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How Electron Flow Controls the Thermochemistry of the Addition of Olefins to Nickel Dithiolenes: Predictions by Density Functional Theory

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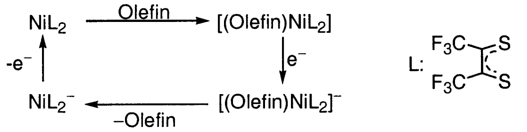
Olefin purification is an important petrochemical process.[1] Although systems based on transition metals can be used, impurities, especially CO and H_2S, often poison and deactivate them. Recently, Wang and Stiefel developed an efficient and convenient method, which begins with a reaction observed over 30 years ago,[2] to remove impurities from olefins with nickel bis(dithiolene) complexes (Scheme 1).[3]

Scheme 1



Under mild conditions, a nearly quantitative addition reaction between olefins and nickel dithiolene complexes produces stable adducts. Furthermore, the nickel dithiolene complex does not react with H_2, CO, or C_2H_2 under the same conditions.[3] When these adducts are reduced electrochemically, the olefin is released, and the anion of the nickel dithiolene complex is generated.[3] This anion can be readily transformed back to the neutral complex. Thus, a rapid binding and releasing of olefins can be achieved and controlled electrochemically.[3,4] Our theoretical computations[5] (Scheme 2, Table 1) indicate that the reaction of a nickel dithiolene complex (**1**) and ethylene is a two-step process, in which the trans-product (**2**) forms first in the direct addition of the olefin to **1**, while the more thermodynamically stable cis-product (**3**) involves isomerization of **2**. The introduction of electron-withdrawing groups (cyano or trifluoromethyl) not only significantly lowers the activation energy (**TS1**) for the formation of trans-product, but it also strongly stabilizes the products (**2**, **3**) such that they are favored by the free energy. However, these substituents leave the barrier for the conformational transformation step (**TS2**) nearly unchanged. On reduction, the previously favored adduct is now strongly disfavored.

Scheme 2

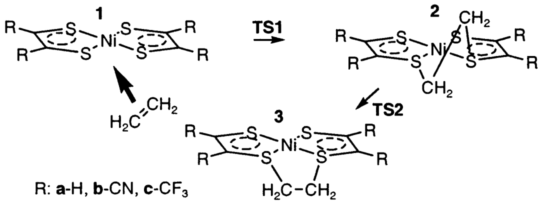


Table 1. Relative Enthalpies ($\Delta H°$, $\Delta H^‡$) and Free Energies ($\Delta G°$, $\Delta G^‡$) of Species in Scheme 2 and Figure 2 (kcal/mol for All Values)

	a		**b**		**c**		**[b]⁻**	
	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG
1 + C_2H_4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TS1	27.63	38.13	18.36	29.22	14.80	27.05		
2	1.04	13.81	−10.47	2.30	−13.85	0.02	5.43	17.49
TS2	18.79	31.86	7.49	20.54	4.31	17.93		
3	−3.20	8.89	−13.38	−1.25	−15.84	−2.65	9.12	20.58

The mechanism of this reaction between olefins and planar nickel bis(dithiolene) complexes was suggested to be a cycloaddition, in which cis-products are preferred.[2] As in many reactions, the interactions between the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) of the Ni complexes, **1**, and olefin are expected to play a critical role in the mechanism. The HOMO and LUMO of **1a** in Figure 1 are π orbitals that are largely based on the interaction between the π orbitals of the two dithiolene ligands and have little Ni d-character. Because of the symmetry, ethylene is unable to attack colaterally S atoms of different ligands in the Ni complexes. In other words, it is orbitally forbidden for ethylene to react with the complexes to generate the cis-product (**3a**) by one step. In the reaction, the C−C double bond in ethylene has to make a diagonal approach to the Ni−S plane, to attack the colateral S atoms, and to form initially the trans-product (**2a**). A rearrangement between trans- and cis-conformations then completes the reaction.

Figure 1. Visualized HOMO and LUMO of **1a**.

No direct (one-step) transition state between **1a** and **3a** was found despite extensive searching. Two transition states, **TS1a** between **1a** plus ethylene and the trans-product **2a** and **TS2a** between **2a** and the cis-product **3a**, are found (Figure 2). Comparing the structural parameters of the two reactants and final products (Table 2), we find that the C−C bond in ethylene increases 0.19 Å from

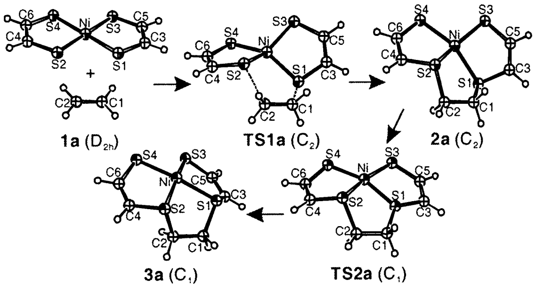


Figure 2. Geometries of all species in (**a**) Scheme 2.

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Table 2. Structural Parameters (Unit for Bond Lengths is Å) of the Species in Figure 2

	1a + C_2H_4	**TS1a**	**2a**	**TS2a**	**3a**
C1−C2	1.338	1.411	1.534	1.543	1.532
C1−S1		2.377	1.858	1.833	1.872
Ni−S1	2.206	2.184	2.241	2.149	2.296
Ni−S3	2.206	2.219	2.235	2.261	2.229
C3−S1	1.705	1.733	1.771	1.770	1.773
C5−S3	1.705	1.727	1.748	1.766	1.744
C3−C5	1.378	1.366	1.354	1.349	1.350

a double bond to a typical single bond, while the dithiolene C−S bonds weaken and increase in length by 0.05 Å on average. On the other hand, the dithiolene C−C bond lengths shorten by 0.03 Å, closer to a C−C double bond in **2a**, **TS2a**, and **3a**. The latter shortening was inferred from the IR spectra of Wing's norbonadiene and norbornene adducts.[2] Although the Ni and four sulfur atoms remain nearly planar in the course of this reaction, there is a tetrahedral distortion for **TS1a** and **2a**, which have twist angles of 38.9° and 50.0°, respectively. This twist enhances the interaction between the LUMO of **1a** and HOMO of ethylene and hence the bonding between the sulfur atoms and the two trans $-CH_2-$ groups of the olefin because the two lobes of the sulfur p orbitals in **1a**'s LUMO with the same sign become closer and produce a better match to the dimension of ethylene's HOMO. Finally, the Ni−S planes in cis-product **3a** are slightly bent toward one another because of the strain in the five-member ring.

According to the enthalpies listed in Table 1, the final product (**3a**) is more stable than the reactants (**1a** + ethylene) and trans-product (**2a**). The activation enthalpies for the two consequential barriers are 27.63 and 17.75 kcal/mol, respectively. Although $\Delta G°$ is unfavorable for the formation of the product for the unsubstituted dithiolene (**3a**), it is favorable when electron-withdrawing groups are introduced. Introduction of cyano, **1b**, or trifluoromethyl, **1c**, significantly lowers the activation enthalpies for the first association step (**TS1**) by ~10 kcal/mol to 18.36 and 14.80 kcal/mol, respectively. As shown in Table 3, the lower barriers can be attributed to the stablilization of the LUMO of Ni−S complexes by the cyano or trifluoromethyl groups. The gap between the LUMOs of these planar complexes and the HOMO of ethylene has decreased from 3.99 eV in **1a** to 1.25 eV in **1b** and 1.36 eV in **1c**. In contrast, the barriers for the trans- to cis-transformation are nearly independent of the substituents.

Table 3. HOMO and LUMO Energies of the Ni−S Complexes and Ethylene and the Difference between the Complexes' LUMO and Ethylene's HOMO (ΔE_{LH}) (eV for All Values)

	HOMO	LUMO	ΔE_{LH}
ethylene	−7.2554	0.5113	
1a	−5.3727	−3.2703	3.99
1b	−7.5754	−6.0094	1.25
1c	−7.6835	−5.8929	1.36

The effect of reduction was only examined for the cyano system (**b**), although similar behavior would be expected for all systems. When the system is reduced, the relative energies of the corresponding anions of species **1b**, **2b**, and **3b** change drastically. As shown in Table 1, for the cyano substituted species, [**2b**]$^-$ and [**3b**]$^-$ are now less stable (ΔH) than [**1b**]$^-$, rather than more stable as they are for the neutral species. The changes in enthalpy $\Delta\Delta H_{1\rightarrow 2}$ and $\Delta\Delta H_{1\rightarrow 3}$ are 15.9 and 20.5 kcal/mol. The free energies indicate that the dissociation of ethylene is now strongly favored. Therefore, as observed by Wang and Stiefel,[2] the reduction can be used to drive the first recycle step; after olefin loss, oxidation can then make the separation "catalytic" (Scheme 1).

In summary, the relative stability of the olefin, nickel bis(dithiolene) adduct is controlled by the electron flow to S from the nickel and ligand substituents. Electron-withdrawing groups lower the barrier for the association of olefins and Ni bis(thiolene) complexes and stabilize cis- and trans-products relative to the reactants, by stabilizing the LUMO of the Ni complexes. When an extra electron is added to the reaction system, the products are so destabilized that dissociation of the olefin becomes the spontaneous process.

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Supporting Information Available: PDB format files of all minima and transition states. This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) Restricted and unrestricted density functional theory (DFT) with Becke three-parameter exchange functional (B3)[6] and the Lee−Yang−Parr correlation functional (LYP),[7] as implemented in Gaussian 98,[8] are used to perform the geometry optimizations. A modified version of Hay and Wadt's LANL2DZ[9] with the two outermost p functions replaced by a new function with (41) split[10] is used for nickel, and the 6-31G* [11] basis set is used for all other elements in the simplified hydrogen-substituted model. Furthermore, an f-polarization function[12] is added to nickel atoms in the cyano- and trifluoromethyl-substituted complexes and their anion forms. The 6-31G* basis set is also used for all atoms (C and N) in cyano groups, and the 6-31 basis set is used for all atoms (C and F) in trifluoromethyl groups. All minima and transition states have been examined by frequency calculations at the same level. All gas-phase thermodynamic functions have been calculated for 298.15 K and 1 atm.

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