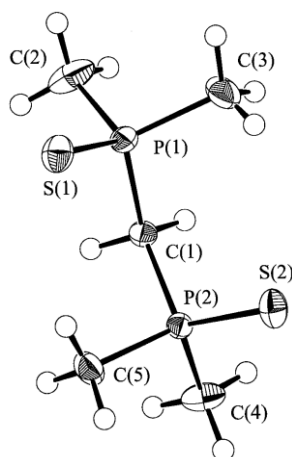


## Reactivity of the bridged-sulfide complex $\text{Pd}_2\text{Cl}_2(\mu\text{-S})(\mu\text{-dmpm})_2$ toward electrophiles ; dmpm = bis(dimethylphosphino)methane

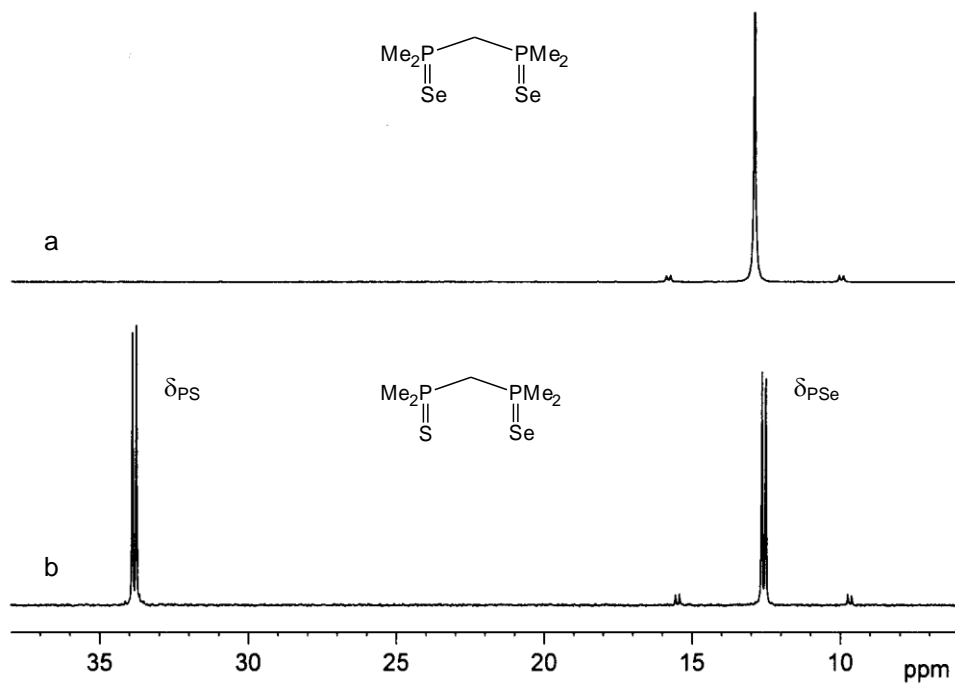
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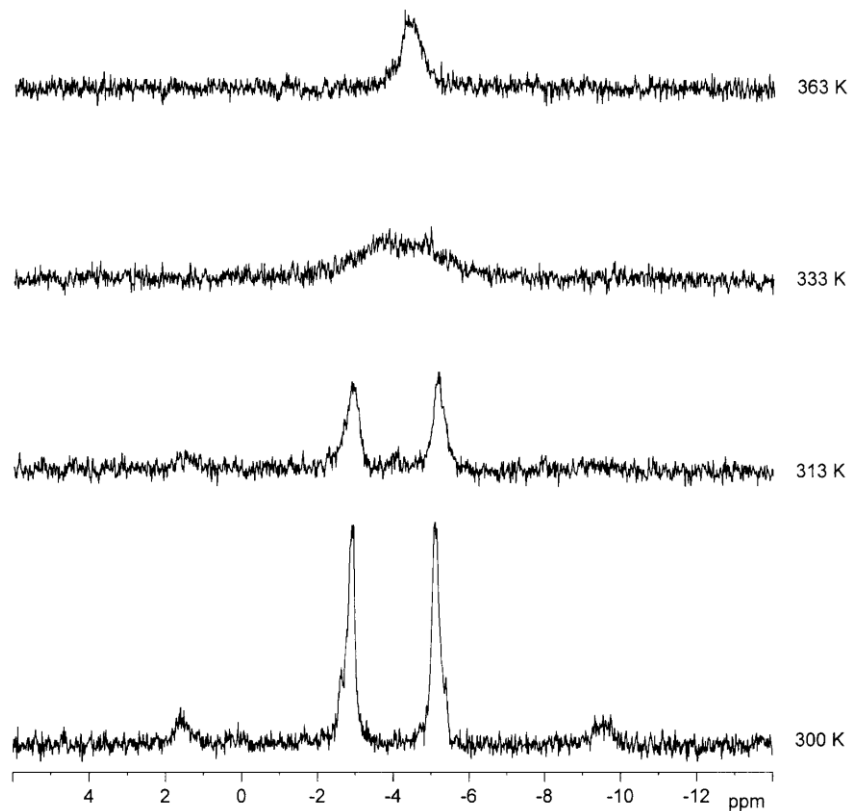
### Supplementary Material



**Figure S1.** ORTEP diagram of  $\text{dmpm}(\text{S})_2$  with 50% probability ellipsoids. Bond lengths (Å) and angles (°):  $\text{S}(1)\text{-P}(1)=1.9504(9)$ ,  $\text{S}(2)\text{-P}(2)=1.9523(9)$ ,  $\text{P}(1)\text{-C}(1)=1.822(2)$ ,  $\text{P}(1)\text{-C}(2)=1.798(3)$ ,  $\text{P}(1)\text{-C}(3)=1.789(3)$ ,  $\text{P}(2)\text{-C}(1)=1.817(2)$ ,  $\text{P}(2)\text{-C}(4)=1.796(3)$ ,  $\text{P}(2)\text{-C}(5)=1.800(3)$ ;  $\text{S}(1)\text{-P}(1)\text{-C}(1)=115.46(8)$ ,  $\text{S}(1)\text{-P}(1)\text{-C}(2)=111.84(10)$ ,  $\text{S}(1)\text{-P}(1)\text{-C}(3)=114.41(10)$ ,  $\text{S}(2)\text{-P}(2)\text{-C}(1)=115.75(9)$ ,  $\text{S}(2)\text{-P}(2)\text{-C}(4)=112.94(10)$ ,  $\text{S}(2)\text{-P}(2)\text{-C}(5)=113.64(9)$ ,  $\text{C}(2)\text{-P}(1)\text{-C}(3)=106.45(13)$ ,  $\text{C}(4)\text{-P}(2)\text{-C}(5)=105.56(12)$ ,  $\text{P}(1)\text{-C}(1)\text{-P}(2)=118.75(12)$ .



**Figure S2.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra ( $\text{CDCl}_3$ ) of (a)  $\text{dmpm}(\text{Se})_2$  and (b)  $\text{dmpm}(\text{S})(\text{Se})$ , both showing the  $^2J_{\text{PP}}$  and  $^1J_{\text{PSe}}$  coupling.



**Figure S3.** VT  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra ( $\text{MeNO}_2\text{-}d_3$ ) of  $[\text{Pd}_2\text{Cl}_2(\mu\text{-SMe})(\text{dmpm})_2]\text{OTf}$  (5). The AA'BB' signal collapses at  $\sim 60^\circ\text{C}$  to give a broad singlet at higher temperature.