Electronic Supplementary Information for Dalton Transactions

Kinetico-mechanistic studies of the acidolysis of Rh-C bonds in monocyclometallated dirhodium(II) acetato complexes; influence of electronic and steric effects.

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Supplementary material

Figure S1.- Observed ^{1}H NMR spectral changes (aromatic zone, CD_3COOD, 65 °C) with time on dissolution of compound $Rh_2P(4\text{-}MeC_6H_4)_3$. Top initial spectrum, bottom after *ca.* 7 h.

FIGURE S1

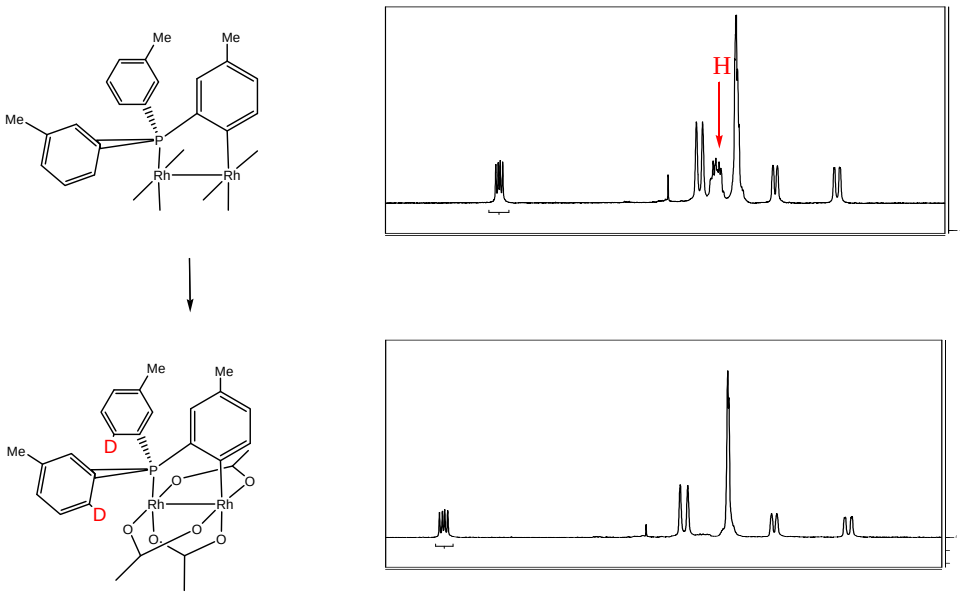
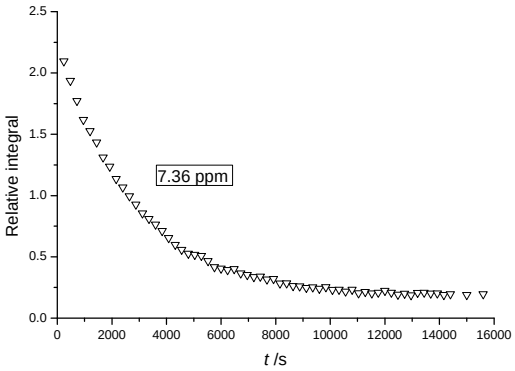


Figure S2.- Changes in the relative integral of selected proton signals for the relevant *ortho* hydrogens on complex $Rh_2P(4\text{-}MeC_6H_4)_3$ with time (CD_3COOD, 400 MHz, 65 °C).



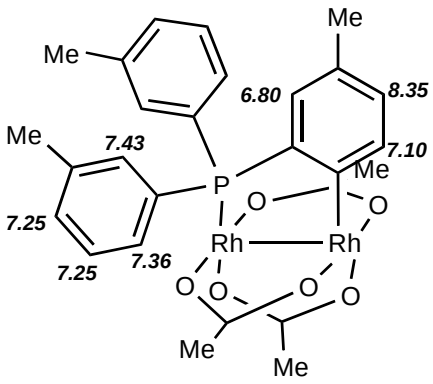


Table S1.- Observed rate constants for the acid cleavage of the Rh-C bonds of the different compounds studied as a function of the temperature.

Compound	T /K	k_{obs} /s^{-1}
Rh_2PPh_3	335	4.6×10^{-6}
	344	1.1×10^{-5}
	353	2.7×10^{-5}
	362	8.2×10^{-5}
$Rh_2P(5\text{-}MeC_6H_4)_3$	343	7.7×10^{-6}
	353	1.7×10^{-5}
	363	3.2×10^{-5}
	373	8.8×10^{-5}
$Rh_2P(4\text{-}MeC_6H_4)_3$	335	4.1×10^{-5}
	344	1.2×10^{-4}
	353	2.9×10^{-4}
	362	4.4×10^{-4}
$Rh_2P(5\text{-}CF_3C_6H_4)_3$	353	1.2×10^{-6}
	363	2.6×10^{-6}
	373	4.2×10^{-6}
	383	6.2×10^{-6}
$Rh_2P(4\text{-}CF_3C_6H_4)_3$	363	2.4×10^{-6}
	373	3.2×10^{-6}
	378	3.7×10^{-6}
	383	4.5×10^{-6}

Table S2.- Characterization data before H/D scrambling exchange for all the complexes studied in this work and indicated in Chart 1.

Compound	^{1}H (300 MHz) in CD_3COOD	^{31}P (121 MHz) in $CDCl_3$	^{19}F (282 MHz) in $CDCl_3$
Rh_2PPh_3	2.26 (s, 3), 2.32 (s, 6), 6.80 (m, 1), 7.07 (m, 1), 7.36 (m, 4), 7.35 (m, 2), 7.42 (m, 2), 8.35 (m, 1)	18.2 ($J_{Rh\text{-}P}$ = 150, $^{2}J_{Rh\text{-}P}$ = 6)	-
$Rh_2P(5\text{-}MeC_6H_4)_3$	2.04 (s, 3), 2.06 (s, 6), 2.39 (s, 6), 2.42 (s, 3), 6.79 (m, 1), 7.16 (m, 1), 7.39 (m, 4), 7.42(m, 4), 7.46 (m, 4), 8.29 (m, 1)	16.8 ($J_{Rh\text{-}P}$ = 158, $^{2}J_{Rh\text{-}P}$ = 6)	-
$Rh_2P(4\text{-}MeC_6H_4)_3$	2.06 (s, 3), 2.16 (s, 6), 2.26 (s, 3), 2.32 (s, 6), 6.80 (m, 1), 7.10 (m, 1), 7.25 (m, 4), 7.36 (m, 2), 7.43 (m, 2), 8.35 (m, 1)	17.7 ($J_{Rh\text{-}P}$ = 150, $^{2}J_{Rh\text{-}P}$ = 6)	-
$Rh_2P(5\text{-}CF_3C_6H_4)_3$	0.94 (broad, 3), 1.35 (broad, 6), 2.15 (s, 6), 2.05 (s, 3), 6.83 (m, 1), 7.10 (m, 1), 7.68 (m, 4), 7.79 (m, 4), 8.86 (broad signal, 1)	19.8 ($J_{Rh\text{-}P}$ = 154)	−66.89 ppm (s, 1), −66.39 ppm (s, 2)
$Rh_2P(4\text{-}CF_3C_6H_4)_3$	2.03 (s, 3), 2.16 (s, 6), 7.27 (m, 1), 7.55 (m, 1), 7.72 (m, 4), 7.88 (d, 2), 8.06 (d, 2), 8.89 (m, 1)	20.7 ($J_{Rh\text{-}P}$ = 156)	−66.82 ppm (s, 1), −66.39 ppm (s, 2)