in which $\Delta\nu$ is the difference in frequency between the two exchanging sites in the stopped-exchange limit. These rate constants were used to determine the Gibbs energy of activation ΔG^{*} at the coalescence temperature T_c from the Erying equation

$$k_c = (k_b/\hbar)T_c e^{-\Delta G^{*}/RT_c}$$

in which k_b = Boltzmann constant, $\hbar$ = Planck's constant/2π, and R = ideal gas constant.

(K) Equilibrium Constants and ΔH and ΔS Measurements. The positions of equilibrium **2a** ⇄ **3a** and **2b** ⇄ **3b** were determined from ^{31}P NMR spectra. Samples of **3a** and **3b** were weighed and dissolved in a known volume of CD_3COCD_3. The concentrations of the solutions were ca. (0.1–2.0) × 10^{-3} M. In the case of equilibrium between **2b** and **3b**, added CH_3CN was present in concentration in the range (0.20–4.0) × 10^{-3} M. In measurement of thermal parameters ΔH and ΔS, equilibrium constants K_{eq} were measured in the temperature ranges −10 to +20 °C. The probe temperatures were calibrated as described in section J of the Experimental Section. The errors of ΔH and ΔS are reported as the standard deviation from the mean value of three independent runs.

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Supplementary Material Available: Plots of ln K_{eq} versus $1/T$ and their numerical values (**3a** ⇄ **2a**; **3b** ⇄ **2b**) and, for **1c** and **2a**, tables giving final coordinates, bond distances, angles, anisotropic displacement parameters for non-hydrogen atoms, and crystal data (11 pages); listings of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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NMR Study of the Chemical Exchange of the Hydrido Ligands in the Bis(bis(diphenylphosphino)ethane)trihydridodiplatinum(II) Cation by T_1, T_2, and HD Isotopic Perturbation

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Proton longitudinal and transverse relaxation rates of hydrido resonances of different isotopomers in $[H_3Pt_2(Dpe)_2][BF_4]$ [Dpe = bis(diphenylphosphino)ethane] show significant differences in the satellite peaks with respect to the central ones that can be used to evaluate the activation energy of the intramolecular exchange process and the chemical shift separation between bridging and terminal sites. An alternative route to get an estimation of the chemical shift values of the bridging and terminal hydrides in this derivative has been pursued by considering the isotopic shift of the three H_3, H_2D, and HD_2 isotopomers at different temperatures.

$[H_3Pt_2(Dpe)_2]^+[BF_4]^-$ [Dpe = bis(diphenylphosphino)ethane] contains five- and four-coordinated Pt atoms linked through two bridging H atoms and has been described as a donor–acceptor complex in which a neutral 16-electron H_2Pt(diphosphine) unit acts as a donor to a cationic 14-electron $[HPt(diphosphine)]^+$ unit.

Neutron diffraction analysis[1] (Figure 1) was performed to directly locate the hydride ligands showing the presence of a marked asymmetry in the μ_2-bridging hydrides. Variable-temperature ^1H NMR studies[2b] were consistent with a rapid exchange of the terminal and bridging hydride ligands, which cannot be "frozen out" down to the lowest accessible temperature.

The use of proton longitudinal relaxation times as structural probes for hydrido ligands has already been reported.[3] Accurate H–H distances can be obtained in polynuclear cluster compounds as well high relaxation rates can support the presence of nonclassical H_2 ligands in mononuclear systems.[4]

Results and Discussion

In the title compound the hydride region shows a pattern of quintets of quintets resulting from the coupling of the hydride resonance with four equivalent phosphorus (^{31}P, $I = {}^1/_2$, natural abundance 100%) and two equivalent Pt nuclei (^{195}Pt, $I = {}^1/_2$, natural abundance 33.8%). The analysis of this spectral pattern provides averaged values for proton–phosphorus and proton–platinum coupling constants (Figure 2).

Table I reports the values for T_1 and T_2 for central and satellite peaks as measured at different temperatures in CD_2Cl_2 solution. The presence of different isotopomers and the fast chemical exchange cause significant differences in the longitudinal and transverse relaxation rates of the satellite peaks with respect to the central ones.

Table I. Spin–Lattice and Spin–Spin Relaxation Times of $[H_3Pt_2(Dpe)_2]^+[BF_4]^-$ for Central and Satellite Peaks at Different Temperatures in CD_2Cl_2 Solution

	temp, °C							
	22	0	−15	−32	−50	−65	−82	−91
	T_1 (ms)							
central peaks	1162	876	698	542	428	439	630	776
satellite peaks	989	785	644	454	331	346	445	555
	T_2 (ms)							
central peaks	1030	807	589	437	218	143	55	45
satellite peaks	847	675	474	335	173	119	44	32

Central Peaks. The T_1 of these resonances is determined mainly by H–H and P–H dipolar interactions modulated by the molecular tumbling; other contributions (chemical shift anisotropy, CSA, and spin rotation, SR) may be present, but they are expected to contribute much less to the overall relaxation rate of the hydride resonances.

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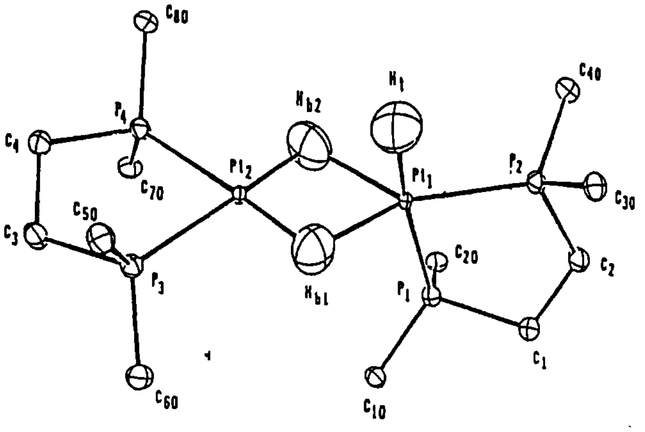

Figure 1. View of the central core of the $[H_3Pt_2(Dpe)_2]^+$ cation as found by neutron diffraction analysis[1] at 20 K. Only the ipso carbons of the phenyl rings are shown, for clarity.

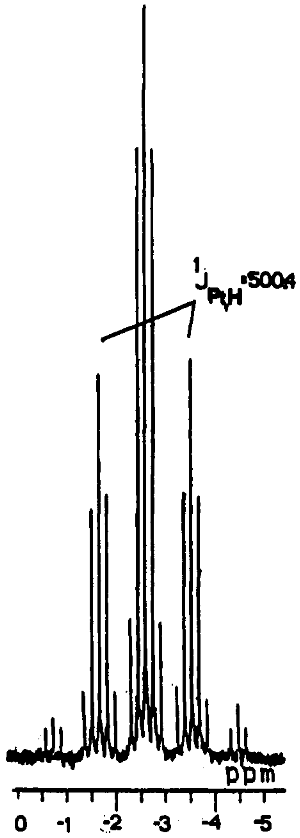

Figure 2. ^1H NMR spectrum (hydride region only) of the $[H_3Pt_2(Dpe)_2]^+$ cation at +23 °C in CD_2Cl_2.

As expected,[5] the T_2 of this set of resonances is lower than T_1 as a consequence of the fast exchange between bridging and terminal sites:

$$\frac{1}{T_2^{\mathrm{obs}}} = \frac{1}{T_2^0} + \frac{1}{T_2^{\mathrm{ex}}} \tag{1}$$

where T_2^0, the transverse relaxation time in the absence of exchange broadening, may be set equal to T_1. The exchange contribution may be evaluated from the equation earlier forwarded by Meiboon and Luz:[6]

$$\frac{1}{T_2^{\mathrm{ex}}} = \sum_i P_i\delta_i^2\tau_M\left[1 - \frac{2\tau_M}{t_{\mathrm{cp}}}\tanh\frac{t_{\mathrm{cp}}}{2\tau_M}\right] \tag{2}$$

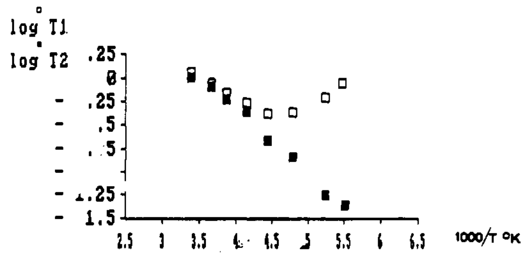

Figure 3. log T_1 and log T_2 vs $1/T$ (K) for the central peaks of the $[H_3Pt_2(Dpe)_2]^+$ cation.

where P_i is the fraction of ith nucleus, δ_i is the chemical shift difference (rad/s) as measured from the center of gravity of the spectrum, τ_M is the average lifetime of the states, and t_{cp} is the time between the 180° pulses in the Carr–Purcell–Meiboon–Gill sequence.

The assumptions in eq 2 are (a) the decay is assumed to be exponential, (b) the spin–spin relaxation times are the same for the two sites in the absence of exchange and equal to T_2^0, and (c) $t_{\mathrm{cp}} \ll T_2$ (typically $t_{\mathrm{cp}} = 0.1$ ms; $T_2 = 44$–1030 ms). In our case, where $t_{\mathrm{cp}}/2\tau_M > 5$, eq 2 simplifies to

$$\frac{1}{T_2^{\mathrm{ex}}} = 0.22(\delta_\omega)^2\tau_M \tag{3}$$

where δ_ω is the separation between bridging and terminal hydrido resonances.

Satellite Peaks. The T_1's of satellite peaks (sat) differ from those of the central peaks (cp) for the dipolar contribution associated with the interaction of a magnetically active Pt nucleus.

$$\frac{1}{T_1^{\mathrm{sat}}} = \frac{1}{T_1^{\mathrm{cp}}} + \frac{1}{T_1^{\mathrm{dd(Pt\text{-}H)}}} \tag{4}$$

The magnitude of this contribution is given by

$$\frac{1}{T_1^{\mathrm{dd(Pt\text{-}H)}}} = \frac{4\gamma_{\mathrm{Pt}}^2\gamma_{\mathrm{H}}^2S(S+1)}{3r^6}f(\tau_c) \tag{5}$$

The increase of the longitudinal relaxation rate of the satellite peaks with respect to the central peaks is quite small (Table I), as expected on the basis of the small γ value for platinum-195. On the other hand, the difference in T_2 between the two sets of resonances is markedly higher; this is due to an additional scalar coupling contribution that selectively affects T_2^{sat}:

$$\frac{1}{T_2^{\mathrm{sat}}} = \frac{1}{T_2^{\mathrm{cp}}} + \frac{1}{T_2^{\mathrm{dd(Pt\text{-}H)}}} + \frac{1}{T_2^{\mathrm{sc}}} \tag{6}$$

$$\frac{1}{T_2^{\mathrm{sc}}} = \frac{{}^1J_{\mathrm{Pt\text{-}H}}{}^2S(S+1)}{3}\left[\tau_M + \frac{\tau_M}{1 + (\omega_H - \omega_{\mathrm{Pt}})^2\tau_M^2}\right] \tag{7}$$

which represents a modulation of the scalar interaction between ^{195}Pt and ^1H nuclei by the intramolecular exchange process characterized as in eq 3 by τ_M.

Since the averaged $^1J_{\mathrm{Pt\text{-}H}}$ values are known, evaluation of eq 7 allows the determination of τ_M. This has been done at different temperatures, and an Arrhenius plot of the log of the exchange rates ($K = 1/\tau_M$) vs $1/T$ provides and activation energy associated with the exchange (17.2 kJ/mol). Now the knowledge of τ_M allows us to get an estimation of δ_ω according to eq 3; from the body of these calculations, the chemical shift separation between bridging and terminal hydrides results as equal to 2.0 ± 0.1 ppm.

Figure 3 shows the behavior of log T_1 and log T_2 vs $1/T$ (K). The compound shows a T_1 minimum close to −50 °C; at this temperature then $\tau_c\omega_0 = 0.62$. It follows that we can estimate the magnitude of the magnetic interaction C whose modulation via τ_c determines the T_1 of the central peaks:

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$$\frac{1}{T_1^{\mathrm{cp}}} = C\tau_{\mathrm{c}} \tag{8}$$

By assuming that C does not vary in the range of temperatures considered in this study, we can compute the τ_c values at each temperature at which T_1's have been measured. An Arrhenius plot of these values vs $1/T$ (K) affords the activation energy associated with the molecular tumbling (8.6 kJ/mol).

For the central peaks C results from several H, H and H, P magnetic interactions, but to a first approximation it may be roughly regarded as the result of the interactions inside the set of the three hydride resonances:

$$C = \frac{2\gamma^4\hbar^2S(S+1)}{r_{\mathrm{H,H}}^6} \tag{9}$$

If we consider that each hydride interacts with the other two, an averaged $r_{\mathrm{H,H}}$ distance of 2.53 ± 0.03 Å is found in good agreement with the 2.399, 2.401, and 2.561 Å obtained for the $r_{\mathrm{H,H}}$ distances from the neutron diffraction study.[1]

H, D Isotopic Perturbation. In this fast-exchanging system an alternative approach to the indirect evaluation of the chemical shifts for bridging and terminal hydrides may be provided by the H, D isotopic perturbation of the equilibria suggested some years ago by Saunders and co-workers.[7]

Actually this technique has already been applied to discuss the solution structure of a binuclear Pt, Re hydride complex,[8] but no quantitative evaluation of the parameters involved in the exchange process was done in that case.

A more detailed application was reported by Shapley et al.[9] in the study of $HOs_3(CO)_{10}CH_3$, and the large H/D Saunders effect observed in its H, D isotopomers was taken as strong evidence for the occurrence of a C–H–Os interaction in this compound.

In order to get more insight into the exchange process of the hydride ligands, we investigated the VT behavior of ^{1}H NMR spectra of a mixture of the three $HD_2Pt_2(Dpe)_2^+$, $H_2DPt_2(Dpe)_2^+$, and $H_3Pt_2(Dpe)_2^+$ isotopomers. Their averaged hydride resonances are at −2.5602, −2.5977, and −2.6320 ppm, respectively. These isotopic shifts are larger than that found upon substitution of H and D in the stereochemically rigid $H_2Os_3(CO)_{10}$ molecule (0.0068 ppm) and thus indicative of the occurrence of an H, D isotopic perturbation of the equilibrium.

The phenomenon is clearly shown by the large variation of the isotopic shift on lowering the temperature. Defining $D_1 = \tau_{\mathrm{H_3}} - \tau_{\mathrm{H_2D}}$ and $D_2 = \tau_{\mathrm{H_2D}} - \tau_{\mathrm{HD_2}}$, we observed the variation of D_1 between 0.0343 and 0.0634 ppm and of D_2 between 0.0375 and 0.0632 ppm in the temperature range +22 to −65 °C. The chemical shift of the three isotopomers is related to the chemical shifts τ_{B} and τ_{T} of the bridging and terminal hydrides by eqs 10–12, where $A = \exp(-\Delta E/RT)$ and ΔE is the energy difference between the forms containing the deuterium in the terminal or in the bridging position.

$$\tau_{\mathrm{H_3}} = \frac{2\tau_{\mathrm{B}} + \tau_{\mathrm{T}}}{3} \tag{10}$$

$$\tau_{\mathrm{H_2D}} = \frac{A\tau_{\mathrm{T}} + (A+1)\tau_{\mathrm{B}}}{1+2A} \tag{11}$$

$$\tau_{\mathrm{HD_2}} = \frac{2\tau_{\mathrm{B}} + A\tau_{\mathrm{T}}}{2+A} \tag{12}$$

Owing to the relatively small chemical shift difference expected between the two exchanging sites, reliable values for bridging and terminal hydride resonances have been found only by introducing in eqs 10–12 $\tau_{\mathrm{H_2D}}$ and $\tau_{\mathrm{HD_2}}$ values corrected by the contribution of the "static" H, D isotopic effect. The best fit of data was obtained by assigning a static H, D isotopic shift of 0.0077 ppm, which is quite close to the value found by us for the μ_2-H resonance in $H_2Os_3(CO)_{10}$.[3b]

Finally, by solving eqs 10–12, we have obtained the following parameters: $\tau_{\mathrm{B}} = 11.20 \pm 0.2$ ppm, $\tau_{\mathrm{T}} = 14.2 \pm 0.4$ ppm, and $E_{\mathrm{A}} = 404 \pm 50$ J/mol. The chemical shift values found by this approach are in good enough agreement with the chemical shift difference evaluated through the analysis of longitudinal and transverse relaxation processes.

Experimental Section

The trihydrido complex, $[Pt_2H_3(Dpe)_2][BF_4]$, and the deuterated analogue, $[Pt_2D_3(Dpe)_2][BF_4]$, were obtained and purified according to the literature.[2a]

A partially deuterated sample was obtained according to the same procedure by using a $NaBD_4/KBH_4$ mixture (molar ratio 3/1). The compound (30 mg) dissolved in 0.5 mL of CD_2Cl_2 was degassed by using Schenk tube techniques and the freeze–thaw methodology.

NMR spectra were recorded on a Jeol GX 270/89 spectrometer operating at 270 MHz.

The spin-lattice relaxation times were measured by using the inversion recovery technique, and spin-spin relaxation times were obtained with the Carr–Purcell–Meiboon–Gill pulse sequence.[5] Each measurement was repeated at least five times, and the weighted average of the relaxation times was used for the calculations. Errors are estimated to be ±2% for T_1 and ±5% for T_2.

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