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 CHClF\(_2\)

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Problem R-99P \((C_{15}H_{45}O_5P_5Pt^{2+} \cdot 2BPh_4^-)\). This problem requires you to interpret the 36.43 MHz \(^{31}\text{P}\) variable temperature NMR spectra of a platinum phosphite complex \(\text{Pt}[(\text{OCH}_3)_3]_5^{2+} \cdot 2\text{BPh}_4^-\). 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 \(\text{P}((\text{OCH}_3)_3\) 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 \((C_{15}H_{45}O_{15}P_{3}Pt^{2+} 2BPh_{4}^-)\). This problem requires you to interpret the 36.43 MHz \(^{31}\text{P}\) variable temperature NMR spectra of a platinum phosphite complex \(\text{Pt[P(OCH}_{3}\text{)}_{3}]_5^{2+} 2\text{BPh}_{4}^-\). 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 \(^1J_{X,Y} = 00.0\) Hz. In your drawings, feel free to use "P" for the \(\text{P(OCH}_{3}\text{)}_{3}\) group. Hint: make sure you consider the NMR active isotope(s) of platinum.

Multiplet a:
- 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:
- 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:
- This is the \(^{31}\text{P}\) signal of the equatorial \(\text{P(OCH}_{3}\text{)}_{3}\) ligands - triplet due to coupling to the two apical \(\text{P(OCH}_{3}\text{)}_{3}\)
- \(\delta\) 77 ppm, t, \(^2J_{\text{P-P}} = 60\) Hz

Multiplet d:
- This is the \(^{31}\text{P}\) signal of the apical \(\text{P(OCH}_{3}\text{)}_{3}\) ligands - quartet due to coupling to the three equatorial \(\text{P(OCH}_{3}\text{)}_{3}\)
- \(\delta\) 56 ppm, q, \(^2J_{\text{P-P}} = 60\) Hz

Multiplet e:
- 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.

Berry pseudorotation of the trigonal-bipyramidal structure (swapping of two apical with two equatorial \(\text{P(OCH}_{3}\text{)}_{3}\)). 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).

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 \((C_{15}H_{45}O_{15}P_5Pt^{2+} \ 2BPh_4^-)\).

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


\[
Pt[P(OCH_3)_3]_5^{2+} \ 2B(C_6H_5)_4^- \\
^{195}Pt I = 1/2, 33.7 abundance
\]

21.5 MHz / 100 MHz \(^1H\)

-69 °C

The a and b signals are the furthest apart, and are the last to coalesce to give f

-98 °C

The c and d signals (central peaks) coalesce second to give g

-130 °C

As the rate of pseudorotation increases, the e and e' signals coalesce first to give h - since they are closest together.

-151 °C

Multiplets a, b, e, e' are \(^{195}Pt\) satellites, which coalesce to give f and h. Multiplets c and d are the central (non \(^{195}Pt\)) signals, which coalesce to give g.

\[
^{2}J_{P,P} = 60 \text{ Hz} \\
^{1}J_{Pt(ap)-Pt} = 2840 \text{ Hz} \\
^{1}J_{Pt(eq)-Pt} = 4100 \text{ Hz}
\]

In the low-temperature spectrum there are distinct \(^{31}P\) signals for the apical and equatorial phosphite ligands - the apical a triplet, the equatorial a quartet due to P-P coupling. Each one has \(^{195}Pt\) 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 \(^{195}Pt\) satellites shows that the exchange is intramolecular, since intermolecular exchange would cause loss of \(^{31}P-^{195}Pt\) coupling. This is a Berry pseudorotation