Nickel-Catalyzed Anionic Cross-Coupling Reaction of Lithium Sulfonimidoyl Alkyldiene Carbenoids With Organolithiums

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Abstract: The mechanistic platform for an over nickel catalyzed anionic cross-coupling reaction (ACCR) of lithium sulfonimidoyl alkyldiene carbenoids (metalloalkenyl sulfoximines) with organometallic reagents is reported herein, affording substituted alkenylmetals and lithium sulfanimides. The Ni catalyzed ACCR of three different types of metalloalkenyl sulfoximines, including acyclic, axially chiral and exocyclic derivatives, with sp organolithiums and sp2 Grignard reagents has been studied. The ACCR of metalloalkenyl sulfoximines with PhLi in the presence of the Ni catalyst and pre-catalyst Ni(PPh3)2Cl2 afforded alkynylmetals, under inversion of configuration at the C atom and complete retention at the S atom. In a combination of experimental and DFT studies, we propose a catalytic cycle of the Ni catalyzed ACCR of lithioalkenyl sulfoximines. Computational studies reveal two distinctive pathways of the ACCR, depending on whether a phosphine or 1,5-cyclooctadiene (COD) is the ligand of the Ni atom. They rectify the underlying importance of forming the key Ni-vinylidene intermediate through an indispensable electron-rich Ni center coordinated by phosphine ligands. Fundamentally, we present a mechanistic study in controlling the diastereoselectivity of the alkenylthium formation via the key lithium sulfinamide coordinated Ni-vinylidene complex, which consequently avoids an unselective formation of an alkyldiene carbene Ni-complex and ultimately racemic alkenyllithium.

Introduction

Myriads of studies of nickel and palladium have extensively expanded not only the research spectrum on organometallic catalysis but also their utilization in cross-coupling reactions. Cross-coupling reactions catalyzed by late transition metals such as Pd and Ni have been widely exploited for the introduction of various functional groups into unsaturated substrates such as alkenes and aromatic rings. Although chemists have shed much light on the nature of catalysis by interchanging transition metals that share isoelectronic properties to mimic their respective complex systems, Ni and Pd have flourished in many other pairs/trios of transition metals in producing fruitful insight to chemists. Anionic Pd complexes have proven to play a crucial role in cross-coupling or Heck reactions through high catalytic activity. In a similar vein, anionic Ni-ate complexes showed promise in overcoming the less efficient oxidative addition of alkyl halides as a Ni-catalyzed cross-coupling partner than that of aryl or alkenyl halide. Especially, Kambe described the formation of anionic Ni-ate complexes from or-

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ganometallic reagents, which show an enhanced nucleophilicity in the cleavage of the C(sp^3)–X bond of alkyl halides.\cite{46} Cornella recently reported that highly reduced Ni-precatalysts, which are stabilized by simple olefinic ligands, exhibit an increased catalytic activity in the Kumada–Corriu–Negishi (KCN) cross-coupling.\cite{5} Despite these advances in anionic cross-coupling reactions (ACCR) and pervasive usage of interchanging Ni and Pd to their respective complex systems, fundamental aspects of electron-rich Ni-ate complexes have not been well-understood and studies in this field remain relatively scarce.

The ubiquitous use of Ni-catalysts in modern chemistry and the increased interest they received in recent years instigated us to carefully examine the mechanism of the Ni-catalyzed ACCR of metalloalkenyl sulfoximines with organolithium or Grignard reagents, yielding substituted alkenylmetals.\cite{6,7} In these reactions, metalloalkenyl sulfoximines react under inversion of configuration at the C α atom and complete retention at the S atom. Combining experimental and computational techniques, we found a new catalytic cycle that includes an anionic Ni^0-ate intermediate induced by organolithium that traverses a putative Ni^2-olate intermediate through α-elimination of the sulfonimidoyl group, which is a nucleofugal leaving group. In this paper, we disclose a complete and detailed mechanism of Ni-catalyzed ACCR of metalloalkenyl sulfoximines.

Metalloalkylidenecarbenoids 1, carrying an electrophilic and a nucleofugal leaving group at the C α atom, are an intriguing class of compounds (Scheme 1a).\cite{8,9} Key reactivity features of 1 are electrophilic and nucleophilic substitution at the C α atom, Fritschi–Buttenberg–Wiechell (FBW) rearrangement, α-elimination, and formation of transition-metal-ate complexes, for example. Lithioalkenyl sulfoximines Li-2\cite{6,7,10–12} are a new group of non-classical alkyldiene carbenoids, displaying characteristic ambiphilic reactivity (Scheme 1b). For example, although electrophilic substitution of Li-2 gives alkenyl sulfoximines 3,\cite{6,10–12} nucleophilic substitution of Li-2 with cuprates furnishes alkenyl cuprates 4 through 1,2-metalate shift of higher-order cuprates.\cite{13} Unlike the classical alkyldiene carbenoids 1, Li-2 carry a chiral nucleofuge, are generally stable in solution up to 0 °C, and do not undergo FBW rearrangement or nucleophilic substitution with organolithium reagents.\cite{14,15} According to experimental and theoretical studies, lithioalkenyl sulfoximines Li-2, which are obtained by lithiation of alkenyl sulfoximines H-2, are monomeric in ethereal solution and dimeric in the crystal (bridging O–Li bonds), contain a fluxional C–Li bond and a Li atom being coordinated by the N atom or in case of a N-sulfonyl group by one of its O atoms.\cite{15,16}

We observed an interesting stereoselective C–C bond formation of metalloalkenyl sulfoximines using organolithium reagents RLi to form alkenyllithiums 5. It traverses through a Ni-ylidenecarbd. which is synthetically derived from either anionic or dianionic Ni^2-ate intermediates, in which the sulfonimidoyl group acted as a nucleofuge as described in Scheme 1c. Of particular interest was the role of the anionic Ni^0-ate complex that leads to the Ni^2-ylidenecarbd. under reduction of the S(VI) atom of the sulfonimidoyl group to S(IV) and extrusion of PhS(O)LiMe. Herein, the extremely electron-rich nickel center is necessary for pushing the electron density to the α-carbon to form a putative Ni^2-ylidenecarbd. intermediate. In cases of vinylidenemediated catalysis, there have been plenty of studies of metal–vinylidenecarbd. complexes involved in various reaction pathways.\cite{16,17} These studies generally demonstrate that the rearrangement of an acetylene to a vinylidene in the coordination sphere of a transition metal is a thermodynamically favorable process and henceforth has been widely employed for approaching the metal–vinylidenecarbd. complex. In closer scrutiny, however, there have been very few examples of metal–vinylidenecarbd. complexes involving Group 10 metals,\cite{18} because they have preferred modes of reactivity with alkenes that do not easily allow formation of metal–vinylidenecarbd. intermediates during the reaction. Instead, Ni(vinylidenoid) intermediates have been accessed in vinylidene transfer reactions from dinuclear Ni-catalysts and 1,1-dichloroalkenes as vinylidene precursors.\cite{19} Herein, we demonstrate that metalloalkenyl sulfoxi-
mines can also lead to Ni\(^0\)-vinylidenes, in which the nickel center is highly reduced.

During synthetic studies of carbocyclic prostacyclin analogs,\(^{[20]}\) we made the intriguing observation that the exocyclic magnesioalkenyl sulfoximines \((E/Z)-M-6\), obtained through metalation of \((E)-H-6\),\(^{[21]}\) seemingly partake in a Ni-catalyzed ACCR with PhMgBr, affording the phenyl-substituted alkylmagnesiums \((E/Z)-M-7\) (Scheme 2).\(^{[6]}\) Furthermore, the acyclic lithioalkenyl sulfoximines \((E/Z)-Li-8\),\(^{[11]}\) prepared by lithiation of \((Z)-H-8\),\(^{[11]}\) were found to apparently participate in Ni-catalyzed ACCR with PhLi, furnishing alkylolithiums \((E/Z)-Li-9\) as intermediates.\(^{[7]}\) In the absence of the Ni-precatalyst no ACCR took place between the metalloalkenyl sulfoximines and PhM.

Shortly after the publication of our preliminary observation with the exocyclic magnesioalkenyl sulfoximines \((E/Z)-Mg-6\), Kocien\'sky reported that cyclic \(\alpha\)-lithioalkenyl ethers engage in copper-catalyzed ACCR with organolithiums.\(^{[22]}\) To date, Ni- and Pd-catalyzed ACCRs of metallo alkyldene carbeneoids with organometallic reagents have not been described with the exception of the examples depicted in Scheme 2, however. This prompted us to carry out a comprehensive study of the Ni-catalyzed ACCR of metalloalkenyl sulfoximines M-2 using experimental and computational techniques.

### Results and Discussion

The magnesioalkenyl sulfoximines \((E/Z,R)-Mg-6\) \((X = Br)\) (50:50 dr), which were obtained through metalation of the alkenyl sulfoximine \((E/R)-H-6\)\(^{[23]}\) with PhMgBr, engaged in an ACCR with PhMgBr (3 equiv) and Ni(dppp)Cl\(_2\) (dppp = 1,3-bis(diphenylphosphino)propane) (6–10 mol%) in ether at 0 °C and gave alkylmagnesiums \((E/Z)-Mg-7a\) \((X = Br)\), which after quenching with CF\(_3\)CO\(_2\)D furnished the deuterated alkenes \((E/Z)-D-7a\) in 80% yield and 50:50 dr (Scheme 3a). A similar ACCR of the lithioalkenyl sulfoximines \((E/Z,R)-Li-6\) (50:50 dr), which were prepared from \((E/R)-H-6\) upon treatment with MeLi, with PhLi (3 equiv) and Ni(dppp)Cl\(_2\) (10 mol%) in diethyl ether at 0 °C for 3–5 h afforded alkylolithiums \((E/Z)-Li-7a\). Quenching of the alkylolithiums with CF\(_3\)CO\(_2\)H gave alkene \((E)-H-7a\) and \((Z)-H-7a\) in 80% yield and 50:50 dr. The ACCR of \((E/Z,R)-Mg-6\) \((X = Br)\) with ClMg(CH\(_2\))\(_2\)OSiBu\(_3\)\(^{[24]}\) (4.3 equiv) in the presence of Ni(dppp)Cl\(_2\) (6 mol%) in diethyl ether at 0 °C for 3 h furnished alkylmagnesiums \((E/Z)-Mg-7b\) \((X = Br, Cl)\). Quenching of the alkylmagnesiums with CF\(_3\)CO\(_2\)H gave alkenes \((E)-H-7b\) and \((Z)-H-7b\) in 27% yield and 50:50 dr.

The acyclic \((E)-configured lithioalkenyl sulfoximine \((E)-Li-8a\), which was obtained from alkenyl sulfoximine \((Z)-H-8a\)\(^{[11]}\) through metalation with MeLi, engaged in an ACCR with PhLi for 3 h afforded alkenes \((E/Z)-Mg-7b\) \((X = Br)\), Ni-catalyzed ACCR of exocyclic metalloalkenyl sulfoximines.

![Scheme 2. Nickel-catalyzed anionic cross-coupling reaction (ACCR) of metalloalkenyl sulfoximines with PhM (M = MgBr, Li).](image)

![Scheme 3. (a) Ni-catalyzed ACCR of exocyclic metalloalkenyl sulfoximines. (b) Ni-catalyzed ACCR of acyclic \((E)-configured lithioalkenyl sulfoximines. (c) Proposed pathway through [1,5]-retro-Brook rearrangement of \(\delta\)-silyloxy alkylolithiums. (d) Synthesis of \((Z)-alkenylsilanes.](image)
(2 equiv) and Ni(PPh3)2Cl2 (5 mol%) in diethyl ether at 0 ℃. To our surprise, quenching of the reaction mixture with CF3CO2H furnished the (Z)-configured alkenylsilane (Z)-H-10a (≥ 98.2: 2 dr) in 82% yield instead of the corresponding alkene derived from protonation of alkenylsilane (Z)-Li-9a or (E)-Li-9a (Scheme 3b). The (E)-configured lithioalkenyl sulfoximine rac-(E)-Li-8b, which was obtained through metatation of (Z)-H-8b [11] with MeLi, similarly engaged in an ACCR with PhLi and Ni(PPh3)2Cl2 and afforded the (Z)-configured alkenylsilane rac-(Z)-H-10b (≥ 98.2: 2 dr) in 59% yield (Scheme 3c). The ACCR of (E)-Li-8a and rac-(E)-Li-8b had initially given alkenyllithiums Li-9a and rac-Li-9b either as (Z)- or (E)-configured isomers or mixtures of both isomers. Regardless of the selectivity of the ACCR, the establishment of an equilibrium between the (E)- and (Z)-isomers of alkenyllithiums Li-9a and rac-Li-9b has to be assumed, because the α-phenyl alkenyllithiums should have a low configurational stability under the reaction conditions. [24]

For example, (Z)-(2-isopropyl-1-phenylvinyl)lithium experienced under ACCR conditions a fast (Z)-isomerization in ether at 0 ℃ (see the Supporting Information for details). From the equilibrium mixture of the isomeric alkenyllithiums the (E)-configured isomers selectively reacted through migration of the silyl group from the O to the C atom under formation of the (Z)-configured alkenylsilanes (Z)-Li-10a and rac-(Z)-Li-10b. Silyl migration in the (Z)-configured isomers should be prohibited because of steric reasons. The formation of alkenylsilanes (Z)-Li-10a and rac-(Z)-Li-10b from the corresponding alkenyllithiums (E)-Li-9a and rac-(E)-Li-9b are examples of a [1,5]-retro-Brook rearrangement involving sp2-hybridized C atoms. [25] Although examples of [1,4]-retro-Brook rearrangement have frequently been described, [25, 26] those of [1,5]-retro-Brook rearrangement are scarce. [25, 27] The alternative route to (Z)-H-10a and rac-(Z)-H-10b starting with a [1,5]-retro-Brook rearrangement of (E)-Li-8a and rac-(E)-Li-8b followed by a Ni-catalyzed CCR of the corresponding α-silyl alkenyl sulfoximines [24] can be excluded, because of the inertness of the lithioalkenyl sulfoximines towards silyl migration. Ultimately, the Ni-catalyzed ACCR of (E)-Li-8 with aryllithiums followed by a [1,5]-retro Brook rearrangement of the intermediate alkenyllithium provides a stereoselective route to acyclic homoallylic alcohols (Z)-10, carrying a synthetically valuable (Z)-alkenylsilane group [28] (Scheme 3d), from allylic sulfoximines and aldehydes. Because of the availability of the exocyclic lithioalkenyl sulfoximines (E)-Li-11,[12a] this route should also give access to the exocyclic silyl-substituted homoallylic alcohols (Z)-12.

Although we initially observed a Ni-catalyzed ACCR of (E/ Z)-M-6, its stereoselectivity remained unclear since we could not differentiate in diastereoselectivity between (E, R)-M-6 and (Z, R)-M-6 or (Z, S)-M-6 and (E, S)-M-6 as illustrated in Scheme 4a. Although the exocyclic metalloalkenyl sulfoximines (E)-Li-8 led to a C–C coupling and an intriguing [1,5]-retro-Brook rearrangement to form the (Z)-alkenylsilanes as depicted in Schemes 2 and 3. However, the ACCR of the (Z)-configured lithioalkenyl sulfoximines (Z)-Li-8 could not be studied, because of a fast and complete isomerization at −35 ℃ to the corresponding (E)-configured diastereomers (E)-Li-8 (see the Supporting Information for details), [11] as revealed by trapping experiments (Scheme 4b). Thus, we had to employ a new class of metalloalkenyl sulfoximines as illustrated in Scheme 4c, in order to investigate the mechanism and stereoselectivity of the ACCR.

The axially chiral lithioalkenyl (N-methyl)sulfoximines (aS,S)-Li-13a and (aR,S)-Li-13a, which are accessible through metatation of the corresponding alkyl sulfoximines (aS,S)-H-13a and (aR,S)-H-13a [23] with MeLi, exist as equilibrium mixtures in which the composition and the rate of isomerization are strongly solvent dependent. Although the dr of the lithioalkenyl (N-methyl)sulfoximines (aS,S)-Li-13a and (aR,S)-Li-13a is 97:3...
in diethyl ether at $-70^\circ$C (95:5 at 0°C) and 97.3 in dimethylsulfoxide (DME) at $-50^\circ$C, it is 33:67 in THF at $-70^\circ$C to 0°C. Lithioalkenyl sulfoximine (aS,S)-Li-13a is configurationally stable in ether and DME at low temperatures for a prolonged period of time (see the Supporting Information for details). Isomerization of the lithioalkenyl sulfoximines is in THF significantly faster than in ether (see the Supporting Information for details). However, at low temperatures both lithioalkenyl sulfoximines (aS,S)-Li-13a and (aR,S)-Li-13a can be efficiently trapped with electrophiles in diethyl ether/HMPA or THF. Isomerization of the lithioalkenyl sulfoximines, which are expected to contain a C-Li bond and Li atom being coordinated by the N atom or N-sulfonfyl O atom, most likely involves a solvent-assisted cleavage of the C-Li bond and formation of N,Li or Q,Li contact ion pairs, which undergo inversion at the anionic C atom and rotation around the C-S bond formed by the formation of the C-Li bond to give the corresponding diastereomer.[11] The unresolved issue within this dynamic scheme is the strong solvent dependency of the equilibrium between (N-methyl)alkenyllithiums (aS,S)-Li-13a and (aR,S)-Li-13a and rate of isomerization. The (N-silylsulfoximine (aS,S)-Li-13c is configurationally stable at $-70^\circ$C in diethyl ether, but forms a 1:3 mixture of diastereomers (aR,S)-Li-13c and (aS,S)-Li-13c at 0°C. The substituent at the N atom of the axially chiral lithioalkenyl sulfoximines exerts a strong influence on the rate of isomerization. In contrast to the (N-methyl)- and (N-silyl)sulfoximines, the (N-sulfonfyl)sulfoximine (aR,S)-Li-13b experiences even at $-70^\circ$C in diethyl ether and THF a fast isomerization to give a mixture of (aR,S)-Li-13b and (aS,S)-Li-13b in 50:50 dr. The origin of the difference in configurational stability of the (N-methyl)- and (N-sulfonfyl)alkenyllithiums is unknown.

The axially chiral metalloalkenyl sulfoxime (aS,S)-Li-13a was considered to be a good stereochemical probe, because it carries diastereotropic methylene groups at the double bond and ACCR will afford enantiomeric alkenes. Moreover, the three types of metalloalkenyl sulfoximines, (aS,S)-Li-13a, (aR,S)-Li-13b, and (aS,S)-Li-13c should also serve to explore the substrate specificity of the ACCR. Finally, the axially chiral metalloalkenyl sulfoximines, which carry sulfinimidoyl groups of different nucleofugacity and Lewis basicity,[12,25] were intended to be probes for the influence of the nucleofuge upon the ACCR.

The dependency of the ACCR of metalloalkenyl sulfoximines on a number of variables, including the Ni-catalyst, Ni-precatalyst, ligands of the Ni atom, sulfinimidoyl group and reaction conditions, was studied by using (aS,S)-Li-13a as substrate. Generally, ACCR was run in diethyl ether, because of the high dr and the configurational stability of the lithioalkenyl sulfoximine in this solvent at low temperatures. Treatment of lithioalkenyl sulfoximine (aS,S)-Li-13a of 96:4 dr in diethyl ether with Ni(COD)$_2$[36] (5 mol%) and salt-free PhLi (2 equiv)[31] at $-60^\circ$C to $-55^\circ$C for 3 h followed by quenching the mixture with CF$_2$CO$_2$D afforded alkenes (aR)-D-14a and (aS)-D-14a with 97% D in 82% yield and 84.16 er (Table 1, entry 1). The er of (aR)-D-14a and (aS)-D-14a was determined by $^1$H NMR spectroscopy of the presence in AgFOD (FOD = 7.7-dimethyl-1,1,2,2,3,3-heptafluoro-octan-4,6-dionato) and Pr(tfc)$_3$[32] (tfc = 3-trifluoroacetyl-d-camphorato) and by GC on a chiral stationary phase. The absolute configuration of (aR)-D-14a was determined based on a comparison of its chiroptical properties with those reported in the literature for (aS)-H-14a and structurally closely related compounds.[33] In addition to (aR)-D-14a and (aS)-D-14a sulfinamide (H)-S-15[34,35] was isolated in 73% yield and >98:2 er. Repetition of the above ACCR experiment with salt-containing PhLi gave similar results.

Because of the difference in the 96:4 dr of (aS,S)-Li-13a (equilibrium ratio) (see, Table S3, Supporting Information) and the 84:16 er of (aR)-H-14a and (aS)-H-14a found in the ACCR, control experiments with (aS,S)-Li-13a (96:4 dr), Ni(COD)$_2$, and PhLi in diethyl ether were run at $-65^\circ$C to $-55^\circ$C. First, the reaction mixture was quenched after 1.5 h and the alkyl en sulfoxime (aS,S)-H-13a was isolated, the dr of which was 92:8. In a second experiment, the reaction mixture was quenched after 15 min, and the alkenes (aR)-H-14a and (aS)-H-14a were isolated (85:15 er), showing that no racemization of (aR)-Li-14a occurred during the reaction. Racemization of (aR)-Li-14a in diethyl ether is slow. For example, (aR)-Li-14a with 62:38 er had after being kept in ether at 0°C for 6 h an er of 59:41.

To reveal the possible influence of phosphines, reaction of (aS,S)-Li-13a (97.3:2.7 dr) with PhLi was conducted with in situ prepared Ni(PPh$_3$)$_2$(COD)$_2$[36] (5 mol%) in diethyl ether at $-60$ to $-55^\circ$C for 3 h followed by quenching the mixture with CF$_2$CO$_2$D, which gave (aR)-D-14a and (aS)-D-14a in 85:15 er and 93% yield (entry 2). In further experiments, the ligand for the Ni atom was further varied in the ACCRs of (aS,S)-Li-13a (97:3:2.7 dr) with PhLi and Ni(COD)$_2$ (entries 3 and 4), and different Ni$^0$-precatalysts were tested (entries 5–7). Complex Ni(PPh$_3$)$_2$Cl$_2$...
proven to be an excellent precatalyst (entry 5), which is converted by PhLi to a Ni[I]-complex.\textsuperscript{17} Alkenes (\textit{aR})-(H)-D-14a and (\textit{aS})-(H)-D-14a were isolated in 80–94% yield and 82:18 to 85:15 er. ACCR of (\textit{aS,S})-Li-13a (97.3 dr) with PhLi and Ni(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} in diethyl ether at 0 °C was less selective. After a reaction time of only 2 min (\textit{aR})-D-14a and (\textit{aS})-D-14a were isolated in 62:38 er and 84% yield. Table 1 reveals that the catalyst, the precatalyst(s) and the ligands of the Ni atom have only a minor influence upon the ACCR. We also studied the ACCR of (\textit{aR,S})-Li-13a, which is configurationally less stable than (\textit{aS,S})-Li-13a. ACCR of (\textit{aR,S})-Li-9a of approximately 95:5 dr with PhLi in ether in the presence of Ni(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} at ~65 °C for 4 h followed by quenching the mixture with CF\textsubscript{3}CO\textsubscript{2}D gave alkenes (\textit{aS})-D-10a and (\textit{aR})-D-10a (98% D) in 64:36 er and 82% yield (entry 8). The selectivity of the ACCR of (\textit{aR,S})-Li-13a is lower than that of diastereomer (\textit{aS,S})-Li-13a. Responsible for the lower selectivity is most likely the competing isomerization of (\textit{aR,S})-Li-13a to the more stable diastereomer (\textit{aS,S})-Li-13a and its respective ACCR.

Previously, alkenyl sulfoximines (\textit{E})-H-6 and (\textit{aS,S})-H-13a were found to be subject to a highly stereoselective Ni\textsuperscript{II}-catalyzed and Lewis acid-promoted cross-coupling reaction with diorganozincs,\textsuperscript{3, 23, 38, 39} which most likely proceeds by a KCN catalytic cycle.\textsuperscript{21, 22} The adaption of this cycle to the ACCR involved (i) an oxidative addition of (\textit{aS,S})-Li-13a to the Ni\textsuperscript{II}-catalyst to afford a Ni\textsuperscript{III}-complex, (ii) a transmetalation with PhLi, and (iii) a reductive elimination to furnish alkenyllithium (\textit{aS})-Li-14a as described in Scheme 5 with the dotted red line. Although the ACCR cycle leads, under retent of configuration, to alkenyllithium (\textit{aS})-Li-14a, the alkenyllithium obtained experimentally in ACCR had the (\textit{aR})-configuration, under inversion of configuration. The observed difference in stereoselectivity led us to deduce that the KCN cycle is not applicable to the ACCR of metalloalkenyl sulfoximines. Moreover, our density functional theory (DFT) calculations indicate that the barrier of the oxidative addition pathway is 27.7 kcal mol\textsuperscript{-1}, which is too high for the given experimental conditions to be mechanistically relevant (see the Supporting Information for details). Therefore, we considered an unconventional and intriguing mechanism, as illustrated in Scheme 5. We imagined that the highly reduced nickel center of the complex, containing a C–Ni bond, may be compelled to form the Ni\textsuperscript{II}-vinylidene complex that is stabilized by lithium sulfonamide coordination and which we were able to locate in our DFT calculations. Our calculations suggest that the reaction may proceed further by coordination of the phenyl anion to the Ni-center of the Ni\textsuperscript{II}-vinylidene to form a Ni\textsuperscript{III}-intermediate with carbanionic character, which requires stabilization by two Li\textsuperscript{+}. Finally, reductive elimination of the Ni\textsuperscript{III}-intermediate extrudes alkenyllithium (\textit{aR})-Li-14a.

Figure 1 illustrates the computed free-energy profile for the proposed mechanism. In our computer model, Ni(PMe\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} was used as the precatalyst and (\textit{aS,S})-Li-13a was employed as representative substrate. Notably, the electron-rich Ni-center in the anionic Ni\textsuperscript{II}-ate intermediate A1 is stabilized by π-backdonation to the anti-bonding orbital of the C=C moiety in the lithioalkenyl sulfoximine, leading to a notable lengthening of the C=C bond from 1.35 to 1.44 Å (see the Supporting Information for details). The carbenoid addition from A1 to the diatomic Ni\textsuperscript{II}-ate complex A10 at 25.1 kcal mol\textsuperscript{-1} is energetically too high to be mechanistically relevant, as indicated in red. This finding is easy to understand given that in the putative intermediate A10, there is no appropriate electron acceptor that may allow for delocalizing the high electron density of the highly reduced nickel center. Of course, the phosphine ligands are notorious for being excellent π-acceptors and, thus, we also tested if the arylphosphine ligand PPh\textsubscript{3} could act as an effective electron acceptor. Our calculations indicate that compared with the model ligand PMe\textsubscript{3}, the PPh\textsubscript{3}-analogue of A10 is indeed lower, but still too high in energy at 20.6 kcal mol\textsuperscript{-1} to be meaningful for the overall chemical reaction (see the Supporting Information for details).

We propose that the productive mechanistic pathway involves the neutral Ni\textsuperscript{II} intermediate A2 located at 4.2 kcal mol\textsuperscript{-1}, which can form the anionic Ni\textsuperscript{II}-ate intermediate A3 through a nucleophilic attack of the carbanion substrate mediated by Li\textsuperscript{+}. We found that this process only requires the passage through the transition state A2-TS at 16.3 kcal mol\textsuperscript{-1}. Subsequently, the transient intermediate A3 must undergo an α-elimination via A3-TS at 20.4 kcal mol\textsuperscript{-1} to form intermediate A4. And again, the presence of Li\textsuperscript{+} is important for this step, as the barrier would be nearly 6 kcal mol\textsuperscript{-1} higher in energy without it (see Supporting Information for details). Intriguingly, Li\textsuperscript{+} also plays a critical role in determining the stereoselectivity. Lithium sulfonamide-coordinated Ni\textsuperscript{II}-vinylidene A4 is energetically preferred over the noncoordinated Ni\textsuperscript{II}-vinylidene A7, a finding which is ultimately responsible for the observed stereoselectivity. The geometry of A4 exposes only one possible site for the addition of a PhLi reagent to the Ni-center, rendering inter-
mediate A5, stabilized by two Li⁺ and located at −17.2 kcal mol⁻¹, the only plausible adduct. Formation of A5 with the opposite configuration at the chiral axis requires a prior isomerization of the Ni⁺⁺-vinylidene intermediate A4. Attempts to locate a transition state for the putative isomerization of A4 were unsuccessful, but the conversion of A4 to A5 having the aR configuration should be fast given the driving force of ΔG ≈ −17 kcal mol⁻¹ and should only be limited by diffusion and collision of A4 with PhLi.

Figure 2 illustrates the optimized structures of A4 and A5, intermediates featuring structural and energetic stabilization by Li⁺-coordination. Ni⁺⁺-vinylidene A4 shows a Ni–C1 bond length of 1.74 Å, clearly indicating a double-bond character. Relatively weak Ni–Li interaction is indicated by the calculated bond length of 2.58 Å. Similar metal–lithium interactions have been previously observed in lithiated Fe- Co-, and Ni-complexes. The short distance between the vinylidene carbon and the Li center of 2.26 Å suggests a strong interaction and is analogous to interactions previously reported for metal–car-
bene complexes stabilized by alkali metals.[41] Taken together, this structural pattern demonstrates why the three-center interaction of Ni–Li–C1 cannot be easily overcome to afford the free Ni2-vinylidyne intermediate A7. Moreover, the two Li+ interact covalently with C1 as shown in A5 with bond lengths of C1–Li1 (2.13 Å) and C1–Li2 (2.10 Å). The elongated bond length of Ni–C1 of 1.85 Å shows that the two Li+ stabilize C1, allowing it to formally remain a carbanion center instead of becoming part of a Fischer-type metal–carbon double bond. Consequently, the Ni-center of A5 has a formal oxidation state of Ni0. Intermediate A5 easily undergoes reductive elimination to form the C–C bond of A6 with a barrier of only 7.6 kcal mol−1, which is 3 kcal mol−1 lower than the barrier of 10.5 kcal mol−1 associated with the alternative transition state A8-TS. Furthermore, transition state A5-TS illustrates the impact of the second Li+. It facilitates the reductive elimination by temporarily increasing the positive charge of the Ni-center without actively participating in the redox process. Finally, alkylLi-amine (aR)-Li-14a coordinated by (S)-Li-15 is extruded from A6 through ligand exchange with (aS,S)-13a to give A2, which can start a new catalytic cycle.

In summary, our computational study suggests an intriguing mechanistic role of Li+ and proposes that the stereoselectivity of ACCR is determined by the electrostatic stabilization of the putative Ni0-complex A5 through coordination of two Li+, which is in accordance with the experimental observations. To test this hypothesis, we examined the decreasing effect of the Li+ when DME is used as the solvent. It is well known that DME can chelate Li+ by formation of Li–O interactions and thereby give rise to the formation of solvent-separated ion pairs.[42] In DME treatment of (aS,S)-Li-13a (97:3 dr) with PhLi and Ni(PPh3)2Cl2 (5 mol%) at −60 to −55 °C for 3 h followed by quenching the mixture with MeI at −55 °C to 0 °C gave a mixture of the methylated alkyl sulfoximines (aS,R)-Me-13a and (aR,R)-Me-13a in 50:50 dr in 74% yield, but only traces of the methylated alkene derived from a methylation of alkylLi-amine (aR)-Li-14a (see below, Scheme 6). Formation of the mixture of the diastereomeric methylated alkyl sulfoximines in 50:50 dr indicates that the Ni0-vinylidyne intermediate A7 and two different isomers of A7/Li-sulfamination (Scheme 6) exist in the reaction path and Li+ is chelated by DME instead of forming A4 (see the Supporting Information for details). Moreover, it is likely that the carbanion intermediate A4 is formed to afford the Ni0 intermediate A5 that undergoes reductive elimination and advances the C–C bond formation with PhLi. However, because of the reduced activity of Li+ it may not accelerate the formation of the Ni0 intermediate A5 from A7 or (aR)- and (aS)-A7/Li-sulfamination intermediates, which might be generated because of the different reaction conditions with DME as solvent.

The anionic Ni0-ate mediated catalytic pathway was established with Ni(PPh3)2Cl2 as precatalyst. However, we also obtained experimental results when employing Ni(PPh3)2(COD) as the precatalyst that were inconsistent with the aforementioned mechanism. Scheme 7 represents a control experiment with (aS,S)-Li-13a (96:4 dr) and stoichiometric amounts of Ni(PPh3)2(COD) at −55 °C in diethyl ether/cyclohexene for 2 h in the absence of PhLi. The Ni-complex did not cause a decomposition of the lithioalkenyl sulfoximine at low temperatures. Instead, the decomposition took place when the temperature was increased to 0 °C, indicating that the reaction pathway of A2 → A3 → A3-TS does not occur when COD is present as an innocent ligand. In this case, the C–S bond cleavage of the lithioalkenyl sulfoximine will be accelerated by the existence of the PhLi reagent at low temperature. Computational studies show that PhLi is not necessary for the Ni(PPh3)2Cl2 system in which the dianionic Ni0 intermediate A10 is located at high energy of 25.1 kcal mol−1, whereas in the Ni(COD)2 system the dianionic Ni0 intermediate B3 (see below) has a relatively low energy. Thus, the use of olefinic ligands such as COD for the Ni-catalyzed ACCR gave the same product with a similar yield (see Table 1) but to our surprise, the reaction path seemed to be different. Recently, formation of anionic Ni0 complexes has been described when COD was employed as innocent ligand.[5] In these complexes, which display an intriguing catalytic activity, the highly reduced Ni0 atom is stabilized by π-back-donation to the C–C bond of the olefinic ligand. Given that we sensed for the reaction pathway of the ACCR with Ni(COD)2 disparities in comparison with the aforementioned one based on Ni(PPh3)2Cl2, we decided to further examine the elusive
mechanism of the ACCR via dianionic Ni

DFT calculations of the ACCR of \((\alpha S, S)-Li-13a\) with PhLi in the presence of Ni(COD)
with theoretical methods.

In the absence of PhLi, the carbenoid addition traversing the transition state B6-TS is associated with a reaction barrier of 23.7 kcal mol
This barrier suggests that the decomposition of the lithioalkenyl sulfoximine via Ni
and B8 is not feasible at low temperatures, when the olefinic ligand is employed, as observed in the control experiment mentioned above. In contrast, the addition of PhLi to B1 leads to the anionic Ni
complex B2, which is stabilized by two olefinic ligands, COD and the lithioalkenyl sulfoximine. Next, the carbenoid addition to the Ni atom generates the dianionic Ni
complex B3 at 1.5 kcal mol

Optimized structures of B2 and B3 are shown in Figure 4. Although the anionic Ni
complex could be stabilized by the C=C bond of the lithioalkenyl sulfoximine for both ligands PMe3 (A1) and COD (B2), only the dianionic Ni
complex B3, carrying COD as ligand, was located at relatively low energy. This differentiates the two distinct mechanisms of the Ni-catalyzed ACCR with the different innocent ligands because the analogous dianionic Ni
complex A10 is associated with a high barrier. Electron-rich \([\text{Ni}^{2-}]\)
engages in \(\pi\)-backdonation to the C=C bond of the lithioalkenyl sulfoximine that displays an elongated C3–C4 bond (1.43 Å) as a consequence. This orbital interaction is also present in A1, in which the alkenyl double bond is found to be 1.44 Å (see the Supporting Information for details). On the way from B2 to the dianionic Ni
complex B3, the interaction between the Ni atom and C=C bond of the lithioalkenyl sulfoximine is resolved and instead the Ni–C3 \(\sigma\)-bond is formed. The other olefinic ligand, COD, accepts an electron from the highly reduced \([\text{Ni}^{2-}]\) metal center, which is indicated by the elongated bond length of
C1–C2 (1.45 Å) in B3, whereas there is no more proper electron acceptor in the PMe3, coordinated system (A10). The proposed formation of the Ni3-ate complexes B2 and B3 is supported by the synthesis of lithium and dillithium Ni3-ate complexes from Ni2 complexes including Ni(COD), and organolithiurns.246 Furthermore, the highly electron-rich [Ni3]2- metal center of B3 can easily push some electron density to the alkyl sulfoximine group, consequently transpiring the C–S bond cleavage with the reduction of sulfur from S(VI) to S(IV). The overall barrier associated with B3-TS is 16.4 kcal mol−1. The transformation of B3 to the Ni0 complex B4 is mediated by two Li+ in an exogenic process. Finally, reductive elimination of B4 via transition state B4-TS affords alkylolithium ([αR]-Li-14a, as observed when Ni(PPh3)3Cl2 was used as precatalyst.

To gain information about the observed lack of a competing ACCR of the lithioalkenyl sulfoximine with alkylolithium ([αR]-Li-14a, ACCRs of (αS,S)-Li-13a (97:3 dr) with vinylithium and α-phenyl vinylithium as model compounds for (αR)-Li-14a were performed (Table 2, entries 1–4). ACCR of (αS,S)-Li-13a (96:4 dr) with vinylithium in the presence of Ni(PPh3)3Cl2 (5 mol%) in diethyl ether was slow at low temperatures (entries 1 and 2). It occurred with reasonable rate only at 0 °C and gave after quenching the reaction mixture with CF3CO2D diene rac-D-14b (83% D) in 86% yield (entry 3). A similar ACCR of (αS,S)-Li-13a (96:4 dr) with α-phenyl vinylithium in the presence of Ni(PPh3)3Cl2 (5 mol%) at 0 °C in diethyl ether for 1.5 h followed by treatment of the reaction mixture with CF3CO2D afforded diene rac-D-14c (42% D) in only 30% yield (entry 4). The rate of the ACCR of (αS,S)-Li-13a with the sp2-organolithiums strongly decreases in the order PhLi > vinylithium > α-phenyl vinylithium. These data suggest that the ACCR of (αS,S)-Li-13a with alkylithium (αR)-Li-14a should be even slower than with α-phenyl vinylithium. Isolation of rac-D-14b and rac-D-14c, having a low D-content, appears to be the result of a lithiation of the corresponding lithioallyl sulfoximine, resulting in a vinyl-allyl isomerization of (αS,S)-Li-13a, by the dienyliithium under formation of the corresponding dillithioallyl sulfoximine and the protonated diene (see the Supporting Information for details). In contrast, attempts to achieve a Ni-catalyzed ACCR of (αS,S)-Li-13a with alkylithiums, including MeLi, nBuLi, and LiCH2SiMe3, were unsuccessful.

In further experiments with axially chiral lithioalkenyl sulfoximines, we studied the influence of the substituent at the N atom upon the ACCR. In stark contrast to the (N-methyl)sulfoximine (αS,S)-Li-13a, the (N-sulfonyl)sulfoximines (αR,S)-Li-13b and (αS,S)-Li-13b (50:50 dr), which were synthesized through metalation of alkyl sulfoximine (αR,S)-H-13b [52] with nBuLi, did not undergo an ACCR with PhLi at −75 °C in diethyl ether for 1 h in the presence of Ni(PPh3)3Cl2 (5 mol%) (Table 2, entry 5). Quenching the reaction mixture with CF3CO2D led to a recovery of the deuterated sulfoximines (αR,S)-D-13b and (αS,S)-D-13b (95% D) in 50:50 dr. Under these conditions, already 30% of the (N-methyl)sulfoximine (αS,S)-Li-13a had been converted to alkylolithium (αR,S)-Li-13a (see above). Correspondingly, no ACCR was observed between the (N-silyl)sulfoximine (αR,S)-Li-13c, which was obtained from alkyl sulfoximine (αR,S)-H-13c on reaction with MeLi, and PhLi in the presence of Ni(PPh3)3Cl2 (5 mol%) at −75 °C (entry 6). After the temperature of the reaction mixture was raised to −5 °C and the mixture quenched with CF3CO2D, alkene rac-D-14a (77% D) was isolated in only 12% yield. Alkyl sulfoximines (αR,S)-D-13c and (αS,S)-D-13c (98% D) were recovered in 73% yield and 50:50 dr (entry 7).

So far the phenyl-substituted alkylithiums (αS,S)-Li-14a and (αR,S)-Li-14a were trapped by protonation and/or deuteration. It was of interest to see, however, whether the alkyl-

Table 2. Ni-catalyzed ACCR based on different lithioalkenyl sulfoximines and alkylithiums.

| Entry | Alkenyl sulfoximine | R′Li | T [°C] | t [h] | Yield [%] | D [%] | er |
|-------|---------------------|------|--------|-------|-----------|-------|----|
| 1     | (αS,S)-Li-13a       | ClH2 | −30    | 3.5   | 39H1     | 41    | 50:50 |
| 2     | (αS,S)-Li-13a       | ClH2 | −20    | 3.5   | 68H1     | 79    | 50:50 |
| 3     | (αS,S)-Li-13a       | ClH2 | 0      | 1     | 86H1     | 83    | 50:50 |
| 4     | (αS,S)-Li-13a       | ClH2 | 0      | 1.5   | 30H1     | 42    | 50:50 |
| 5     | (αR,S)-Li-13b       | PhLi | −75    | 1     | –        | –     | –   |
| 6     | (αS,S)-Li-13b       | PhLi | −75    | 1     | –        | –     | –   |
| 7     | (αS,S)-Li-13c       | PhLi | −5     | 5     | 12       | 77    | 50:50 |

[a] A mixture of (αS,S)-D-13a and (αR,S)-D-13a (70:30 dr) and the corresponding diastereomeric allylic sulfoximines in a ratio of 92:8 was recovered in 47% yield. [b] A mixture of (αS,S)-D-13a and (αR,S)-D-13a (75:25 dr) and the corresponding diastereomeric allylic sulfoximines (fully deuterated at the α-position) in a ratio of 92:8 was recovered in 12% yield. [c] Amount of unreacted sulfoximine was not determined.
lithiums can also be intercepted with other electrophiles. Therefore, experiments were carried out by using methyl iodide, dibromoethane, and isobutyraldehyde as trapping reagents (Scheme 8).

![Scheme 8. Trapping of axially chiral alkenyllithiums with electrophiles.](image)

First, the ACCR of (aS,S)-Li-13a (97:3 dr) with PhLi was run in the presence of Ni(PPh$_3$)$_2$Cl$_2$ or Ni(PPh$_3$)$_2$(COD) [8] (5 mol%). Treatment of thus obtained alkylolithiums (aR)-Li-14a and (aS)-Li-14a (85:15 er) with Mel at −55 °C to 0 °C afforded the disubstituted axially chiral alkenes (aR)-14d and (aS)-14d in 82% yield and 85:15 er. Determination of the er was done by GC on a chiral stationary phase and by $^1$H NMR spectroscopy in the presence of AgFOD and Pr(fcl)$_n$ [32]. The absolute configuration of (aR)-14d was assigned based on its chiroptropic properties in comparison with those of (aR)-H-14a. Addition of a cold (−55 °C) solution of (aR)-Li-14a and (aS)-Li-14a in diethyl ether to a solution of 1,2-dibromoethane in ether at 0 °C gave the axially chiral bromoalkanes (aS)-14e and (aR)-14e in 68% yield and 78:22 er. Determination of the er was done by $^1$H NMR spectroscopy in the presence of AgFOD and Pr(fcl)$_n$ [32]. The absolute configuration of (aR)-14a was assigned based on its chiroptropic properties in comparison with those of (aR)-H-14a. Trapping of (aR)-Li-14a and (aS)-Li-14a in diethyl ether at −50 °C to 0 °C with $i$PrCHO furnished a mixture of diastereomeric alcohols, (aS,R)-14f and (aS,S)-14f, in a ratio of 54:46 to 79% yield, which were separated by medium-pressure liquid chromatography (MPLC). The configuration of the stereogenic center of the alcohols was not determined. The minor diastereomer had an er of 84:16 as determined by $^1$H NMR spectroscopy in the presence of AgFOD and Pr(fcl)$_n$ [32]. The configuration of the chiral axis of (aS,R)-14f and (aS,S)-14f was assigned in analogy to that of (aR)-14a.

Conclusions

The ACCR of metalloalkenyl sulfoximines with PhLi in the presence of the Ni$^0$-catalyst yielded alkenyllithiums and lithium sulfinamide under inversion of configuration at the C atom and complete retention at the S atom. Utilizing NiCl$_2$ as the precatat- staltic at optimal conditions of −60 °C, COD and phosphine ligands or Ni(COD)$_2$, as catalyst proved to be ideal in attaining a favorable yield and er. In search of establishing the first ACCR with nickel, we discovered an interesting feature in which the oxidative addition step does not initiate the ACCR catalytic cycle, further supported by computational studies. Moreover, in conjunction with DFT calculations, we were able to differentiate the distinct pathways with respect to the two different innocent ligands PPh$_3$ and COD for the reaction system. Fundamentally, the role of Li$^+$ is vital. On the one hand, it stabilizes the electron-rich metal center in the Ni$^0$-intermediates and on the other hand it participates in controlling the reaction barriers that lead to the key Ni$^0$-vinyllidine and dianionic Ni$^0$-ate intermediates of the ACCR pathways. The mechanism of the Ni catalyzed ACCR of lithioalkenyl sulfoximines is distinctly different from that of the Cu catalyzed ACCR of lithioalkenyl sulfoximines [31], which has been postulated as key step a 1,2-metallate shift [31] of higher-order cuprates under displacement of the nucleofuge at the sp$^3$ C atom.

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Conflict of interest

The authors declare no conflict of interest.

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The experiments were run in the presence of cyclohexene in order to trap the (4-tert-butyl)cyclohexylidenecarbene (M. Topolski, H. M. Walborsky, J. Org. Chem. 1994, 59, 5506–5510), which might have been generated in the decomposition of the Ni-complex derived from (aS,S)-13a and Ni(PPh₃)₂(COD). However, formation of 7-(4-(tert-butyl)cyclohexylidene)-bicyclo[4.1.0]heptane was not observed. Instead, 1,2-bis(4-(tert-butyl)cyclohexylidene)ethane (see the Supporting Information for details) could be detected by GC-MS analysis besides several unidentified compounds.