Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Table 1. Geometrical parameters (degree and Å) for the located stationary points.

Structure	State	Angle		Bond distance			
		H-M-R	M-O-C	M-H	M-R	R-H	M-CO
CpCo(CO)	^{1}A		179.0				1.7
CpCo(CO)	^{3}A		175.0				1.7
CpRh(CO)	^{1}A		179.4				1.8
CpRh(CO)	^{3}A		172.9				1.8
CpCo(CO)···HC$(CH_3)_3$	^{1}A	17.3	179.1	1.7	2.6	1.1	1.7
CpCo(CO)···HC$(CH_3)_3$	^{3}A	0	174.9	2.4	3.5	1.1	1.7
CpCo(CO)···HSi$(CH_3)_3$	^{3}A	18.2	173.6	1.9	3.2	1.5	1.7
CpRh(CO)···HC$(CH_3)_3$	^{1}A	12.8	179.6	1.8	2.8	1.1	1.8
CpRh(CO)···HSi$(CH_3)_3$	^{3}A	13.0	172.1	2.0	3.4	1.5	1.8
CpCo(CO)H	^{2}A		176.8	1.4			1.7
CpRh(CO)H	^{2}A		177.2	1.5			1.8
Cp(CO)H-Co-C$(CH_3)_3$	^{1}A	81.1	177.3	2.0	1.4	2.3	1.7
Cp(CO)H-Co-Si$(CH_3)_3$	^{1}A	63.8	178.9	2.2	1.4	2.0	1.7
Cp(CO)H-Rh-C$(CH_3)_3$	^{1}A	79.3	177.3	1.5	2.1	2.3	1.8
Cp(CO)H-Rh-C$(CH_3)_3$	^{3}A	70.8	147.4	1.5	2.1	2.1	1.9
Cp(CO)H-Rh-Si$(CH_3)_3$	^{1}A	72.0	178.6	2.3	1.5	2.4	1.8