact nature of this motion nor its rates.

²H SSNMR is ideally suited to the study of molecular-level dynamics. The ²H electric field gradient (EFG) tensor is very sensitive to a variety of modes of motion over a wide range of temperature-dependent exchange rates.²² Variable-temperature (VT) ²H SSNMR provides direct and convincing evidence for a rotating H–Pt–H unit. The Pt-deuterated complex *trans*-D₂Pt(P^tBu₃)₂, **1-D2**, was prepared. Experimental VT ²H SSNMR spectra are shown in Figure 3 (left). For comparison,

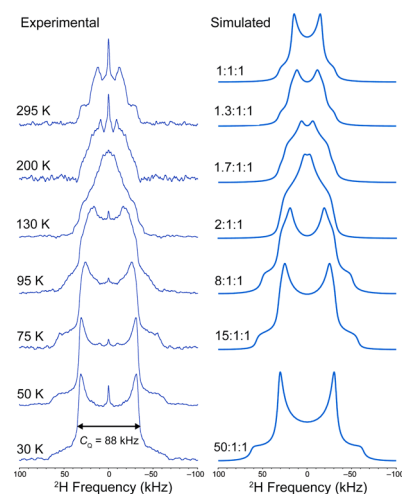


Figure 3. Experimental VT ²H SSNMR of **1-D2** (left) and accompanying simulations of the rotor motion using a *n*:1:1 population model of the various rotational states (right). See text for details (a minor impurity, indicated by the isotropic central “spike”, is not modeled).²⁴

a room-temperature ²H SSNMR spectrum of the “jammed rotor” complex *trans*-D(Cl)Pt(P^tBu₃)₂, **2-D**, was obtained, showing a quadrupolar coupling constant (C_Q) of 110 kHz, indicating a static platinum hydride (Figure S12).²³ Notably, a similar C_Q is observed for **1-D2** only at very low temperatures and about half of that value at room temperature: For **1-D2**, the ²H SSNMR spectrum acquired at 30 K was simulated with a C_Q of 88(2) kHz and an asymmetry parameter (η_Q) of 0.0(1). These ²H EFG tensor parameters (see SI for definitions) are in agreement with those from DFT calculations, indicating that the mode and/or rate of motion at 30 K does not result in a motional averaging of the principal components of the ²H EFG tensors, which would lead to a reduced apparent C_Q and perhaps even a distinct η_Q . The spectra remain relatively unchanged until warming to 75 K, where the effects of motion begin to result in increased values of η_Q (Figure 3, left). Further

increases in temperature result in further increases in η_Q and accompanying decreases in C_Q . At 295 K, the highest temperature used in the experimental study,²⁵ $C_Q = 40$ kHz and $\eta_Q = 0.1$ are observed.

A detailed analysis of the motion must take into account the symmetry of the molecule, as influenced in part by crystal packing. Although the idealized symmetry of the $R_3P-Pt-PR_3$ framework in **1** is D_{3d} , its crystallographic symmetry is only C_i . The H–Pt–H unit is exactly linear. Due to the inversion center, the unique potential energy landscape that unfolds upon a 0° – 180° rotation of the rotator repeats exactly from 180° – 360° . Thus, while there are six minima along the path of a 360° rotation of one of the hydrides, repetition due to C_i symmetry allows for formal treatment as a system with three minima. The minima, shown in Figure 4, are not degenerate in the point

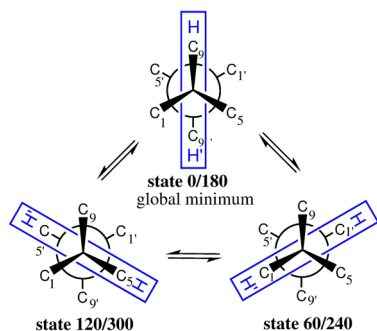


Figure 4. Newman projection along P–Pt–P, illustrating the minima for hydride rotation. Carbon atoms are labeled as in Figure 1.

group of the local symmetry (C_i), although states 60/240 and 120/300, as it turns out (below), are energetically very close. ^2H SSNMR spectra were simulated using the EXPRESS software package.²⁶ Initially, simulations involved simple 2-, 3-, and 6-site jump models (Figure S18) with exchange rates (ν_{ex}) in the intermediate motional regime ($10^3 < \nu_{\text{ex}} < 10^7$ Hz). However, none of these simulations agree with the experimental data. Experimentally varying the echo delay at 120 K results in very little change in the ^2H powder pattern shape, indicating that the exchange is in the fast motion limit ($\nu_{\text{ex}} > 10^7$ Hz) even at that temperature (Figure S19). The temperature-dependent spectral changes appear to arise from different populations associated with each of the energy minima (rotational states shown in Figure 4) at different temperatures.²⁷ The best model for the populations of the states assumes that one conformation is unique and has the lowest energy, while the remaining two conformations, slightly higher in energy, are very similar in energy. The simulated ^2H SSNMR spectra using n :1:1 population distributions (with $n > 1$; n representing the relative population of the global minima states) are shown in Figure 3, right. When the VT populations are plotted in a Van't Hoff fashion (Figure S24), it is predicted that the higher-energy conformations are uphill from the global minimum states by $\sim 0.27(3)$ kcal mol $^{-1}$.

We modeled the energy landscape with DFT (Figure 5), using the C_i -symmetric heavy atom framework directly as obtained from the crystal structure. The Pt–H distance was fixed at the DFT-optimized value (1.657 Å), and the H–Pt–P angle was fixed at 90° . The platinum hydride orientation was varied by incrementing the H–Pt–P–C torsion angle and fixing the other hydride exactly *trans*. In this restricted geometry optimization, simulating the environment in the crystal, the

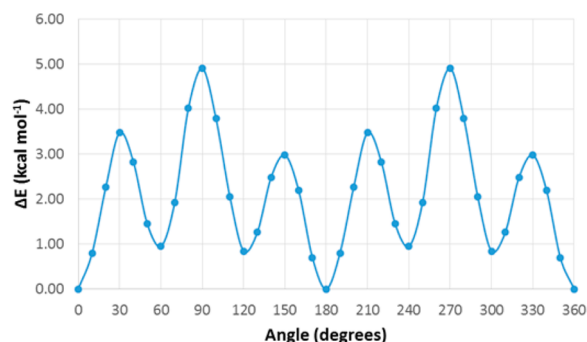


Figure 5. Energy landscape from DFT, using B3LYP. Basis sets include 6-31G** for C, H, and P; LANL2DZ for Pt.

heavy atom framework was not allowed any internal movement, but the *tert*-butyl methyl groups were allowed to rotate. The result (Figure 5) is in qualitative agreement with the experimental data: one global minimum (in fact, the same as suggested by the initial crystallographic refinement) and two other local minima per 180° rotation. The two uphill minima are very similar in energy, consistent with the best model of the experimental ^2H VT NMR data. The quantitative agreement between experiment and theory is not perfect: the energetic separation between the minima is about $0.27(3)$ kcal mol $^{-1}$ experimentally and 0.89 kcal mol $^{-1}$ computationally. Also, the highest barrier between minima, to be consistent with experimental information (fast exchange at 120 K), is ~ 3.0 kcal mol $^{-1}$ or lower (SI, page S26), while the highest barrier computes as 4.9 kcal mol $^{-1}$.

The landscape shown in Figure 5 appears qualitatively appropriate but would have to be scaled (y -axis, energy) by a factor of ~ 0.5 to 0.3 to be quantitatively correct. Possible reasons for this discrepancy include the lack of dispersion forces in the DFT treatment (notoriously hard to treat with DFT),²⁸ in addition to the general problem that very extensive optimization of functional and basis sets would be needed to reduce the error to 1 kcal mol $^{-1}$ or less.

In conclusion, we have demonstrated for the first time that a linear *trans*-dihydride can be a molecular rotor with a very low barrier, even at low temperatures, in the solid state. We expect that this will open the door to more examples in this class of molecules and enlarge the field of facile rotors in the solid state. Further work will be directed to designing systems with controlled motion using different stators and to incorporating a dipole moment.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b08213.

Experimental and computational details (PDF)

Crystal data (CIF)

Crystal data (CIF)

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Notes

The authors declare no competing financial interest.

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- (28) An attempt to improve the quality of the potential energy landscape by adding dispersion corrections Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104. was only partially successful: while the span decreased (from 4.9 to 2.3 kcal mol⁻¹), the order of the minima switched from “one low, two high” to “two low, one high”, inconsistent with the experimental data (a 1:n:n fit is inferior to an n:1:1 fit (for n > 1, see Figure S20 for details)).