Supplementary Material (ESI) for Dalton Transactions

Supporting Information

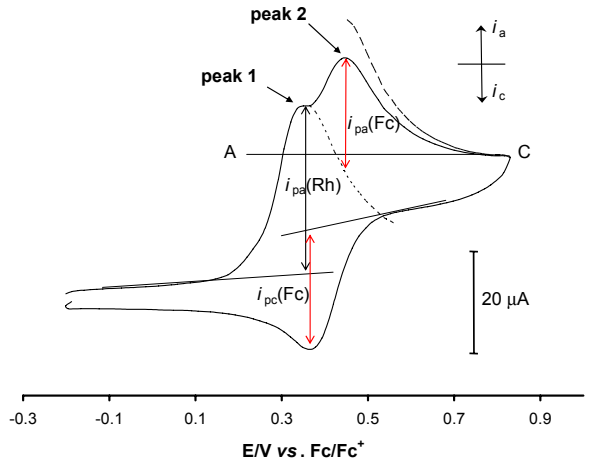
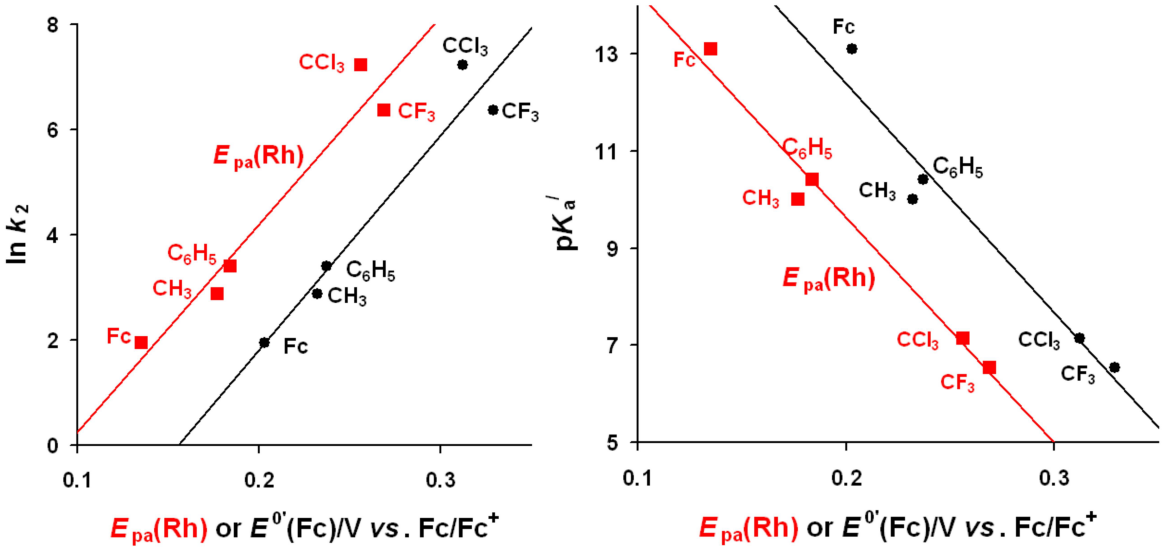


Figure S1: The decay current of rhodium(I) oxidation (peak 1) is estimated by multiplying the decaying current of Fc oxidation (peak 2) from the basis line AC with the ratio i_{pa}(Rh)/i_{pc}(Fc) to allow for the two electron flow during rhodium(I) oxidation as compared to the one electron flow during Fc oxidation. The artificially obtained line is shown as ----- . This line is then translatorily shifted without distortion to coincide exactly with the E_{pa} value of the rhodium(I) oxidation peak (peak 1) and is indicated by ……. The anodic peak current i_{pa}(Fc) of the ferrocenyl group can then be measured as the current between peak 2 and the newly obtained anodic decay current for rhodium(I) oxidation. This method is used since both Rh and Fc are part of the same complex, implying that the diffusion rate of rhodium(I) and Fc should be the same even though rhodium(I) oxidation represents a two electron and Fc a one electron process (the molecule does not divide in any way to allow different diffusion rates for the Rh and Fc fragments).



(a) **(b)**

Figure S2: (a) Linear dependence of the ln of the second-order rate constant of the substitution of the $(FcCOCHCOR)^-$ ligand with phen from [Rh(FcCOCHCOR)(cod)], lnk_2, and E_{pa}(Rh) (top) or $E^{o'}$(Fc) (bottom) in [Rh(FcCOCHCOR)(cod)]. (b) The relationship between $E^{o'}$(Fc) (top) or E_{pa}(Rh) (bottom) of [Rh(FcCOCHCOR)(cod)] and the $pK_a^{/}$ of the free uncoordinated $FcCOCH_2COR$ ligand. R is indicated on the graph.

Table S1: Electrochemical data and conditions for complexes **1** - **5** measured in 0.1 mol dm^{-3} $[N(^nBu_4)][PF_6]/CH_3CN$ on a glassy carbon electrode at 25.0(1) °C *vs.* Fc/Fc^+. The concentration of **3** was 0.7 mmol dm^{-3}, other complexes had concentration 1.0 mmol dm^{-3}.

ν/m Vs^{-1}	rhodium		ferrocenyl group					rhodium		Ferrocenyl group				
	E_{pa} /V	i_{pa} /μA	E_{pa} /V	ΔE_p /mV	$E^{o''}$ /V	i_{pc}/ μA	i_{pc}/i_{pa}	E_{pa} /V	i_{pa} /μA	E_{pa} /V	ΔE_p /mV	$E^{o''}$ /V	i_{pc}/ μA	i_{pc}/i_{pa}
	[Rh(FcCOCHCOCF$_3$)(cod)], **1**							[Rh(FcCOCHCOC$_6$H$_5$)(cod)], **4**						
50	0.255	23	0.368	75	0.329	17	0.98	0.172	24	0.271	67	0.237	18	0.98
100	0.269	33	0.369	79	0.329	24	1.02	0.184	34	0.273	74	0.237	25	0.97
150	0.281	39	0.372	88	0.328	28	1.01	0.189	42	0.277	79	0.237	31	0.98
200	0.281	46	0.372	91	0.327	32	1.04	0.197	48	0.279	85	0.237	36	0.98
	[Rh(FcCOCHCOCCl$_3$)(cod)], **2**							[Rh(FcCOCHCOFc)(cod)], **5** first ferrocenyl group						
50	0.244	24	0.355	92	0.309	19	0.98	0.123	15	0.233	64	0.201	*	*
100	0.256	33	0.360	95	0.312	25	0.98	0.135	25	0.238	71	0.203	*	*
150	0.264	40	0.352	98	0.313	29	0.98	0.142	33	0.240	76	0.202	*	*
200	0.268	46	0.361	100	0.311	33	1.00	0.145	39	0.243	81	0.203	*	*
	[Rh(FcCOCHCOCH$_3$)(cod)], **3**							[Rh(FcCOCHCOFc)(cod)], **5** second ferrocenyl group						
50	0.170	19	0.268	71	0.232	12	0.98	-	-	0.343	81	0.303	13	*
100	0.177	29	0.270	76	0.232	17	1.02	-	-	0.346	88	0.302	23	*
150	0.187	36	0.270	78	0.232	21	1.00	-	-	0.347	92	0.301	28	*
200	0.192	42	0.270	81	0.23	25	0.99	-	-	0.348	95	0.300	31	*

* not accurately determinable