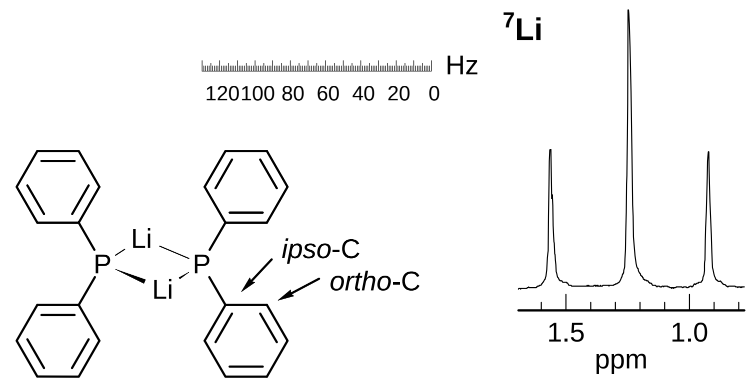
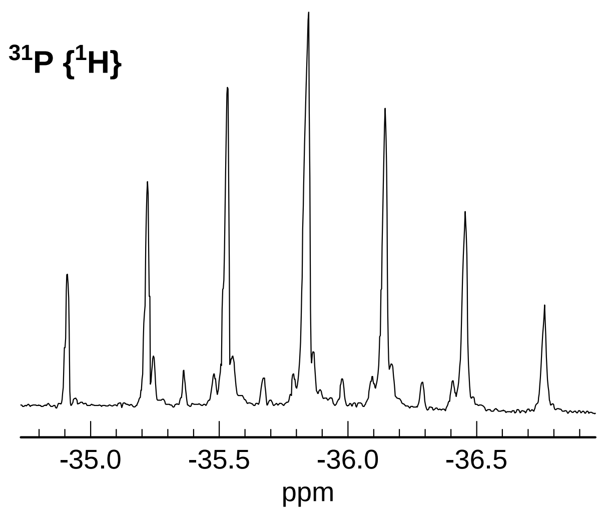
Problem R-08O. Analyze the ^{7}Li, ^{31}P and ^{13}C NMR spectra of lithium diphenylphosphide dimer $(Ph_2PLi)_2$ ($C_{24}H_{20}LiP$). The spectra were measured at -110 °C in ether. All nuclei are at *natural abundance* (Reich, H. J.; Dykstra, R. D. *Organometallics* **1994**, *13*, 4578). The Hz scale applies to all spectra.

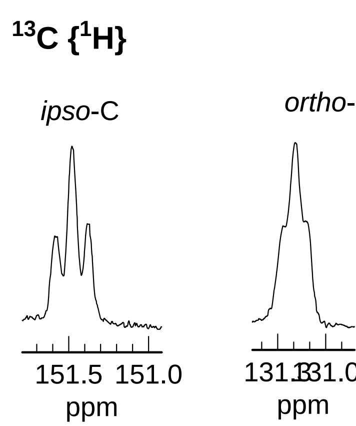
(a) Analyze the 139.96 MHz ^{7}Li NMR spectrum. Report all couplings in the standard format ($^nJ_{XY}$ = 112 Hz).



(b) Analyze the 145.8 MHz proton decoupled ^{31}P NMR spectrum (report couplings and explain the peaks). Include the series of small peaks between the larger ones in your analysis:



(c) Provide a reasonable explanation for why the *ipso* and *ortho* carbons of the phenyl groups in the proton decoupled 90.6 MHz ^{13}C NMR spectrum are triplets.



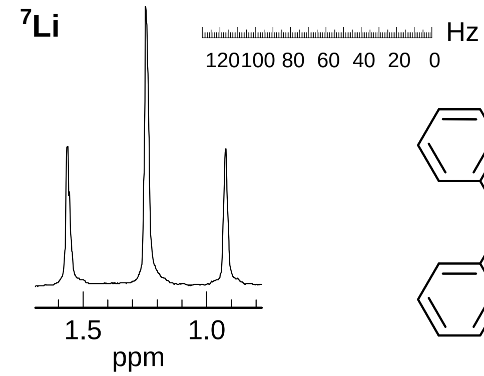
PLT ex-3-08-09-gq.plt

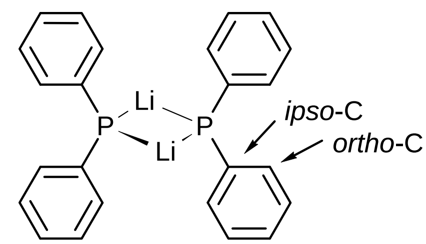
20 **Problem R-08O**. Analyze the ^{7}Li, ^{31}P and ^{13}C NMR spectra of lithium diphenylphosphide dimer $(Ph_2PLi)_2$. The spectra were measured at -110 °C in ether. All nuclei are at *natural abundance* (Reich, H. J.; Dykstra, R. D. *Organometallics* **1994**, *13*, 4578). The Hz scale applies to all spectra.

(a) Analyze the 139.96 MHz ^{7}Li NMR spectrum. Report all couplings in the standard format ($^nJ_{XY}$ = 112 Hz).

4

Triplet, $J_{Li\text{-}P}$ = 45 Hz
^{7}Li coupled equally to two ^{31}P nuclei





(b) Analyze the 145.8 MHz proton decoupled ^{31}P NMR spectrum (report couplings and explain the peaks). Include the series of small peaks between the larger ones in your analysis:

^{7}Li I = 3/2 92.6% 38.87 MHz (^{1}H = 100 MHz)

^{6}Li I = 1 7.4% 14.71 MHz

Large peaks: 1:2:3:4:3:2:1 septet, $^1J_{PLi}$ = 45 Hz
^{31}P coupled equally to two ^{7}Li (I = 3/2)

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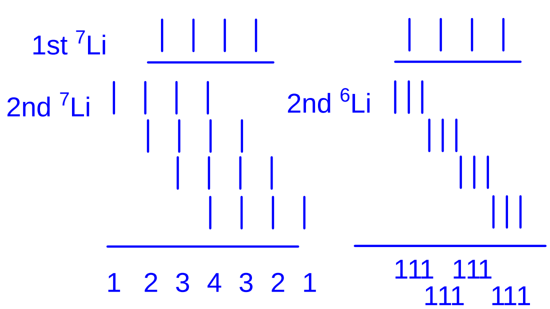
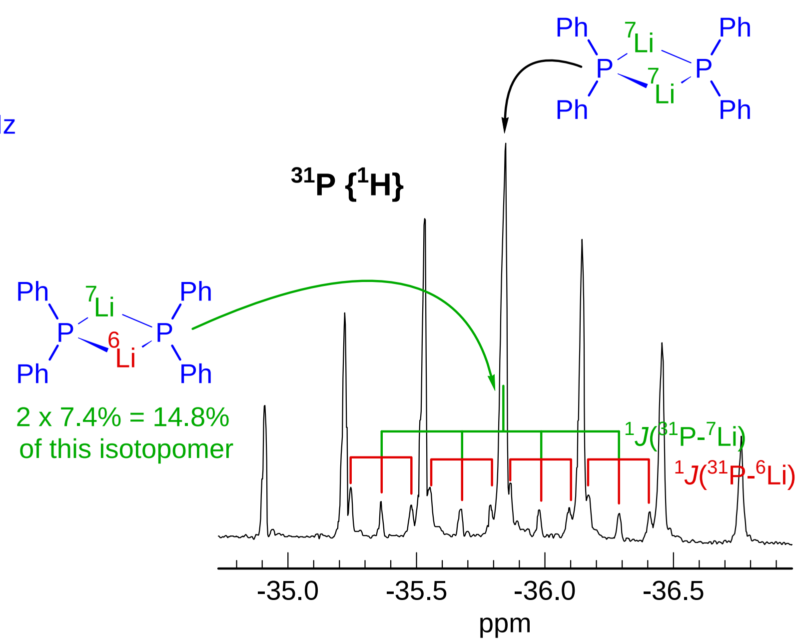
Small peaks due to natural abundance of ^{6}Li
1:1:1:1 quartet of 1:1:1 triplets
^{31}P coupled to one ^{7}Li and one ^{6}Li
$^1J_{P7Li}$ = 45 Hz, $^1J_{P6Li}$ = 16.7 Hz





(c) Provide a reasonable explanation for why the *ipso* and *ortho* carbons of the phenyl groups in the proton decoupled 90.6 MHz ^{13}C NMR spectrum are triplets.

6

There must be a large P-P coupling across the lithiums (greater than about 200 Hz, as it turns out). This results in a "virtually coupled" situation (ABX with ν_{AB} = 0), in which the X (in this case ^{13}C signals) appears to be coupled to both phosphorus nuclei