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New Insight into Reactions of $Ni(S_2C_2(CF_3)_2)_2$ with Simple Alkenes: Alkene Adduct versus Dihydrodithiin Product Selectivity Is Controlled by $[Ni(S_2C_2(CF_3)_2)_2]^-$ Anion

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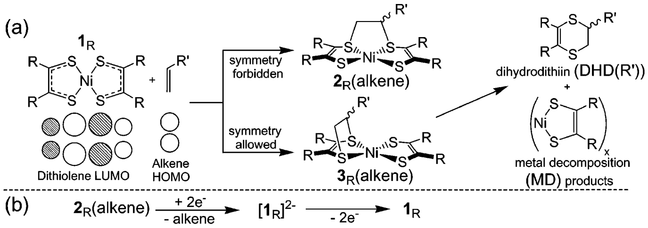
Chemical technology heavily relies on alkenes (olefins) as feedstocks and synthetic intermediates, and their utilization often involves transition metals.[1] In most metal-mediated reactions, the alkene coordinates to the metal in at least one step of the reaction sequence, rendering such systems easily poisoned by impurities in crude alkenes, which often bind more strongly to the metal than the alkene. Metal complexes that bind alkenes through chelated ligands, instead of at the metal center, should be more resistant to deactivation by contaminants, as emphasized by Wang and Stiefel in 2001.[2] It was reported that neutral nickel bis(dithiolene) complexes ($\mathbf{1}_R$ in Scheme 1, R = CN, CF_3) form adducts with linear alkenes, such as ethylene or 1-hexene, where the alkene binds through the ligand S-atoms (Scheme 1a, structure $\mathbf{2}_R$(alkene) was suggested), even in the presence of H_2S or CO. This unusual tolerance toward poisoning led the authors to propose an olefin purification scheme in which the dithiolene-bound alkene is released by electrochemical reduction and $\mathbf{1}_R$ is regenerated by oxidation (Scheme 1b).[2]

Understanding the mechanism of alkene binding to nickel (bis)-dithiolenes will be crucial for tuning the selectivity of such systems and for developing novel applications, but key mechanistic questions are unresolved. Orbital symmetry should prevent compounds $\mathbf{1}_R$, in their singlet ground state, from forming interligand alkene adducts (Scheme 1a, $\mathbf{2}_R$(alkene)) in a concerted, synfacial manner.[3,4] In fact, early structural proposals suggested intraligand binding (Scheme 1a, $\mathbf{3}_R$(alkene)).[5] Crystallographic characterization of an adduct of $\mathbf{1}_{CF3}$ with norbornadiene,[6] however, showed interligand binding, in contrast to orbital symmetry predictions. To address the orbital symmetry problem, a DFT contribution suggested a two-step mechanism for alkene addition, in which the alkene approaches the dithiolene complex in an antifacial fashion, giving an intermediate with tetrahedrally distorted geometry at nickel.[7]

Reactions of simple alkenes (linear monoolefins) with $\mathbf{1}_R$ (R = CF_3, CN) were claimed to proceed selectively to give alkene adducts, and competitive pathways leading to other products were not mentioned.[2] However, dithiolenes with aryl substituents ($\mathbf{1}_{aryl}$, e.g., aryl = C_6H_4(*p*-F)) react with norbornadiene (NBD) to give, in addition to $\mathbf{2}_{aryl}$(NBD), a significant amount of dihydrodithiin (DHD)/metal decomposition (MD) derivatives, likely via orbitally allowed $\mathbf{3}_{aryl}$(NBD) (see Scheme 1a).[3c]

In the present study, we reexamined the reactions of $\mathbf{1}_{CF3}$ with simple alkenes. We found that neutral $\mathbf{1}_{CF3}$ reacts with ethylene or 1-hexene to give *primarily* DHD/MD products and little or no alkene adduct (Scheme 1a). Clearly, if $\mathbf{1}_{CF3}$ is to be useful in olefin purification schemes,[2] this lack of selectivity for stable alkene adducts needs to be addressed. We report that the product distribution can be impacted dramatically by adding monoanionic $[\mathbf{1}_{CF3}]^-$ to $\mathbf{1}_{CF3}$/alkene reaction mixtures, such that adducts $\mathbf{2}_{CF3}$(alkene) can be obtained as dominant products, rather than DHD/MD products. We also provide unambiguous evidence that ethylene, in the stable adduct, binds to $\mathbf{1}_{CF3}$ in a 1:1, interligand fashion (Scheme 1a, $\mathbf{2}_{CF3}$(ethylene)). Finally, the mechanistic implications of these results are discussed.

Scheme 1



Reactions between compound $\mathbf{1}_{CF3}$ and alkenes (ethylene and 1-hexene) were followed by NMR spectroscopy (^{19}F and ^1H). To our knowledge, NMR methods have not been used previously to probe the reactions of metal bis(dithiolenes) with simple, terminal alkenes. Experiments were conducted under strictly water-free conditions, since we found that trace water significantly affects the reactivity in these systems (see below). Reacting compound $\mathbf{1}_{CF3}$ (8.8 mM) with ethylene (~25 mM) for 2.5 h at ambient temperature in $CDCl_3$ formed DHD(H) (Scheme 1a) in 70% yield.[8,9] Upon overnight reaction, conversion to DHD(H)/MD products was near-quantitative (90%). DHD derivatives were identified by comparison of ^{19}F and ^1H data with those of independently prepared samples.[10] No adduct ($\mathbf{2}_{CF3}$(ethylene)) was observed in the reaction between $\mathbf{1}_{CF3}$ and ethylene.

We then investigated the effect of having anion $[\mathbf{1}_{CF3}]^-$ present. Compound $\mathbf{1}_{CF3}$ quantitatively oxidizes up to 1 equiv of decamethylferrocene (Fc*) to give the ion pair $[Fc^*]^+[\mathbf{1}_{CF3}]^-$. When we employed Fc* to reduce 22% of $\mathbf{1}_{CF3}$ (originally 9.7 mM), the resulting $\mathbf{1}_{CF3}/[\mathbf{1}_{CF3}]^-$ (78:22) mixture reacted (25 °C, 16 h, in $CDCl_3$) with excess ethylene to afford $\mathbf{2}_{CF3}$(ethylene) in 55% yield and DHD(H) in 24% yield.[8,9] Compound $\mathbf{2}_{CF3}$(ethylene) was identified by its AA′BB′ pattern in the ^1H NMR spectrum and by its two sets of fluorine signals (Figure 1).[11] Photolysis of $\mathbf{2}_{CF3}$(ethylene) released the alkene, regenerating $\mathbf{1}_{CF3}$,[12] in accord with the expected photochemistry[13] of such adducts.

Thus, a clean, high-yielding synthesis of $\mathbf{2}_{CF3}$(ethylene) requires a considerable concentration of $[\mathbf{1}_{CF3}]^-$. We prepared a 1:1 mixture of $\mathbf{1}_{CF3}$ and $[Fc^*]^+[\mathbf{1}_{CF3}]^-$ (both species ~10 mM in CH_2Cl_2), and reaction (50 °C, 1 h) with excess ethylene formed $\mathbf{2}_{CF3}$(ethylene) in 71% yield (isolated). X-ray quality crystals were grown under ethylene atmosphere from benzene. The structure (Figure 1) clearly shows interligand adduct ($\mathbf{2}_{CF3}$(ethylene)). While a crystal structure of $\mathbf{2}_{CF3}$(NBD) has been reported,[6] the present structure is the first example involving a simple, acyclic alkene. Notable is a bowl-

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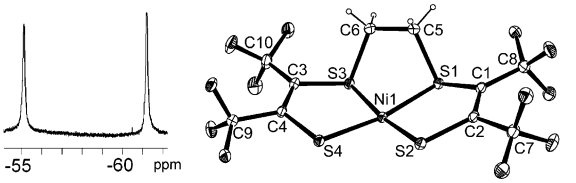


Figure 1. ^{19}F NMR spectrum (470 MHz, $CDCl_3$, 343 K)[11] of $\mathbf{2}_{\mathrm{CF3}}(C_2H_4)$ (left) and its X-ray crystal structure (right, 20% probability ellipsoids). Distances and angles (Å, deg): Ni1−S1, 2.163(1); Ni1−S2, 2.159(1); Ni1−S3, 2.165(1); Ni1−S4, 2.162(1); S1−C5, 1.842(3); S3−C6, 1.854(3); C1−C2 ≈ C3−C4, 1.356(4); S1−Ni1−S2, 92.07(3); S3−Ni1−S4, 92.14(3).

type distortion (centroid$_{C1,C2}$−Ni1−centroid$_{C3,C4}$ = 22°), similar to $\mathbf{2}_{\mathrm{CF3}}$(NBD).[6] Also, the C_2H_4 bridge is twisted (torsion $S_1C_5C_6S_3$ = 19.7°), leading to C_1 molecular symmetry (Figure 1).

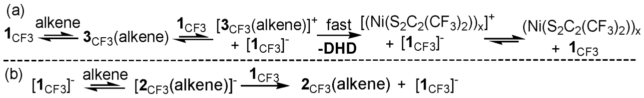
1-Hexene also reacts with $\mathbf{1}_{\mathrm{CF3}}$ to give mainly decomposition products in the absence of $[\mathbf{1}_{\mathrm{CF3}}]^-$. Reaction between $\mathbf{1}_{\mathrm{CF3}}$ (14 mM) and 1-hexene (0.14 M) (25 °C, 1.9 h, in $CDCl_3$), afforded some (12% yield) interligand adduct, of type $\mathbf{2}_{\mathrm{CF3}}$(1-hexene), even if no reductant was added, but DHD(^{n}Bu) was the main product (73% yield).[8,9,14] When we reduced 5.8% of $\mathbf{1}_{\mathrm{CF3}}$ (14 mM initially) with Fc*, the ~94:6 mixture of $\mathbf{1}_{\mathrm{CF3}}/[\mathrm{Fc}^*]^+[\mathbf{1}_{\mathrm{CF3}}]^-$ yielded, upon reaction with 1-hexene, stable adducts (61% yield) and some DHD(^{n}Bu) (27% yield) (25 °C, 2.9 h, in $CDCl_3$).

The 1-hexene reactions gave much more complex NMR spectra than the ethylene reactions, because of the C_1 symmetry of the resulting adducts and endo/exo isomerism. We observed three different types of 1-hexene adducts, in the approximate ratio 1:2:4, and propose that the two major species are interligand adducts $\mathbf{2}_{\mathrm{CF3}}$(1-hexene), as endo and exo isomers. The minor species might be binuclear, with two nickel bis(dithiolene) units connected by an alkyl bridge (Supporting Infoformation). Reduction with Na in THF-d_8 released 1-hexene from the equilibrium mixture of alkene adducts, in agreement with reports[2,6,15,16] about electrochemical reversibility of alkene binding to sulfur centers. For a selectively deuterated alkene, (*E*)-1-D-1-hexene, stereospecific binding was observed, and photolysis released unchanged (*E*)-1-D-1-hexene.

In addition to Fc*, additives such as water, acetone, organic sulfides, and trialkylphosphines also favor larger adduct/DHD ratios. Water[17] and acetone[18] react with $\mathbf{1}_{\mathrm{CF3}}$ to produce $[\mathbf{1}_{\mathrm{CF3}}]^-$. Presumably, SR_2 and PR_3 also reduce $\mathbf{1}_{\mathrm{CF3}}$. If the adduct/DHD selectivity reversal is due to $[\mathbf{1}_{\mathrm{CF3}}]^-$, then independently synthesized[18] $[\mathbf{1}_{\mathrm{CF3}}]^-$ should induce the same effect. Indeed, $\mathbf{1}_{\mathrm{CF3}}$ (19 mM) reacted with 1-hexene (0.15 M) to give $\mathbf{2}_{\mathrm{CF3}}$(1-hexene) as the major product ($\mathbf{2}_{\mathrm{CF3}}$(1-hexene)/DHD(^{n}Bu) ≈ 3:1) when $[\mathrm{NEt}_4]^+[\mathbf{1}_{\mathrm{CF3}}]^-$ (0.9 mM) was present. These observations confirm the importance of $[\mathbf{1}_{\mathrm{CF3}}]^-$ in determining product selectivity.

Full understanding of the reaction mechanism will require very detailed kinetic studies, but preliminary kinetics,[19] for 1-hexene, provide some insight. In the simplest mechanistic scenario, $[\mathbf{1}_{\mathrm{CF3}}]^-$ catalyzes the production of $\mathbf{2}_{\mathrm{CF3}}$(alkene). If $[\mathbf{1}_{\mathrm{CF3}}]^-$ accelerates one of two parallel reactions, then k_{obs} for decay of $\mathbf{1}_{\mathrm{CF3}}$ should increase with increasing $[\mathbf{1}_{\mathrm{CF3}}]^-$ concentration. However, we observed the opposite: While higher anion concentrations favor alkene adducts over decomposition products, $[\mathbf{1}_{\mathrm{CF3}}]^-$ actually *slows* the decay of $\mathbf{1}_{\mathrm{CF3}}$ (time traces in the Supporting Information). Therefore, if $[\mathbf{1}_{\mathrm{CF3}}]^-$ catalyzes formation of $\mathbf{2}_{\mathrm{CF3}}$(alkene), it must simultaneously inhibit DHD production to account for the decreased rate. The pathway leading to decomposition products may be suppressed as shown in Scheme 2. In this proposal, the symmetry-allowed adduct $\mathbf{3}_{\mathrm{CF3}}$(alkene) quickly degrades to DHD/MD products upon oxidation by $\mathbf{1}_{\mathrm{CF3}}$.[20] Higher $[\mathbf{1}_{\mathrm{CF3}}]^-$ concentrations shift the $\mathbf{3}_{\mathrm{CF3}}$(alkene)/$[\mathbf{3}_{\mathrm{CF3}}$(alkene)$]^+$ equilibrium to the left, slowing the decomposition pathway (Scheme 2a). Such a proposal may explain why small amounts of $[\mathbf{1}_{\mathrm{CF3}}]^-$ are produced in the reaction between NBD and *neutral* $\mathbf{1}_{\mathrm{CF3}}$, as observed by Geiger.[16] It is possible that $[\mathbf{1}_{\mathrm{CF3}}]^-$ also reacts directly with alkenes to give the intermediate[21] $[\mathbf{2}_{\mathrm{CF3}}$(alkene)$]^-$ which is oxidized by $\mathbf{1}_{\mathrm{CF3}}$ to yield $\mathbf{2}_{\mathrm{CF3}}$(alkene) (Scheme 2b).

Scheme 2



We conclude that $\mathbf{1}_{\mathrm{CF3}}$ reacts with simple alkenes to give, preferentially, DHD and metal decomposition products, unless $[\mathbf{1}_{\mathrm{CF3}}]^-$ is present. Our results suggest that the mechanism of stable adduct formation ($\mathbf{2}_{\mathrm{CF3}}$(alkene)) is more complicated than previously thought and probably involves charged intermediates. Interestingly, additives such as water or organic sulfides favor larger adduct/DHD ratios, very likely because these species are sufficiently reducing to produce $[\mathbf{1}_{\mathrm{CF3}}]^-$.[17,18] An electrochemical process, as originally envisioned by Wang and Stiefel,[2] might indeed be efficient for olefin purification: if the charge-neutral metal complex is generated in situ by oxidation from the monoanion, in the presence of the alkene, a sufficient amount of monoanion will be present to influence the reactivity toward interligand adducts. More detailed studies of this potentially industrially useful reaction are in progress.

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Supporting Information Available: Experimental details (PDF) and crystallographic information for $\mathbf{2}_{\mathrm{CF3}}$(ethylene) (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(4) Compounds $\mathbf{1}_{\mathrm{R}}$ might possibly react in their triplet state, which was computed (DFT, for $\mathbf{1}_{\mathrm{Me}}$) to be uphill by 60 kJ/mol in ground-state geometry, as proposed in Szilagyi, R. K.; Lim, B. S.; Glaser, T.; Holm, R. H.; Hedman, B.; Hodgson, K. O.; Solomon, E. I. *J. Am. Chem. Soc.* **2003**, *125*, 9158.
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(8) Yields based on $\mathbf{1}_{\mathrm{CF3}}$, using product integration (^{1}H/^{19}F NMR) versus internal standard (see Supp. Info.). For reactions where a fraction of $\mathbf{1}_{\mathrm{CF3}}$ was reduced with Fc*, yields are based on $\mathbf{1}_{\mathrm{CF3}}$ present after reduction.
(9) When DHD(R′) was formed, corresponding amounts of MD products were visible as a manifold of ^{19}F resonances, for ill-defined $(\mathrm{Ni}(S_2C_2(CF_3)_2))_x$.
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(11) Spectra are temperature-dependent (Supp. Info. (Figure S6)).
(12) Expectedly, some $\mathbf{1}_{\mathrm{CF3}}$ reacted with the released alkene to produce DHD-(H) and associated decomposition products.
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(14) Similarly, large DHD(^{n}Bu)/$\mathbf{2}_{\mathrm{CF3}}$(1-hexene) product ratios were observed in CD_2Cl_2 and toluene-d_8 when $[\mathbf{1}_{\mathrm{CF3}}]^-$ was not present.
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(17) UV−vis data show reduction of $\mathbf{1}_{\mathrm{CF3}}$ by H_2O (Supp. Info., S21 and S22).
(18) $\mathbf{1}_{\mathrm{CF3}}$ is reduced by ketones, nitriles, amides, amines, and DMSO: Davison, A.; Edelstein, N.; Holm, R. H.; Maki, A. H. *Inorg. Chem.* **1963**, *2*, 1227.
(19) In $CDCl_3$ or toluene-d_8 in the presence of excess 1-hexene. In the absence of $[\mathbf{1}_{\mathrm{CF3}}]$, decay of $\mathbf{1}_{\mathrm{CF3}}$ is pseudo-first-order, as reported in ref 2.
(20) While adducts of type $\mathbf{2}_{\mathrm{CF3}}$(alkene) are not easily oxidized by $\mathbf{1}_{\mathrm{CF3}}$ (ref 16), compounds $\mathbf{3}_{\mathrm{CF3}}$(alkene) are be expected to be more easily oxidized since they contain an ene-1,2-dithiolate unit (Supp. Info. (S25)).
(21) This proposal is novel, and transition states for this mechanism have not yet been computed. However, in the context of alkene release, the *thermodynamics* of $[\mathbf{2}_{\mathrm{CN}}(\mathrm{ethylene})]^-$ versus $[\mathbf{1}_{\mathrm{CN}}]^-$ + ethylene were computed. (ref 7): ΔH = 38 kJ/mol (not prohibitively uphill).

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