Supporting information.

The supporting information contains:

1. Simulated and experimental $^{31}$P NMR spectrum of [Rh(P$_4$HMes$_4$)(cod)] (3)

2. Variable temperature $^{31}$P{$_1$H} NMR spectra of [Rh$_2$(μ-P$_2$H$_2$Mes$_2$)(μ-PH$_2$Mes)(cod)$_2$] (4)

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

-31P NMR (THF/[D$_8$], 25 °C, for the predominant isomer): 39.34 (m, PA, $^1$J$_{AC}$ = 167.55, $^1$J$_{AY}$ = 85.32, $^2$J$_{AB}$ = 16.54, $^2$J$_{AD}$ = 57.96, $^3$J$_{AX}$ = 5.29 Hz), -23.31 (m, PB, $^1$J$_{BD}$ = 272.71, $^1$J$_{BY}$ = 160.60, $^1$J$_{BX}$ = 335.24, $^2$J$_{BC}$ = 55.29), -34.41 (m, PC, $^1$J$_{CD}$ = 205.56), -61.16 (m, PD).
2. Variable temperature $^{31}\text{P}^{1\text{H}}$ NMR spectra of $[\text{Rh}_2(\mu-P_2\text{HMes}_2)(\mu-P\text{HMes})(\text{cod})_2]$ (4)