Supporting Information

Rhodium Complexes in P–H Bond Activation Reactions

Víctor Varela-Izquierdo,[a] Ana M. Geer,*[b] Bas de Bruin,[c] José A. López,[a] Miguel A. Ciriano,[a] and Cristina Tejel*[a]

chem_201903981_sm_miscellaneous_information.pdf
Selected crystallographic data for \( [(Tp)(H)Rh(\mu-PPh_2)_2Rh(PHPh_2)_2] \) 0.5H_2O (7·0.5H_2O). Crystal data for 7·0.5H_2O: C_{57}H_{54}BN_{6}O_{0.5}P_{4}Rh_{2}, \( M_r = 1171.57 \), monoclinic, space group \( P2_1/n \), \( a = 10.1225(9), b = 23.858(2), c = 22.240(2) \) Å, \( \beta = 96.3060(10), V = 5338.6(8) \) Å³, \( Z = 4, \rho_{\text{calc}} = 1.458 \) g cm\(^{-3} \), \( F(000) = 2388, T = 100(2) \) K, MoK\( \alpha \) radiation (\( \lambda = 0.71073 \) Å, \( \mu = 0.783 \) mm\(^{-1} \)). Data were collected with a yellow needle (0.32 × 0.06 × 0.02 mm). Of 38802 measured reflections (2\( \theta \): 2.5-53.1º), 11057 were unique (\( R_{\text{int}} = 0.0572 \)). Final agreement factors were \( R_1 = 0.0412 \) (8020 observed reflections) and \( wR_2 = 0.0941 \). Data/restraints/parameters 11057/1/653; GOF = 1.020. Largest peak and hole in the final difference map 0.813 and -0.643 e Å\(^{-3} \).

Selected crystallographic data for \([Rh(Tp)(IMes)(PHPh_2)]\) (11). Crystal data for 11: C_{42}H_{45}BN_{8}PRh, \( M_r = 806.55 \), triclinic, space group \( P-1 \), \( a = 13.3019(12), b = 17.3033(16), c = 18.1535(17) \) Å, \( \alpha = 87.9497(14), \beta = 71.6254(14), \gamma = 88.4523(14), V = 3962.2(6) \) Å³, \( Z = 4, \rho_{\text{calc}} = 1.352 \) g cm\(^{-3} \), \( F(000) = 1672, T = 100(2) \) K, MoK\( \alpha \) radiation (\( \lambda = 0.71073 \) Å, \( \mu = 0.512 \) mm\(^{-1} \)). Data were collected with a yellow prismatic block (0.23 × 0.21 × 0.14 mm). Of 42447 measured reflections (2\( \theta \): 2.3-60.0º), 21181 were unique (\( R_{\text{int}} = 0.0214 \)). Final agreement factors were \( R_1 = 0.0294 \) (17823 observed reflections) and \( wR_2 = 0.0676 \). Data/restraints/parameters 21181/0/969; GOF = 1.020. Largest peak and hole in the final difference map 0.465 and -0.444 e Å\(^{-3} \).

Selected crystallographic data for \([Rh(Tp)(H)(POPh_2)(PHPh_2)]\) (14). Crystal data for 14: C_{33}H_{32}BN_{6}OP_{2}Rh, \( M_r = 704.30 \), monoclinic, space group \( Cc \), \( a = 13.8971(11), b = 15.5914(12), c = 14.8704(11) \) Å, \( \beta = 99.7810(10), V = 3175.2(4) \) Å³, \( Z = 4, \rho_{\text{calc}} = 1.473 \) g cm\(^{-3} \), \( F(000) = 1440, T = 100(2) \) K, MoK\( \alpha \) radiation (\( \lambda = 0.71073 \) Å, \( \mu = 0.676 \) mm\(^{-1} \)). Data were collected with a yellow irregular block (0.15 × 0.12 × 0.08 mm). Of 13804 measured reflections (2\( \theta \): 3.9-54.0º), 6783 were unique (\( R_{\text{int}} = 0.0266 \)). Final agreement factors were \( R_1 = 0.0343 \) (6352 observed reflections) and \( wR_2 = 0.0845 \). Data/restraints/parameters 6783/3/406; GOF = 1.036. Largest peak and hole in the final difference map 0.856 and -0.708 e Å\(^{-3} \).
Selected NMR Spectra:

Figure S1. Selected region of: a) $^1$H NMR spectrum, b) $^1$H-selnOe and c) $^1$H-seltocsy irradiating the resonance corresponding to the Ph$^{01}$ proton (marked with a ray) of complex [[(Tp)(H)Rh($\mu$-PPh$_2$)$_2$]]$_2$ (3) in [D$_6$]-benzene. The hydride region of the $^1$H and $^1$H($^{31}$P) NMR spectra are shown in the blue inset, whereas the $^{31}$P($^1$H) NMR spectrum of 3 is shown in the green inset.
Figure S2. Selected region of the $^1$H NMR spectrum of [Rh(Tp)(H)(PMe$_2$Ph)(PPh$_2$)] (5) in [D$_6$]-benzene. The hydride region of the $^1$H and $^1$H($^3$P) NMR spectra are shown in the blue inset, whereas the $^{31}$P{$^1$H} NMR spectrum of 5 is shown in the green inset.

Figure S3. Selected regions of the $^1$H NMR spectrum of [Rh(Tp)(H)(PHPh$_2$)(PPh$_2$)] (6) in [D$_8$]-toluene at $-70$ °C. Selected regions of the $^1$H($^3$P) NMR spectrum are shown in the blue inset, whereas the $^{31}$P{$^1$H} NMR spectrum of 6 is shown in the green inset.
Figure S4. Selected region of the $^1$H NMR spectrum of [(Tp)(H)Rh$^\text{III}$($\mu$-PPh$_2$)$_2$Rh($^1$PPh$_2$)$_2$] (7) in [D$_6$]-benzene. The hydride region of the $^1$H and $^1$H($^3$1P) NMR spectra are shown in the blue inset.

Figure S5. Selected regions of the $^{31}$P($^1$H) NMR spectrum (in black) and simulated (in red) of [(Tp)(H)Rh$^\text{III}$($\mu$-PPh$_2$)$_2$Rh($^1$PPh$_2$)$_2$] (7) in [D$_6$]-benzene. A selected region of the $^1$H,$^3$1P-hmbc NMR spectrum is shown on the right.
**Figure S6.** Selected region of the $^1$H NMR spectrum of 8 in [D$_6$]-benzene, showing the signals of the hydrido-phosphanido complex [Rh(Tp)(H)(PMePh$_2$)(PPh$_2$)] 8a. The hydride region of the $^1$H and $^1$H$^{31}$P NMR spectra are shown in the blue inset, whereas the $^{31}$P($^1$H) NMR spectrum of 8 is shown in the green inset.

**Figure S7.** $^{31}$P($^1$H) NMR of the reaction mixture after mixing [Rh(Tp)(C$_2$H$_4$)(PPh$_3$)] (6.7 %) [Rh($^{2}$-Tp)(PPh$_3$)(PHPh$_2$)] (10b, 41.3 %) [Rh(Tp)(H)(PPh$_3$)(PPh$_2$)] (10a, 14.7 %) [Rh(Tp)(H)(PHP$_2$)(PPh$_3$)] (6, 20.2 %) [(Tp)(H)Rh($^{\mu}$-PPh$_2$)$_2$] (3, 1.5 %) PPh$_3$ (15.6 %)

$^{31}$P($^1$H) NMR of the reaction mixture after mixing [Rh(Tp)(C$_2$H$_4$)(PPh$_3$)] (2) and PPh$_3$ in [D$_6$]-benzene. The blue insets show the hydride (down) and ethylene (up) regions of the $^1$H NMR spectrum.
Figure S8. Van ’t Hoff plots for the equilibria $[\text{Rh}(\kappa^2\text{-Tp})(\text{PMePh}_2)(\text{PHPh}_2)] \quad (8b) \rightleftharpoons [\text{Rh}(\text{Tp})(\text{H})(\text{PMePh}_2)(\text{PHPh}_2)] \quad (8a)$ (in blue) and $[\text{Rh}(\kappa^2\text{-Tp})(\text{PPh}_3)(\text{PHPh}_2)] \quad (10b) \rightleftharpoons [\text{Rh}(\text{Tp})(\text{H})(\text{PPh}_3)(\text{PHPh}_2)] \quad (10a)$ (in red).

Figure S9. $^1\text{H}$ NMR spectrum of $[\text{Rh}(\kappa^2\text{-Tp})(\text{IMes})(\text{PHPh}_2)] \quad (11)$ in [D$_6$]-benzene and a selected region of the $^1\text{H},^1\text{H}$-noesy NMR spectrum showing the negative cross-peaks due to the chemical exchange of the pyrazolate protons.
Figure S10. Selected regions of the $^1$H (down) and $^1$H($^{31}$P) (up) NMR spectra of [Rh($^{\kappa_2}$-Tp)(BzMe)(PHPh$_2$)] (12) in [D$_6$]-benzene. The $^{31}$P($^1$H) NMR spectrum is shown in the green inset.

Figure S11. Selected region of the $^1$H NMR spectrum of [[Rh(Tp)($^{\eta_1}$-$^{1}$Et)(C,P-CH$_2$CH$_2$PPh$_2$)] (13) in [D$_6$]-benzene. A selected region of the $^1$H,$^1$H-cosy NMR spectrum is shown in the upper part.
Figure S12. Selected region of the $^1$H NMR spectrum of [Rh(Tp)(H)(POPh$_2$)(PHPh$_2$)] (14) in [D$_6$]-benzene. The hydride region of the $^1$H and $^1$H($^3$P) NMR spectra are shown in the blue inset, whereas the $^3$P($^1$H) NMR spectrum of 14 is shown in the green inset.

Figure S13. Selected regions of the $^1$H,$^3$P-hmbc NMR spectra of [Rh(Tp)(H)(POPh$_2$)(PHPh$_2$)] (14) in [D$_6$]-benzene with correlation times corresponding to $J$(H,P)= 10 Hz (left) and $J$(H,P)= 400 Hz (right).
Figure S14. $^1$H NMR spectrum of [{(Tp)(η$^1$-Et)Rh(µ-OPPh$_2$)}$_2$] (15) in [D$_6$]-benzene. The $^{31}$P{$^1$H} NMR spectrum of 15 is shown in the green inset.

Figure S15. $^{31}$P{$^1$H} NMR spectra in [D$_6$]-benzene of: i) a mixture of the dinuclear complex [{(Tp)(η$^1$-Et)Rh(µ-OPPh$_2$)}$_2$] (15) and OPHPh$_2$ (bottom), ii) after warming for 2h at 60 °C (middle) and iii) after warming for 14h at 60 °C (top), showing the full transformation into the mononuclear complexes [Rh(Tp)(η$^1$-Et)(POPh$_2$)(POHPh$_2$)] (16) and [Rh(Tp)(H)(POPh$_2$)(POHPh$_2$)] (17).
Figure S16. Selected regions of the $^1$H NMR spectrum of a mixture of [Rh(Tp)(η$^1$-Et)(POPh$_2$)(POHPh$_2$)] (16, in red) and [Rh(Tp)(H)(POPh$_2$)(POHPh$_2$)] (17, in gray) in [D$_6$]-benzene.

**R = Et 16, H 17**