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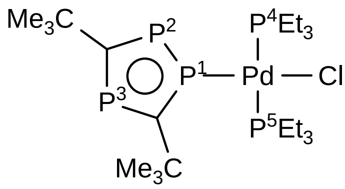
Problem R-12N. Analyze the ^{1}H decoupled 32.4 MHz ^{31}P NMR spectra of a palladium-phosphine complex shown on the next page (Bartsch, R.; Carmichael, D.; Hitchcock, P. B.; Meidine, M. F.; Nixon, J. F.; Sillett, G. J. D. *J. Chem. Soc., Chem. Commun.* **1988**, 1615).

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



$C_{22}H_{28}ClP_5Pd$

4 This is the P closest to the two PEt$_3$ groups, so expect triplet splitting. The dtd (J = 502, 49, 22 Hz) at δ -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 δ -17, $^{1}J_{P1\text{-}P2}$ = 502 Hz, $^{2}J_{P1\text{-}P4/5}$ = 49 Hz, $^{2}J_{P1\text{-}P3}$ = 20 Hz

4 P^2 should also show the large ^{1}J to P^1, so it must be the dd (J = 500, 45 Hz) at δ 18. P^1 and P^2 form an <u>AB</u>XY$_2$ system, would need to do an AB quartet calculation to get accurate chemical shifts

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

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

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

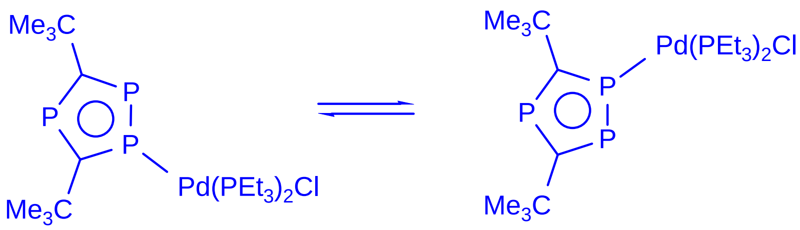
3 This is the signal with double area at δ -122, d, J = 48 Hz

P^4, P^5 δ -122, $^{1}J_{P4/5\text{-}P1}$ = 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.

8 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

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Problem R-12N. 32.4 MHz $^{31}P\text{-}\{^{1}H\}$ NMR spectra.
Solvent toluene-d_8
(Source: *Chem. Commun.* **1988**, 1615)