Problem R-12N (C_{22}H_{28}ClP_4Pd).
32.4 MHz $^{31}$P-$^{1}$H NMR spectra in toluene-d$_8$
Source: Chem. Commun. 1988, 1615 (digitized hard copy)

(a) Identify all signals in the low temperature spectrum (-75 °C), and report approximate coupling constants using the form: $\delta$, $^XJ_{1-2}$ = ____ Hz. Use the numberings shown on the structure. For each signal briefly give your reasoning for the assignment.

(b) Identify the process which is responsible for the changes in the NMR spectrum at the higher temperatures (-30 °C and +50 °C). The signal at -122 ppm in the +50 °C spectrum is a triplet. Draw a structure or an equation.

(c) What is the proton frequency (MHz) of the spectrometer which was used for these spectra?

(a) Identify all signals in the low temperature spectrum (-75 °C), and report approximate coupling constants using the form: $\delta$, $^XJ_{i,j}$ = ____ Hz. Use the numberings shown on the structure. For each signal briefly give your reasoning for the assignment.

This is the P closest to the two PEt$_3$ groups, so expect triplet splitting. The dtd ($J = 502, 49, 22$ Hz) at $\delta$ -17 is the only signal that shows a triplet, so this must be P$^1$, which should also be coupled to both P$^2$ and P$^3$, as observed.

P$^1$  
$\delta$ -17, $^1J_{P1,P2} = 502$ Hz, $^2J_{P1,P4/5} = 49$ Hz, $^2J_{P1,P3} = 20$ Hz

P$^2$ should also show the large $^1J$ to P$^1$, so it must be the dd ($J = 500, 45$ Hz) at $\delta$ 18. P$^1$ and P$^2$ form an ABXY$_2$ system, would need to do an AB quartet calculation to get accurate chemical shifts.

P$^2$  
$\delta$ 18, $^1J_{P1,P2} = 500$ Hz, $^2J_{P1,P3} = 40$ Hz

P$^3$ is coupled to both P$^1$ and P$^2$ (dd, $J = 46, 25$ Hz), so it has to be the $\delta$ 112 signal.

P$^3$  
$\delta$ 112, $^2J_{P3,P2} = 40$ Hz, $^2J_{P3,P1} = 20$ Hz

This is the signal with double area at $\delta$ -122, d, $J = 48$ Hz.

P$^4$, P$^5$  
$\delta$ -122, $^1J_{P4/5,P1} = 46$ Hz

(b) Identify the process which is responsible for the changes in the NMR spectrum at the higher temperatures (-30 °C and +50 °C). The signal at -122 ppm in the +50 °C spectrum is a triplet. Draw a structure or an equation.

The Pd migrates back and forth between P$^1$ and P$^2$, so their chemical shifts are averaged, and both P$^3$ and P$^4/P^5$ become triplets, equally coupled to both. Since the two coupling constants are fairly close (expect the P$^4/P^5$ coupling to be $(49+0)/2 = 25$, and P$^3$ coupling to be $(40+20)/2 = 30$ Hz in size, the P$^1/P^2$ signal becomes an approximate quartet.

The exchange is intramolecular, since the coupling between P$^1/P^2$ and P$^4/P^5$ is maintained in the high temperature spectrum.

(c) What is the proton frequency (MHz) of the spectrometer which was used for these spectra?

32.4x$(100/40.49) = 80$ MHz
Problem R-12N \(\text{(C}_{22}\text{H}_{28}\text{ClP}_{4}\text{Pd)}\).  
32.4 MHz \(^3\text{P}\{-\text{^1H}\} \text{NMR spectra in toluene-d}_6\)  
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