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Fe Catalysis

Fe or Fe-NO Catalysis? A Quantum Chemical Investigation of the $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ -Catalyzed Cloke-Wilson RearrangementJohannes E. M. N. Klein,^[a] Gerald Knizia,^[b] Burkhard Miehlich,^[a] Johannes Kästner^[b] und Bernd Plietker^{[a]*}

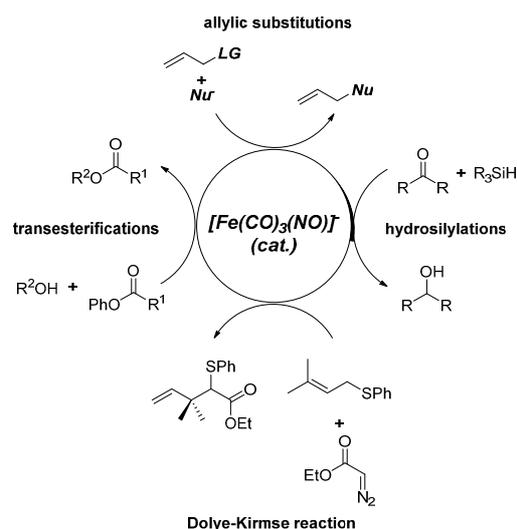
Abstract: We report a quantum chemical investigation of the $\text{Bu}_4\text{N}[\text{Fe}(\text{CO})_3(\text{NO})]$ -catalyzed Cloke-Wilson rearrangement of vinyl cyclopropanes. It was found that allylic C-C bond activation can proceed via a $\text{S}_{\text{N}}2'$ or $\text{S}_{\text{N}}2$ -type mechanism. The

application of the recently reported Intrinsic Bond Orbital (IBO) method for all structures indicates that one Fe-N π -bond is directly involved. Further analysis shows that during the reaction oxidation occurs at the NO-Ligand exclusively.

Introduction

Fe-catalyzed reactions have become a well-established tool for organic transformations.^[1] In many cases, Fe-catalysts display remarkable reactivity and selectivity. Aside from the purely empirical observation of such reactivity and selectivity, a fundamental understanding of catalytic processes of this type is not well developed. A particular challenge in the field of mechanistic investigations is the strong and reactivity dictating ligand to metal interaction. This can lead to unusual oxidation states and bonding scenarios.^[2,3] This holds particularly true for complexes with NO-ligands, which have been identified as non-innocent decades ago.^[3,4] The development of spectroscopic and quantum chemical methods which allow to analyze changes in the electronic configuration of the metal during a catalytic cycle, is therefore of great interest.

The ferrate $\text{Bu}_4\text{N}[\text{Fe}(\text{CO})_3(\text{NO})]$ has demonstrated its ability as a potent catalyst in the past years (Scheme 1).^[5] In contrast to the formally isoelectronic Collman-reagent,^[6] $[\text{Fe}(\text{CO})_4]^{2-}$, allylic substitution, hydrosilylation, transesterification and carbene-transfer reactions are known to be catalyzed by $\text{Bu}_4\text{N}[\text{Fe}(\text{CO})_3(\text{NO})]$.



Scheme 1. Examples of $\text{Bu}_4\text{N}[\text{Fe}(\text{CO})_3(\text{NO})]$ -catalyzed reactions.^[5]

We recently showed in a spectroscopic and theoretical study, of the NO-complex that it is best described through several mesomeric structures in which the Fe possesses the oxidation state 0 and is bound through two covalent Fe-N π -bonds to an anionic NO-Ligand.^[7] A covalent σ -bond between the ligand and metal is not observed. These findings were based on *ab initio* CASSCF-calculations and the recently introduced IBO-analysis of Kohn-Sham-wave functions (IBO: intrinsic bond orbital).^[8]

In the present study, the IBO-analysis is employed for the elucidation of the mechanism of the $\text{Bu}_4\text{N}[\text{Fe}(\text{CO})_3(\text{NO})]$ -catalyzed Cloke-Wilson rearrangement (Scheme 2) with focus on changes in bonding of the Fe-NO unit along the reaction coordinate,^[9,10] shedding light into the process of allylic C-C bond activation.^[11]

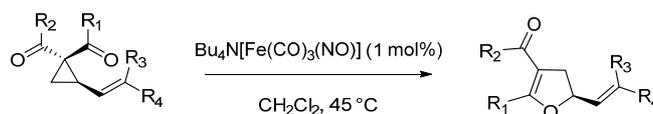
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Results and Discussion

The starting point for the study presented herein was the observation that vinyl cyclopropanes result in an efficient Cloke-Wilson rearrangement giving the corresponding dihydrofurans using catalytic amounts of $\text{Bu}_4\text{N}[\text{Fe}(\text{CO})_3(\text{NO})]$ in the absence of ligands (Scheme 2).^[12] This reaction represents a special case of allylic substitution and in our opinion, is suitable for understanding the underlying principles of such mechanisms since the addition of phosphine or carbene ligands is not mandatory for this reaction.

Based on our previous study regarding the electronic ground state of $[\text{Fe}(\text{CO})_3(\text{NO})]^-$, we have analyzed this reaction using Kohn-Sham density functional theory (DFT). We used the BP86-functional^[13] in combination with Grimme's D3^[14] dispersion correction. Structural parameters were obtained using the split-valence basis set def2-SV(P)^[15] and energies were recomputed using the triple- ζ basis set def2-TZVP.^[15]



Scheme 2. The $\text{Bu}_4\text{N}[\text{Fe}(\text{CO})_3(\text{NO})]$ -catalyzed Cloke-Wilson rearrangement.

The conductor-like screening model (COSMO)^[16] was used in order to simulate solvation effects of CH_2Cl_2 ($\epsilon = 7.98$ ^[17] at 45 °C). As thermal corrections based on the harmonic approximation are prone to error we restrain ourselves to the discussion of ZPE-corrected energies (ΔE_{ZPE}). ΔG values are given for completeness at the reaction temperature of 318 K.

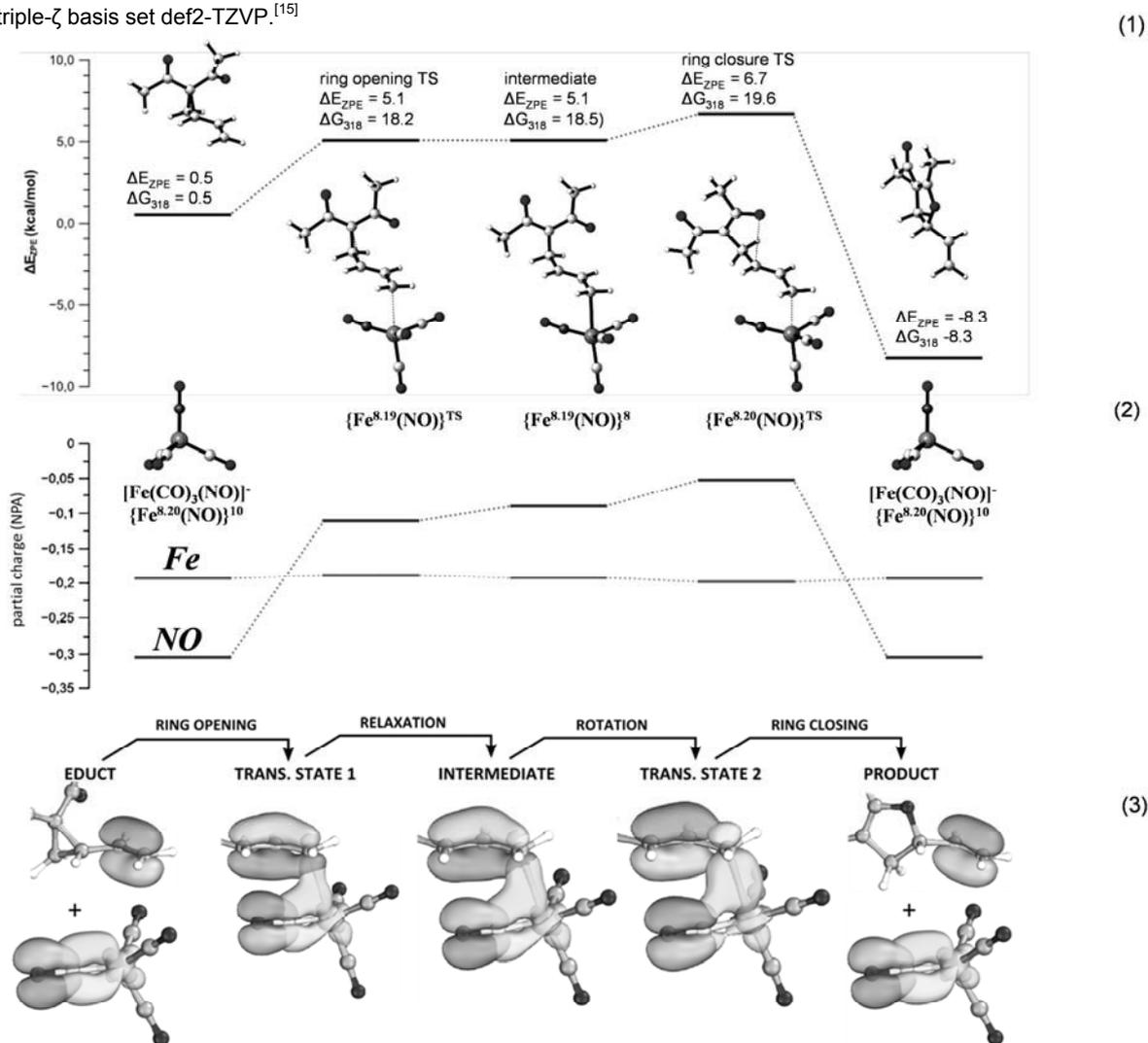


Figure 1. (1) Quantum chemical calculation of the $\text{S}_{\text{N}}2'$ -path of the Cloke-Wilson rearrangement (BP86-D3/def2-SV(P)//def2-TZVP/COSMO($\epsilon = 7.98$)); (2) Changes in partial charges along the reaction coordinate (NPA) and (3) Electron flow along the $\text{S}_{\text{N}}2'$ -path (the IBOs of the active Fe-N π -bond. This bond changes along the reaction coordinate to a Fe-C σ -bond which reduces the terminal C atom of the vinyl moiety. The reduction causes the vinyl C-C bond to shift and results in C-C bond breaking of the cyclopropane. At the catalyst the loss of the Fe-N bond is compensated by the change of one O π -lone pair into a N-O π -bond. The slightly antibonding character at the Fe disappears.)

We first computed the reaction path of the S_N2' -mechanism (Figure 1, (1)). The path consists of: (i) nucleophilic attack of the ferrate onto the allylic C-C bond in the vinyl cyclopropane substrate, (ii) formation of an intermediate and (iii) ring closure resulting in the dihydrofurane product. The intermediate is a reflection of the complex reaction coordinate marking the transition of the cyclopropane opening to a rotational motion, which leads to the dihydrofurane product. As such, the intermediate should not be regarded as a stable intermediate but the turning point between these two motions. The transition state for the ring opening and the intermediate are energetically nearly degenerate and the activation barrier of this reaction is determined by the transition state of the ring closure ($6.7 \text{ kcal mol}^{-1}$ for the depicted conformer of the VCP/the orientation of the NO-Ligand). Several conformers regarding the orientation of the acyl groups and the NO-Ligand (equatorial positions) could be modelled. In certain cases no transition state for the ring opening and no intermediate were identified. In these cases only the transition state of ring closure is identified. All these conformers have very similar activation barriers with regards to the ring closure $\Delta E_{ZPE} = 6.4\text{--}7.8 \text{ kcal mol}^{-1}$ ($\Delta G_{318} = 19.5\text{--}20.5 \text{ kcal mol}^{-1}$). When placing the NO-Ligand in the axial position, the activation barrier of the ring closing transition state is significantly higher $\Delta E_{ZPE} = 14.6 \text{ kcal mol}^{-1}$ ($\Delta G_{318} = 26.5 \text{ kcal mol}^{-1}$) (for details see ESI).

With the computed mechanism in hand we addressed the role of the NO-Ligand. We first computed partial charges at the stationary points of the reaction coordinate using Natural Population Analysis (NPA) (Figure 1, (2)).^[18] We find that the partial charge of the Fe-atom does not significantly change during the reaction, whereas the combined partial charge of the NO-Ligand changes significantly to more positive values. This is in good agreement with our previous description of the electronic ground state being composed of a reduced (NO)⁻-ligand bound to Fe(0).

Applying the previously proposed extended Enemark-Feltham notation^[7] supports this description and indicates electron transfer solely from the NO-Ligand (Figure 1).^[19] The use of formal oxidation states would not be suitable in the present case.

The interactions of the Fe-NO unit with the substrate were analyzed using the IBO-analysis at all stationary points of the reaction coordinate (Figure 1, (3)).^[8] The results show that only one of the Fe-N d-p π -bonds is involved. The nucleophilic attack occurs via the Fe transforming one of the Fe-N d-p π -bonds into a bonding interaction between the Fe and the substrate.^[20] In the ground state of $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ Pauli-repulsion leads to the absence of pronounced N-O π -bonds. Instead, O π -lone pairs are formed with partial N-O bonding and O-Fe anti-bonding character. This facilitates the temporary conversion of a Fe-N π -bond into a Fe-substrate bonding interaction and the loss of a Fe-N d-p π -bond is compensated by the formation of a N-O π -bond. The NO-ligand serves as an electron reservoir which can donate or accept electrons as needed during a catalytic transformation. The orbitals orthogonal to the involved Fe-N d-p π -bond are largely uninfluenced by these events (Figure 2).

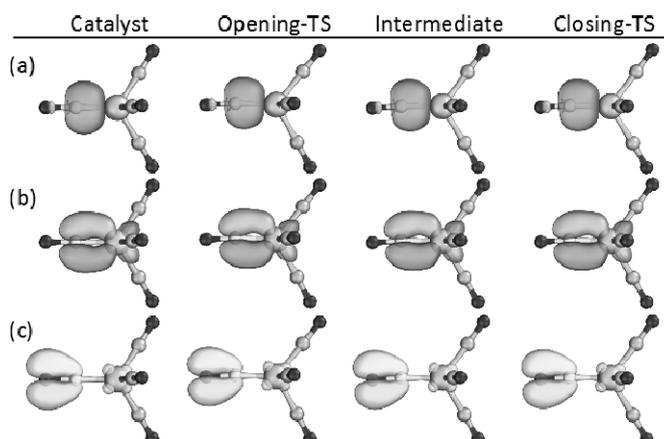


Figure 2. Depiction of the orthogonal IBOs of the O-N-Fe fragment. (a): N lone pair, (b) N-O π -bond, (c) delocalized O π -lone pair with weak O-N bonding character and weak O-Fe antibonding character.

The attempt to compute a direct S_N2 -substitution mechanism (Figure 3) of the C-C bond resulted in the unexpected observation that this path is only marginally higher in energy than the previously investigated S_N2' -path.^[21] The scenario is rather similar to the previously described reaction path and sometimes no transition state for the cyclopropane ring opening or an intermediate are observed *in silico*. The activation barriers (ring closure to the dihydrofurane) are $\Delta E_{ZPE} = 7.8\text{--}9.2 \text{ kcal mol}^{-1}$ ($\Delta G_{318} = 21.3\text{--}22.5 \text{ kcal mol}^{-1}$) and differ little from the S_N2' -path. A distinction based on DFT calculations cannot be made and both paths are likely to contribute (for additional isomers see ESI). The NPA partial charges of these paths indicate oxidation of the NO-ligand, similar to the S_N2' -path with no changes at the Fe center. As for the S_N2' -path, IBOs were computed at all stationary points along the reaction coordinate. Again, we find that only one Fe-N d-p π -bond is significantly involved in the nucleophilic attack. The orthogonal IBOs do not undergo any pronounced changes. Both for the S_N2' and the S_N2 -path, the role of the NO-ligand is to store, deliver and absorb electrons.

Conclusion

In summary, we have presented a quantum chemical investigation giving insight into the mode of action of $\text{Bu}_4\text{N}[\text{Fe}(\text{CO})_3(\text{NO})]$, a catalyst often employed by our group. These results show that the Fe-NO motif is essential for the catalytic potency. Electrons are transferred from a covalent Fe-N π -bond to the substrate and back resulting in formal oxidation of the NO-ligand during this process. The results presented here might also have implications for other electron rich Fe-NO complexes which can even be found in nature.^[22]

As neither the Fe nor the NO unit themselves are capable of the presented catalytic transformation, the answer to the question raised in the title we believe to be: Fe-NO catalysis.

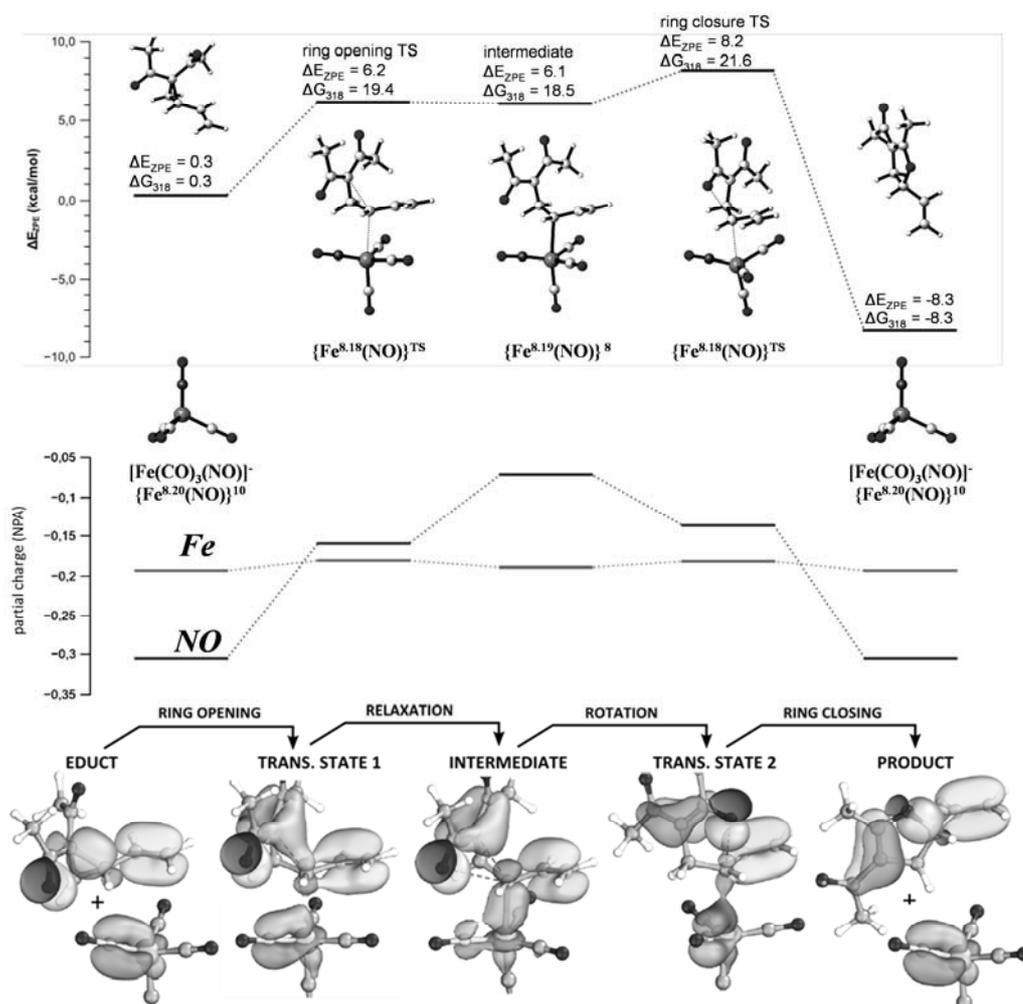


Figure 3. (1) Quantum chemical calculation of the S_N2 -path of the Cloke-Wilson rearrangement (BP86-D3/def2-SV(P)//def2-TZVP/COSMO($\epsilon = 7.98$)); (2) Changes in partial charges along the reaction coordinate (NPA) and (3) Electron flow along the S_N2 -path (The IBOs of the active Fe-N π -bond, the transformation of the cyclopropane bond into a delocalized C-C π -bond and the transformation of a O lone pair into a O-C σ -bond is shown. The C-C bond breaking is supported by the vinyl moiety.)

Keywords: cyclopropane • rearrangement • iron • catalysis • quantumchemistry

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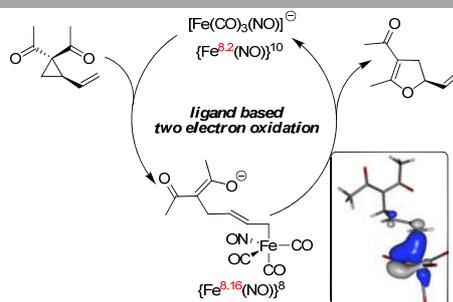
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FULL PAPER

Fe- or Fe-NO catalysis? The $\text{Bu}_4\text{N}[\text{Fe}(\text{CO})_3(\text{NO})]$ -catalyzed Cloke-Wilson rearrangement of activated vinyl cyclopropanes occurs readily at 45 °C in the absence of added ligands. Quantum chemical calculations show that the initial electron transfer originates from one Fe-N π -bond resulting in formal oxidation of the NO-ligand.



Fe Catalysis

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