Supporting Information

The Mechanism of Ethylene Addition to Nickel bis(oxothiolene) and Nickel bis(dioxolene) Complexes

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Table S1. Mulliken and natural charges (NBO) on sulfur and oxygen atoms on $Ni(S_2C_2(CN)_2)_2$, $Ni(O_2C_2(CN)_2)_2$, and for two isomers of $Ni(SOC_2(CN)_2)_2$. Solvent corrected values are given.

Complex		Mulliken	NBO
$Ni(S_2C_2(CN)_2)_2$	S	0.134	0.372
$Ni(O_2C_2(CN)_2)_2$	O	-0.389	-0.524
Cis-$Ni(SOC_2(CN)_2)_2$	S	0.329	0.347
Cis-$Ni(SOC_2(CN)_2)_2$	O	-0.362	-0.517
Trans-$Ni(SOC_2(CN)_2)_2$	S	0.170	0.333
Trans-$Ni(SOC_2(CN)_2)_2$	O	-0.424	-0.528

Table S2. Energy difference (eV) between the HOMO of ethylene and LUMO of nickel complexes. Solvent corrected values are given.

Complex	HOMO	LUMO	ΔE (eV)
C_2H_4	-9.68	1.53	
$Ni(S_2C_2(CN)_2)_2$	-9.26	-3.92	**5.76**
$Ni(O_2C_2(CN)_2)_2$	-8.04	-4.39	**5.29**
Cis-$Ni(SOC_2(CN)_2)_2$	-8.48	-4.38	**5.30**
Trans-$Ni(SOC_2(CN)_2)_2$	-8.37	-4.45	**5.23**

Table S3. Calculated reduction potentials with respect to Fc/Fc^{+}.

Half reactions	E^0 (V)
$Ni(mnt)_2 + e^- \rightarrow [Ni(mnt)_2]^-$	0.69[a]
$1_{\_Ni\_SS} + e^- \rightarrow 1_{\_Ni\_SS}^-$	0.76[b]
$2_{\_Ni\_SS} + e^- \rightarrow 2_{\_Ni\_SS}^-$	-0.83[b]
$1_{\_Ni\_OO} + e^- \rightarrow 1_{\_Ni\_OO}^-$	0.15
$1_{\_Ni\_OS\_cis} + e^- \rightarrow 1_{\_Ni\_OS\_cis}^-$	0.64
$1_{\_Ni\_OS\_trans} + e^- \rightarrow 1_{\_Ni\_OS\_trans}^-$	0.56
$2y_{\_Ni\_OO} + e^- \rightarrow 2y_{\_Ni\_OO}^-$	-0.21
$2_{\_Ni\_(O)S\_cis} + e^- \rightarrow 2_{\_Ni\_(O)S\_cis}^-$	-0.24
$2_{\_Ni\_O(S)\_cis} + e^- \rightarrow 2_{\_Ni\_O(S)\_cis}^-$	-0.16
$2_{\_Ni\_OS\_trans} + e^- \rightarrow 2_{\_Ni\_OS\_trans}^-$	0.03

[a]The experimental value from the reference 17 (mnt = $S_2C_2(CN)_2$).
[b]The calculated value from the reference 22.

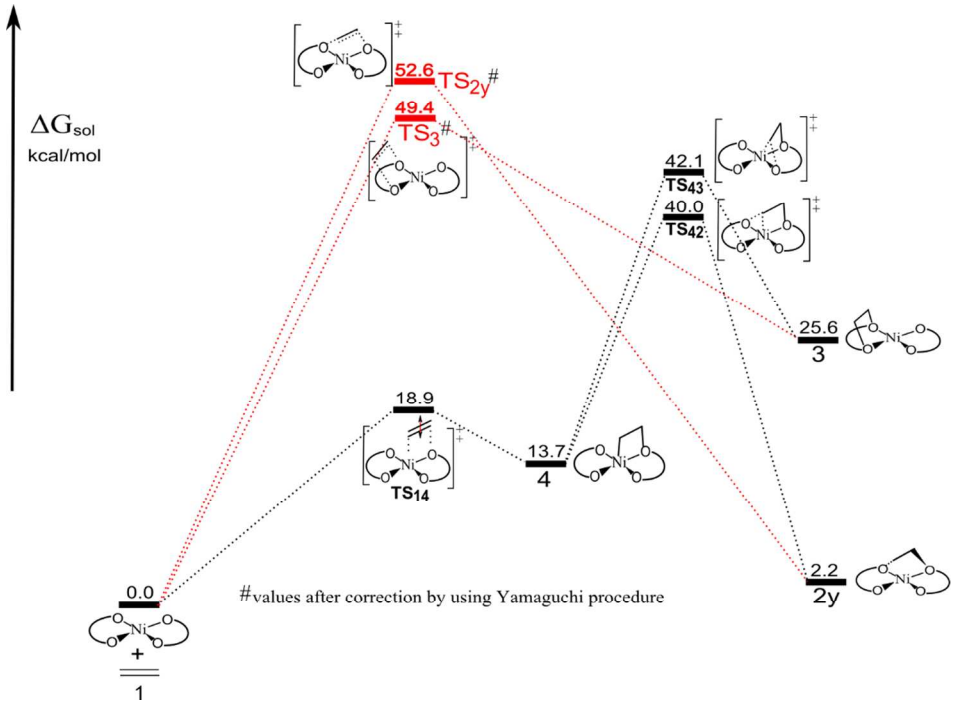

Figure S1. Energy profile for the ethylene approach to the Ni-O bonds, together with reaction routes for direct ethylene approaches, for the 1_{OO} complex. The relative free energies in solvent ($CHCl_3$) are shown.

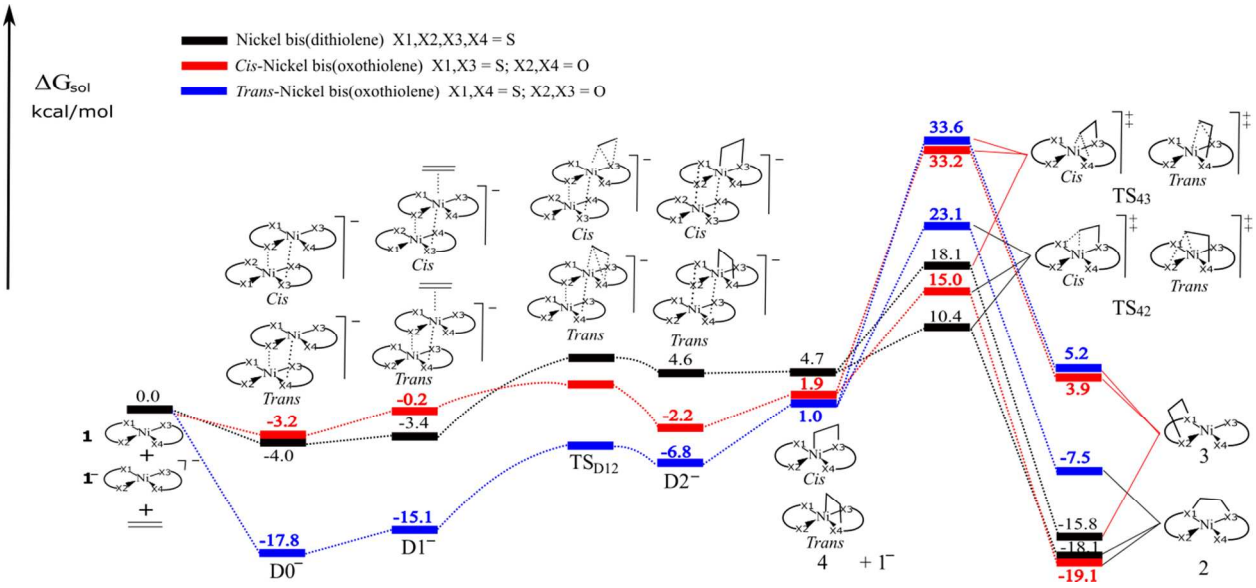

Figure S2. Energy profiles for the anion co-catalyzed pathways (dimer mechanism) for the original dithiolene complex (black levels)[20,21] as well as trans- (blue levels) and cis- (red levels) oxothiolene complexes. The relative free energies in solvent ($CHCl_3$) are shown.

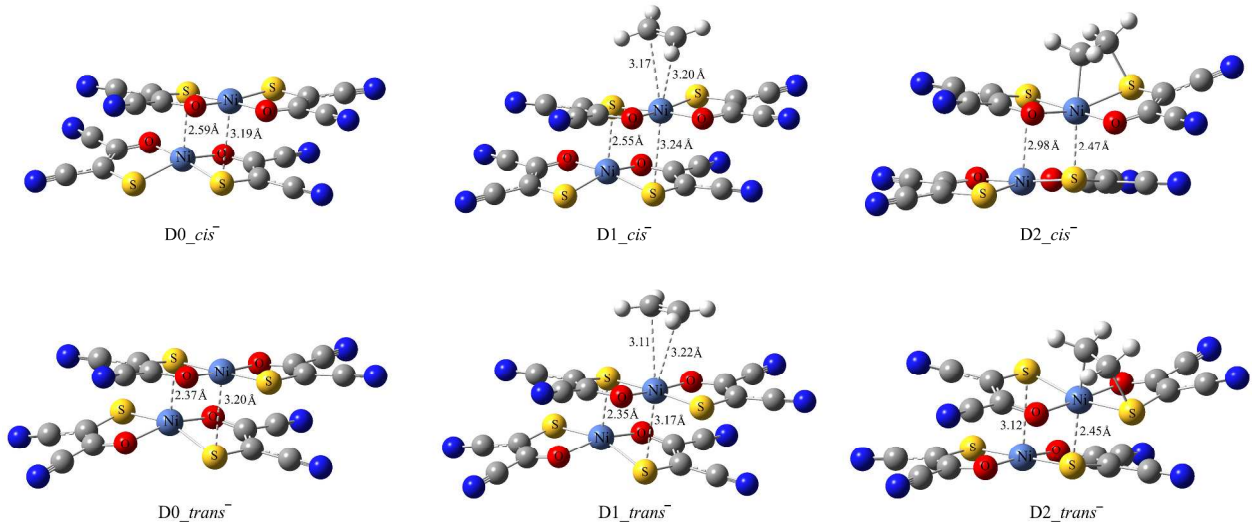

Figure S3. Optimized geometries for the anionic bimetallic species of the nickel bis(oxothiolene) complexes involved in Figure S2.

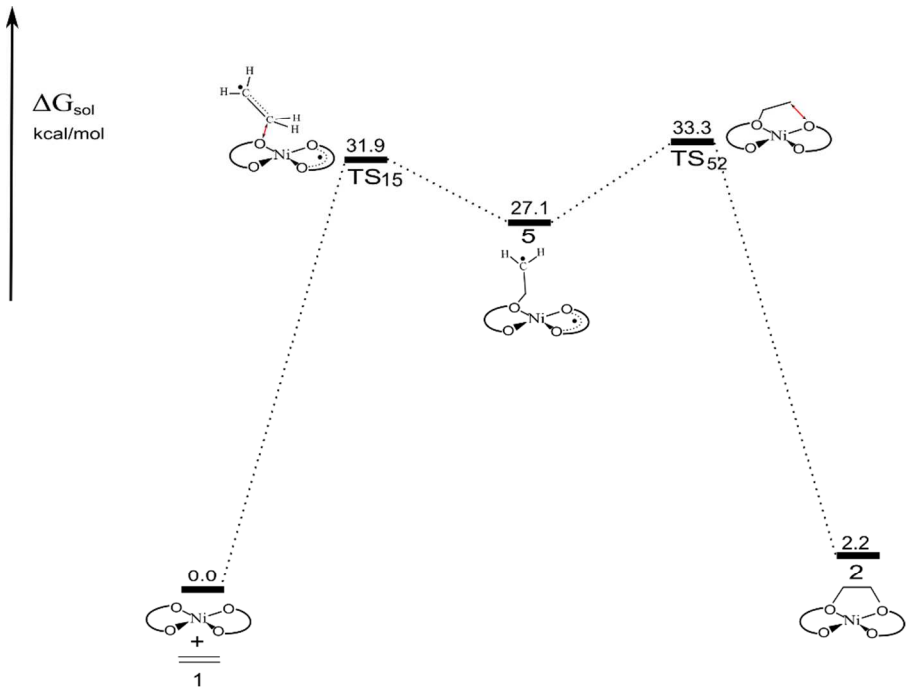

Figure S4. Energy profiles of biradical mechanism for the reactions of $\mathbf{1_{oo}}$ with ethylene, to form the interligand adduct $\mathbf{2_{oo}}$. The relative free energies in solvent ($CHCl_3$) are shown.