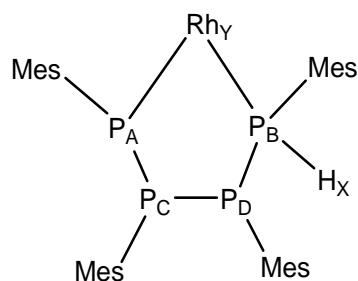
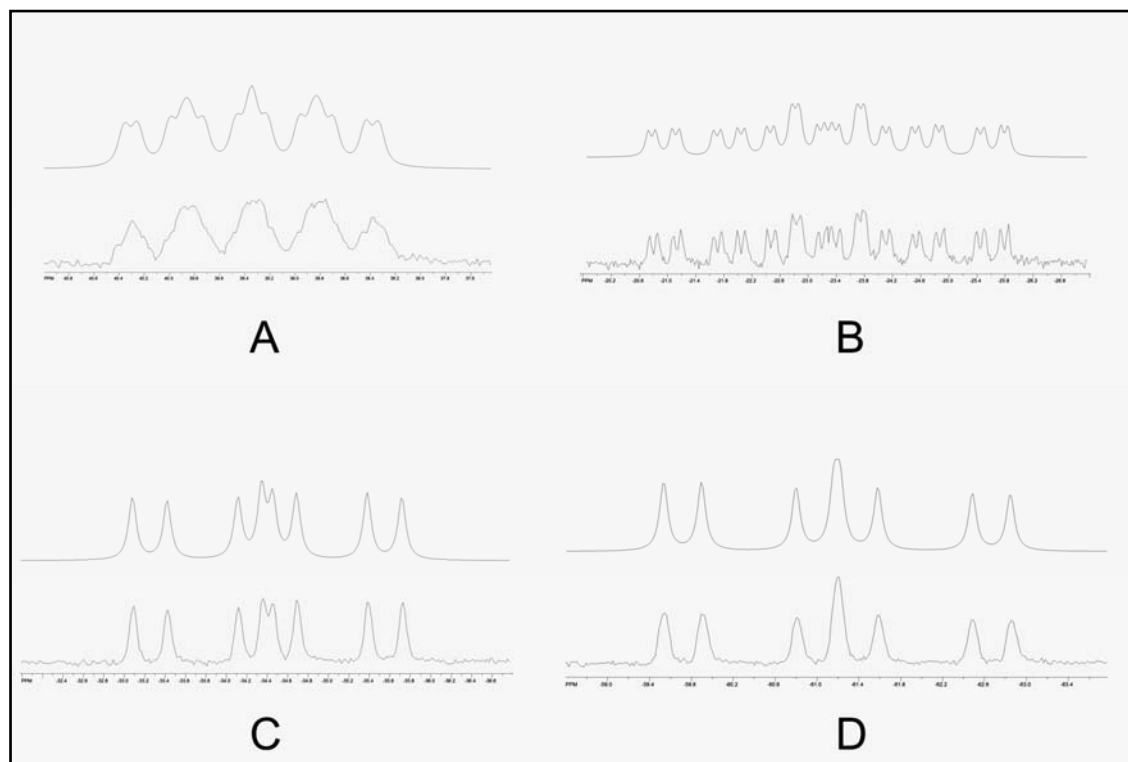


Supporting information.

The supporting information contains:

1. Simulated and experimental ^{31}P NMR spectrum of $[\text{Rh}(\text{P}_4\text{HMe}_4)(\text{cod})]$ (**3**)
2. Variable temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $[\text{Rh}_2(\mu\text{-P}_2\text{HMe}_2)(\mu\text{-PHMe})(\text{cod})_2]$ (**4**)

1. Simulated (top) and experimental (bottom) ^{31}P NMR spectrum of $[\text{Rh}(\text{P}_4\text{HMe}_4)(\text{cod})]$ (**3**)



^{31}P NMR (THF/ $[\text{D}_8]$, 25 °C, for the predominant isomer): 39.34 (m, P_A , $^1J_{\text{AC}} = 167.55$, $^1J_{\text{AY}} = 85.32$, $^2J_{\text{AB}} = 16.54$, $^2J_{\text{AD}} = 57.96$, $^3J_{\text{AX}} = 5.29$ Hz), -23.31 (m, P_B , $^1J_{\text{BD}} = 272.71$, $^1J_{\text{BY}} = 160.60$, $^1J_{\text{BX}} = 335.24$, $^2J_{\text{BC}} = 55.29$), -34.41 (m, P_C , $^1J_{\text{CD}} = 205.56$), -61.16 (m, P_D).

2. Variable temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $[\text{Rh}_2(\mu\text{-P}_2\text{HMes}_2)(\mu\text{-PHMes})(\text{cod})_2]$ (4)

