Supplementary Information

Table S1. Structural data for the intermediate species in the H_2-evolving catalytic cycle of [Ni(xbsms)Ru(CO)$_2$Cl$_2$] (BP86 in DMF)

Bond (Å)/angle (°)	**[NiRu]$^-$** (initial and final steps)	**[NiHRu]**	**[NiHRu]$^-$**	**[NiRu(H$_2$)]**	**[NiRu]**
Ni-Ru	2.733	2.934	2.823	2.982	2.819
Ru-H$_1$		**1.614**	**1.629**	**1. 813**	
Ru-H$_2$				**1.700**	
Ni-H$_1$		**2.342**	**1.951**	**1.850**	
Ni-H$_1$-Ru		**93.9**	**103.7**	109.0	
Hinge Ni-2S-Ru	97.9	106.7	101.0	110.0	100.9
Hinge 2S-Ni-2S	171.5	176.4	173.8	174.2	174.2

Table S2. Mulliken spin densities for the intermediate species in the H_2-evolving catalytic cycle of [Nixbsms)Ru(CO)$_2$Cl$_2$] (BP86 in DMF)

Atom	**[NiRu]$^-$**	**[NiHRu]**	**[NiHRu]$^-$**	**[NiRu(H$_2$)]**	**[NiRu]**
Ru	**0.601**	0.0	0.015	0.027	0.649
Ni	**-0.425**	0.0	**–0.674**	**–0.674**	0.124
Cl_2	0.116	0.0	0.005	0.012	0.143
S_1	–0.080	0.0	–0.104	–0.111	0.026
S_2	–0.079	0.0	–0.072	–0.080	-0.002
S_3	–0.079	0.0	–0.072	–0.080	-0.002
S_4	–0.079	0.0	–0.104	–0.111	0.025

Table S3. Atomic (ESP) charges for the intermediate species in the H_2-evolving catalytic cycle of [Ni(xbsms)Ru(CO)$_2$Cl$_2$] (BP86 in DMF except for X-ray which was gas-phase optimized)

Atom	[Ni(xbsms)Ru(CO)$_2$Cl$_2$]	**[NiRu]$^-$**	**[NiHRu]**	**[NiHRu]$^-$**	**[NiRu(H_2)]**	**[NiRu]**
Ru	0.108	0.720	0.462	0.680	0.031	0.385
Ni	0.235	0.322	0.277	0.275	0.260	0.320
Cl_1	–0.467					
Cl_2	–0.406	–0.806	–0.717	–0.816	–0.530	-0.707
H_1			**–0.209**	**–0.274**	**–0.323**	
H_2					**0.845**	
S_1	–0.162	–0.503	–0.272	–0.446	–0.387	-0.298
S_2	–0.112	–0.317	–0.183	–0.272	–0.277	-0.206
S_3	–0.113	–0.316	–0.182	–0.274	–0.279	-0.207
S_4	–0.163	–0.493	–0.276	–0.452	–0.395	-0288
Total 4S	–0.550	–1.629	–0.913	–1.443	–1.338	-0.998
$C_{21}O_{21}$	0.058	–0.270	–0.092	–0.189	0.063	-0.132
$C_{22}O_{22}$	0.058	–0.270	–0.090	–0.190	0.060	-0.132

Table S4. Mayer bond orders for the intermediate species in the H_2-evolving catalytic cycle of [Ni(xbsms)Ru(CO)$_2$Cl$_2$] (BP86 in DMF except for X-ray which was gas-phase optimized)

Atoms	[Ni(xbsms)Ru(CO)$_2$Cl$_2$]	**[NiRu]$^-$**	**[NiHRu]**	**[NiHRu]$^-$**	**[NiRu(H$_2$)]**	**[NiRu]**
Ru-H_1			0.697	0.617	0.464	
Ru-H_2					0.312	
Ni-H			0.126	0.262		
Ru-Cl_1	0.083					
H_1-H_2					0.374	
Ru-C_{21}	1.257	1.428	1.313	1.371	1.192	1.359
Ru-C_{22}	1.258	1.430	1.314	1.371	1.190	1.360
Ru-Cl_2	0.807	0.364	0.462	0.394	0.611	0.457
Ru-S_1	0.626	0.593	0.616	0.636	0.681	0.596
Ru-S_4	0.627	0.594	0.612	0.635	0.683	0.599
Ni-S_1	1.050	0.775	1.023	0.735	0.770	1.054
Ni-S_4	1.052	0.776	1.025	0.729	0.772	1.055
Ni-S_2	0.916	0.696	0.930	0.752	0.757	0.896
Ni-S_3	0.915	0.704	0.929	0.755	0.759	0.899
C_{21}-O_{21}	2.546	2.347	2.471	2.408	2.558	2.414
C_{22}-O_{22}	2.546	2.349	2.471	2.407	2.560	2.414

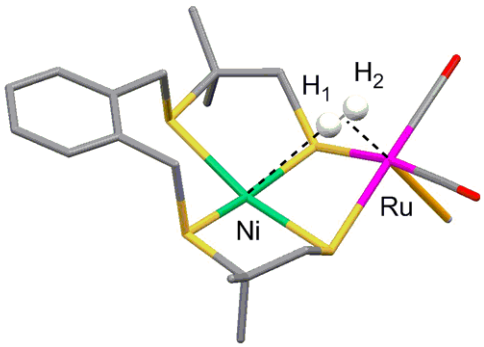

Figure S1. Molecular structure of **[NiRu(H$_2$)].** The nickel atom is depicted in green, ruthenium in magenta, chloride in orange and sulfurs in yellow.