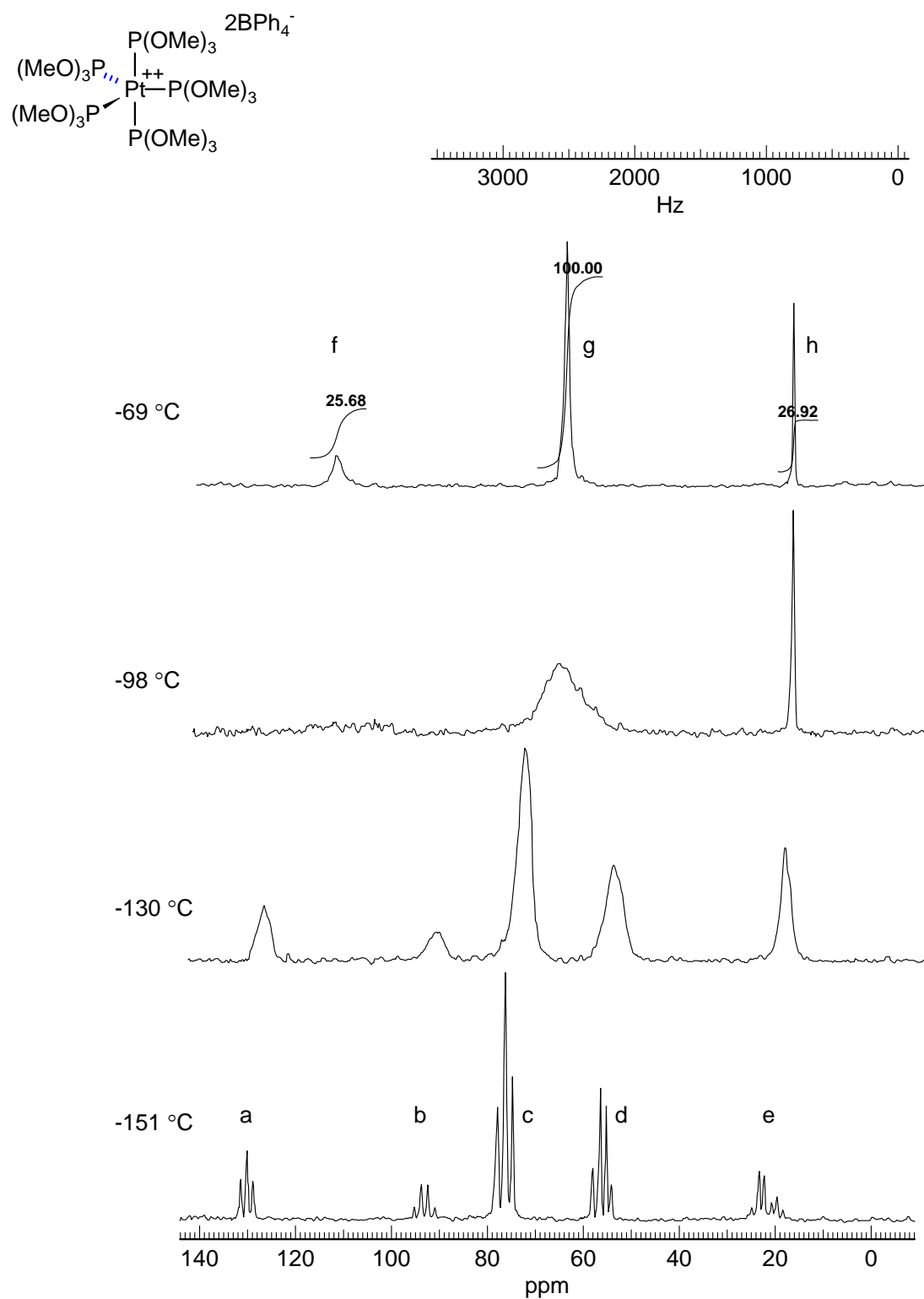


**Problem R-99P** ( $\text{C}_{15}\text{H}_{45}\text{O}_{15}\text{P}_5\text{Pt}^{2+} 2\text{BPh}_4^-$ ).

Temperature dependent 36.43 MHz  $\{^1\text{H}\}$   $^{31}\text{P}$  NMR Spectra in  $\text{CHClF}_2$

Source: *J. Am. Chem. Soc.* **1974**, 96, 5760 (digitized from hard copy)



**Problem R-99P** ( $C_{15}H_{45}O_{15}P_5Pt^{2+} 2BPh_4^-$ ). This problem requires you to interpret the 36.43 MHz  $^{31}P$  variable temperature NMR spectra of a platinum phosphite complex  $Pt[P(OCH_3)_3]_5^{++} 2BPh_4^-$ . The spectrum was taken with proton decoupling.

(a) Analyze the low temperature (-151 °C) spectrum. Explain the origin of each of the marked multiplets a to e with reference to the structure of the compound. Report coupling constants. Use the form  $^nJ_{X-Y} = 00.0$  Hz. In your drawings, feel free to use "P" for the  $P(OCH_3)_3$  group. Hint: make sure you consider the NMR active isotope(s) of platinum.

Multiplet a:

Multiplet b:

Multiplet c:

Multiplet d:

Multiplet e:

(b) What molecular process is responsible for the changes in the NMR spectrum as a function of temperature? Is it intra- or intermolecular? Explain how you know.

(c) For the spectra at -98 °C and -69 °C, explain why multiplet f is broad and multiplet h is relatively sharp (at still higher temperature both f and h become sharp).

**Problem R-99P** ( $\text{C}_{15}\text{H}_{45}\text{O}_{15}\text{P}_5\text{Pt}^{2+} 2\text{BPh}_4^-$ ). This problem requires you to interpret the 36.43 MHz  $^{31}\text{P}$  variable temperature NMR spectra of a platinum phosphite complex  $\text{Pt}[\text{P}(\text{OCH}_3)_3]_5^{++} 2\text{BPh}_4^-$ . The spectrum was taken with proton decoupling.

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Multiplet a:

3

This is one of the  $^{195}\text{Pt}$  satellites of the central triplet c corresponding to the equatorial P  
 $^1J_{\text{P-Pt}} \approx 3940$  Hz (actual value reported in paper 4100 Hz)

Multiplet b:

3

This is one of the  $^{195}\text{Pt}$  satellites of the central quartet d corresponding to the apical P  
 $^1J_{\text{P-Pt}} \approx 2800$  Hz (actual value reported in paper 2840 Hz)

Multiplet c:

3

This is the  $^{31}\text{P}$  signal of the equatorial  $\text{P}(\text{OMe})_3$  ligands - triplet due to coupling to the two apical  $\text{P}(\text{OMe})_3$   
 $\delta$  77 ppm, t,  $^2J_{\text{P-P}} = 60$  Hz

Multiplet d:

3

This is the  $^{31}\text{P}$  signal of the apical  $\text{P}(\text{OMe})_3$  ligands - quartet due to coupling to the three equatorial  $\text{P}(\text{OMe})_3$   
 $\delta$  56 ppm, q,  $^2J_{\text{P-P}} = 60$  Hz

Multiplet e:

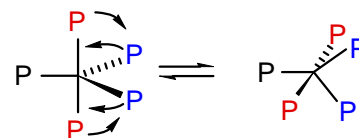
3

These are the other two  $^{195}\text{Pt}$  satellites of the central peaks, the q and t are distorted because they are coupled to each other (leaning)

(b) What molecular process is responsible for the changes in the NMR spectrum as a function of temperature? Is it intra- or intermolecular? Explain how you know.

5

Berry pseudorotation of the trigonal-bipyramidal structure (swapping of two apical with two equatorial  $\text{P}(\text{OMe})_3$ ). The process is intramolecular since the the P-Pt coupling is not lost



(c) For the spectra at -98 °C and -69 °C, explain why multiplet f is broad and multiplet h is relatively sharp (at still higher temperature both f and h become sharp).

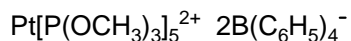
5

The peak f resulted from coalescence of a and b. which are much further apart than the signals e and e', which means at a and b coalesce at much higher temperature than e and e' (it requires a higher pseudorotation rate to fully average a and b)

**Problem R-99P** ( $\text{C}_{15}\text{H}_{45}\text{O}_{15}\text{P}_5\text{Pt}^{2+} 2\text{BPh}_4^-$ ).

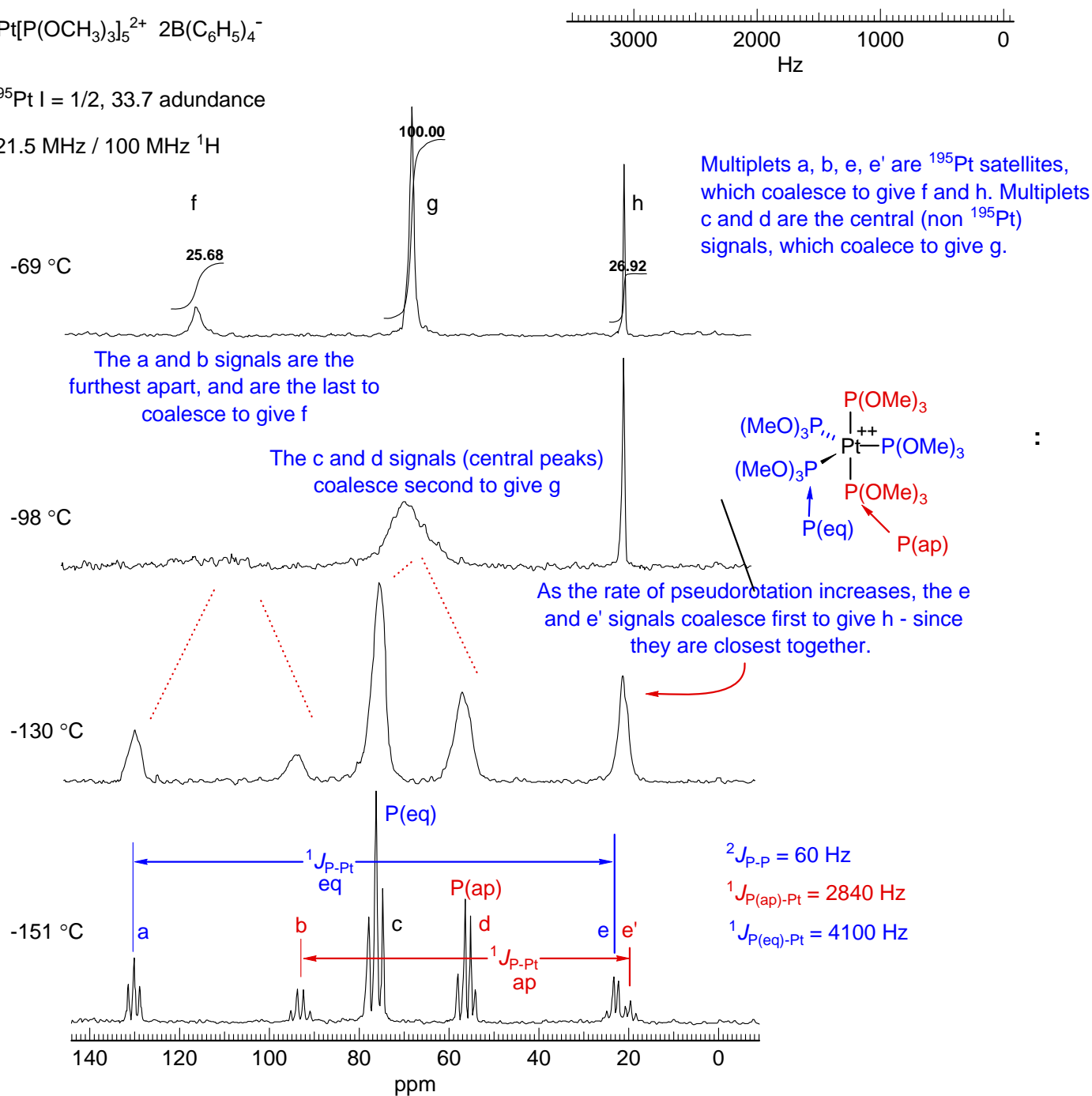
Temperature dependent 36.43 MHz  $\{^1\text{H}\}$   $^{31}\text{P}$  NMR Spectra in  $\text{CHClF}_2$

Source: *J. Am. Chem. Soc.* **1974**, 96, 5760 (digitized from hard copy)



$^{195}\text{Pt}$  I = 1/2, 33.7 abundance

21.5 MHz / 100 MHz  $^1\text{H}$



In the low-temperature spectrum there are distinct  $^{31}\text{P}$  signals for the apical and equatorial phosphite ligands - the apical a triplet, the equatorial a quartet due to P-P coupling. Each one has  $^{195}\text{Pt}$  satellites, which are also triplets and quartets. The e and e' signals are quite close, and coupled to each other, so there is a lot of leaning, much less for the a and b signals (also coupled to each other) since they are far apart. The fact that the e and e' signals coalesce with each other to form h, and the a and b signals to form f, proves that the sign of the PtP coupling constant is the same for the apical and equatorial P (not surprising).

The fact that the high temperature spectrum still has  $^{195}\text{Pt}$  satellites shows that the exchange is intramolecular, since intermolecular exchange would cause loss of  $^{31}\text{P}$ - $^{195}\text{Pt}$  coupling. This is a Berry pseudorotation