ChemPubSoc Europe

DOI: 10.1002/chem.201904862

CHEMISTRY A European Journal Full Paper

Cross-Coupling Reactions

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

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Abstract: The mechanistic platform for a novel nickel^0-catalyzed anionic cross-coupling reaction (ACCR) of lithium sulfonimidoyl alkylidene carbenoids (metalloalkenyl sulfoximines) with organometallic reagents is reported herein, affording substituted alkenylmetals and lithium sulfinamides. The Ni^0-catalyzed ACCR of three different types of metalloalkenyl sulfoximines, including acyclic, axially chiral and exocyclic derivatives, with sp^2 organolithiums and sp^2 and sp^3 Grignard reagents has been studied. The ACCR of metalloalkenyl sulfoximines with PhLi in the presence of the Ni^0-catalyst and precatalyst Ni(PPh$_3$)$_2$Cl$_2$ afforded alkenyllithiums, 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^0-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^0-vinylidene intermediate through an indispensable electron-rich Ni^0-center coordinated by phosphine ligands. Fundamentally, we present a mechanistic study in controlling the diastereoselectivity of the alkenyllithium formation via the key lithium sulfinamide coordinated Ni^0-vinylidene complex, which consequently avoids an unselective formation of an alkylidene 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.[1] 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.[1d] Anionic Pd complexes have proven to play a crucial role in cross-coupling or Heck reactions through high catalytic activity.[2] 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.[3] Especially, Kambe described the formation of anionic Ni-ate complexes from or-

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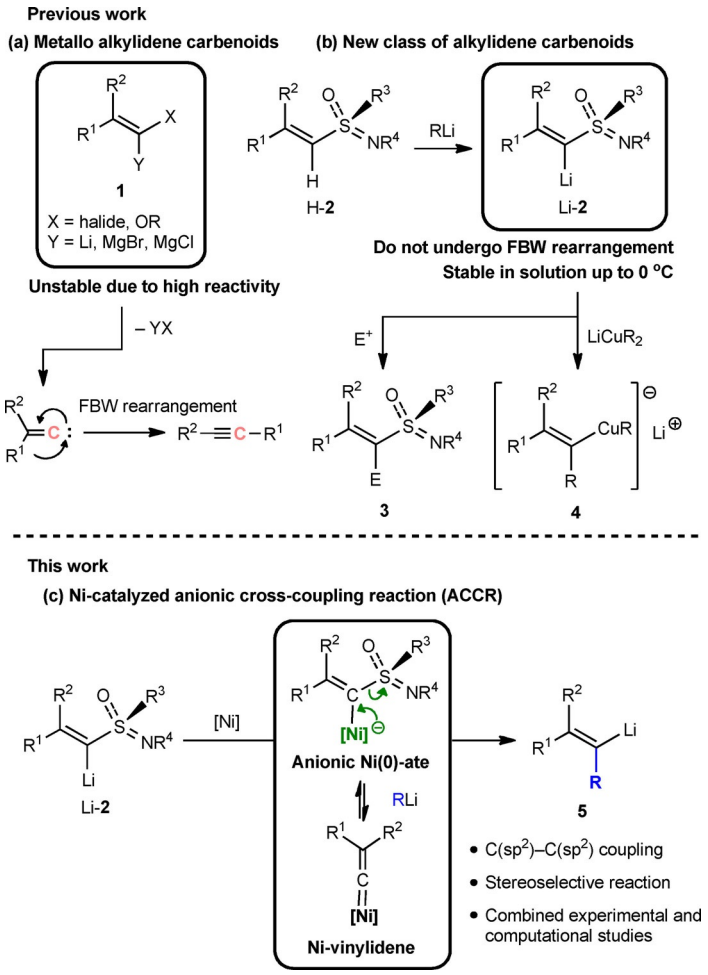
Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/chem.201904862.

ganometallic reagents, which show an enhanced nucleophilicity in the cleavage of the C(sp^3)–X bond of alkyl halides.[4] 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.[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.[6,7] In these reactions, metalloalkenyl sulfoximines react under inversion of configuration at the C 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^0-vinylidene 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.



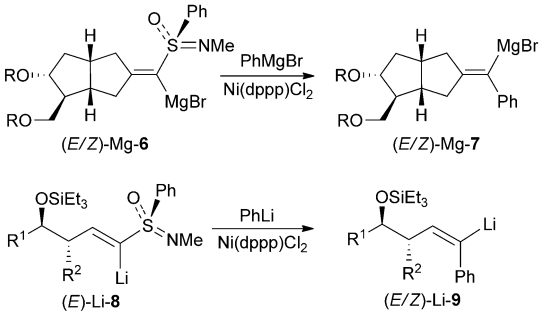
Scheme 1. (a) Metallo alkylidene carbenoids. (b) Lithium sulfonimidoyl alkylidene carbenoids. (c) Ni-catalyzed ACCR.

Metallo alkylidene carbenoids **1**, carrying an electrofugal and a nucleofugal leaving group at the Cα atom, are an intriguing class of compounds (Scheme 1 a).[8,9] Key reactivity features of **1** are electrophilic and nucleophilic substitution at the Cα atom, Fritsch–Buttenberg–Wiechell (FBW) rearrangement, α-elimination, and formation of transition-metal-ate complexes, for example. Lithioalkenyl sulfoximines Li-**2**[6,7,10–12] are a new group of non-classical alkylidene carbenoids, displaying characteristic ambiphilic reactivity (Scheme 1 b). For example, although electrophilic substitution of Li-**2** gives alkenyl sulfoximines **3**,[6,10,12] nucleophilic substitution of Li-**2** with cuprates furnishes alkenyl cuprates **4** through 1,2-metalate shift of higher-order cuprates.[13] Unlike the classical alkylidene 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.[14] According to experimental and theoretical studies, lithioalkenyl sulfoximines Li-**2**, which are obtained by lithiation of alkenyl sulfoximines H-**2**, are monomeric in etheral 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.[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-vinylidene intermediate, which is synthetically derived from either anionic or dianionic Ni^0-ate intermediates, in which the sulfonimidoyl group acted as a nucleofuge as described in Scheme 1 c. Of particular interest was the role of the anionic Ni^0-ate complex that leads to the Ni^0-vinylidene intermediate under reduction of the S(VI) atom of the sulfonimidoyl group to S(IV) and extrusion of PhS(O)N(Li)Me. Herein, the extremely electron-rich nickel center is necessary for pushing the electron density to the α-carbon to form a putative Ni^0-vinylidene intermediate. In cases of vinylidene-mediated catalysis, there have been plenty of studies of metal–vinylidene complexes in reaction pathways.[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–vinylidene complex. In closer scrutiny, however, there have been very few examples of metal–vinylidene complexes involving Group 10 metals,[18] because they have preferred modes of reactivity with alkynes that do not easily allow formation of metal–vinylidene intermediates during the reaction. Instead, Ni_2(vinylidenoid) intermediates have been accessed in vinylidene transfer reactions from dinuclear Ni-catalysts and 1,1-dichloroalkenes as vinylidene precursors.[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 alkenylmagnesiums (*E*/*Z*)-M-**7** (Scheme 2).[6] Furthermore, the acyclic



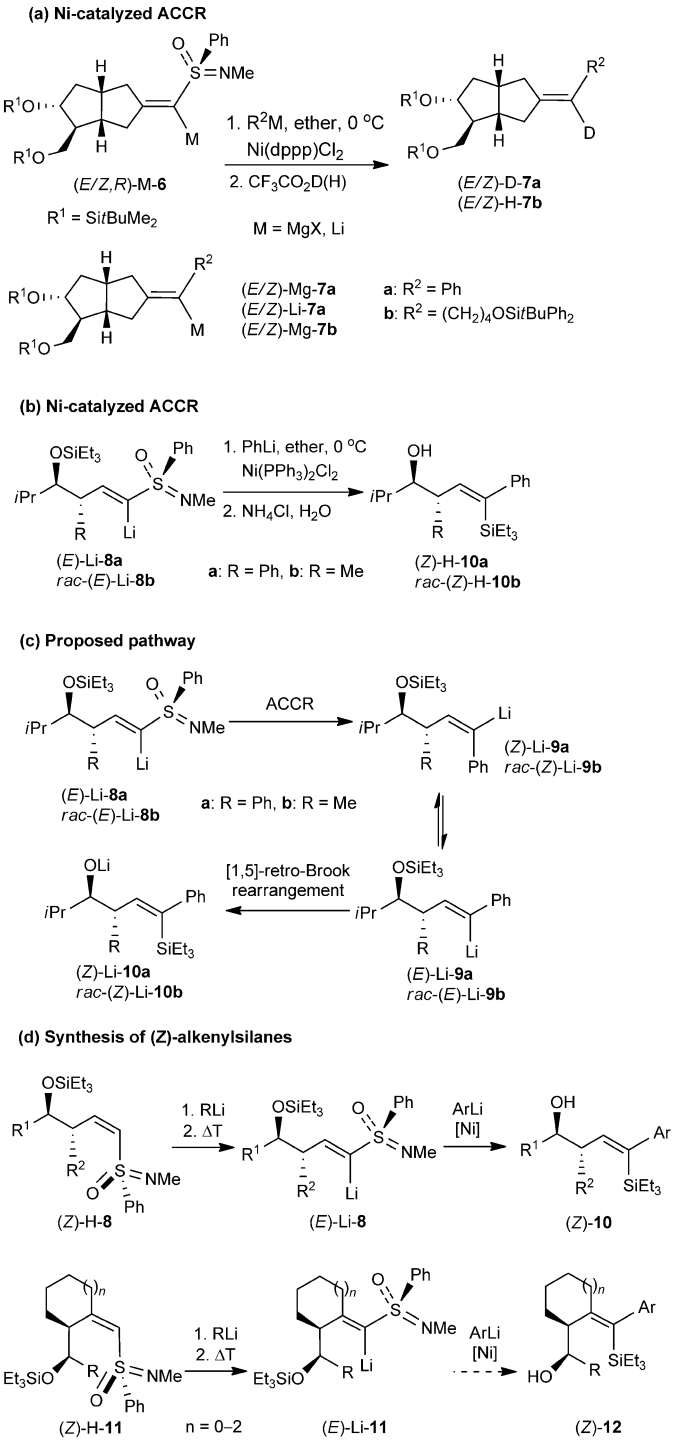
Scheme 2. Nickel-catalyzed anionic cross-coupling reaction (ACCR) of metalloalkenyl sulfoximines wtih PhM (M = MgBr, Li).

lithioalkenyl sulfoximines (*E*)-Li-**8**,[11] prepared by lithiation of (*Z*)-H-**8**,[11] were found to apparently participate in a Ni-catalyzed ACCR with PhLi, furnishing alkenyllithiums (*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**, Kocieński reported that cyclic α-lithioalkenyl ethers engage in a copper-catalyzed ACCR with organolithiums.[22] To date, Ni- and Pd-catalyzed ACCRs of metallo alkylidene carbenoids 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 for 3 h and gave alkenylmagnesiums (*E*/*Z*)-Mg-**7a** (X = Br), which after quenching with CF_3CO_2D furnished the deuterated alkenes (*E*/*Z*)-D-**7a** (93% D) 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 alkenyllithiums (*E*/*Z*)-Li-**7a**. Quenching of the alkenyllithiums with CF_3CO_2H gave alkenes (*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 $ClMg(CH_2)_4OSitBuPh_2$[6] (4.3 equiv) in the presence of Ni(dppp)Cl_2 (6 mol%) in diethyl ether at 0 °C



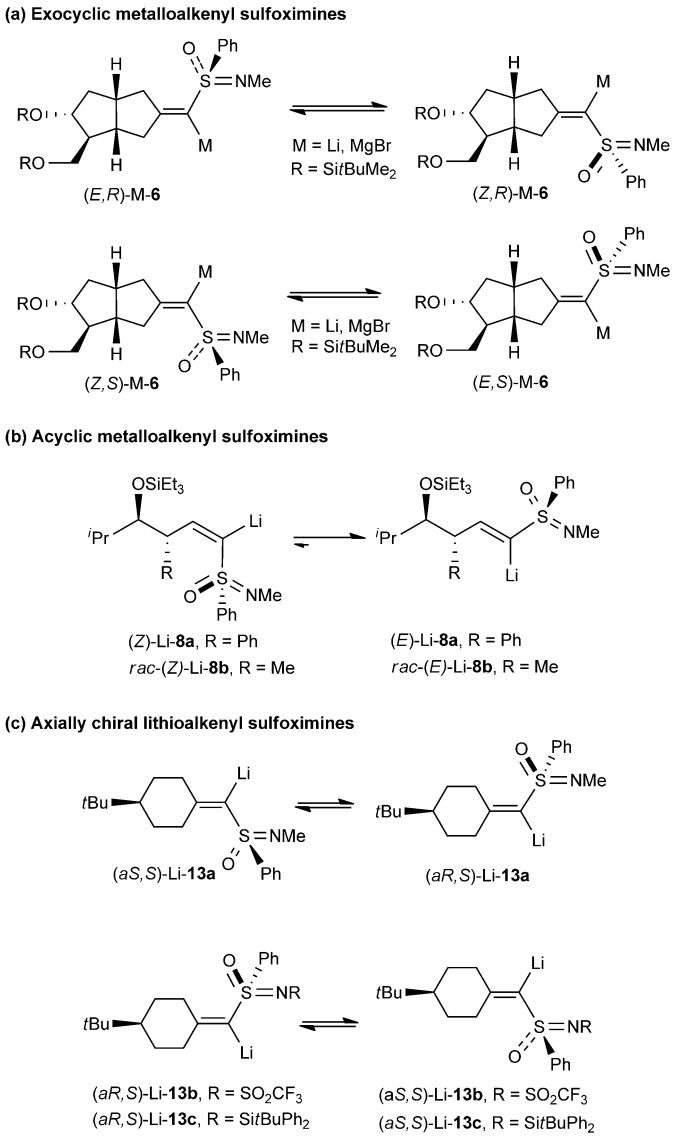
Scheme 3. (a) Ni-catalyzed ACCR of exocyclic metalloalkenyl sulfoximines. (b) Ni-catalyzed ACCR of acyclic (*E*)-configured lithioalkenyl sulfoximines. (c) Proposed pathway through [1,5]-retro-Brook rearrangement of δ-silyloxy alkenyllithiums. (d) Synthesis of acyclic and cyclic aryl-substituted homoallylic alcohols, carrying a (*Z*)-configured alkenylsilane group.

for 3 d furnished alkenylmagnesiums (*E*/*Z*)-Mg-**7b** (X = Br, Cl). Quenching of the alkenylmagnesiums with CF_3CO_2H 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

(2 equiv) and $Ni(PPh_3)_2Cl_2$ (5 mol%) in diethyl ether at 0 °C. To our surprise, quenching of the reaction mixture with CF_3CO_2H furnished the (*Z*)-configured alkenylsilane (*Z*)-H-**10a** (≥98:2 *dr*) in 82% yield instead of the corresponding alkene derived from protonation of alkenyllithium (*Z*)-Li-**9a** or (*E*)-Li-**9a** (Scheme 3b). The (*E*)-configured lithioalkenyl sulfoximine *rac*-(*E*)-Li-**8b**, which was obtained through metalation of (*Z*)-H-**8b**[11] with MeLi, similarly engaged in an ACCR with PhLi and $Ni(PPh_3)_2Cl_2$ and afforded the (*Z*)-configured alkenylsilane *rac*-(*Z*)-H-**10b** (≥98:2 *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*,*E*)-isomerization in ether at 0 °C (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 sp^2-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 alkenyllithiums 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**,[12g] 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*,*R*)-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 are configurationally stable at −70 °C in diethyl ether and diethyl ether/hexamethylphosphoramide (HMPA) and can be trapped with electrophiles, isomerization is fast at −35 °C, forming 1:1 mixtures of the diastereomers (see the Supporting Information for details). In addition, the ACCR of the acyclic lithioalkenyl sulfoximines (*E*)-Li-**8** led to a C–C coupling and an intriguing [1,5]-retro-Brook rearrangement to form the (*Z*)-alkenylsilanes as described 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 °C to the corresponding (*E*)-configured diastereomers (*E*)-Li-**8** (see the Supporting Information for details),[12] 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.



Scheme 4. (a) Isomerization of exocyclic metalloalkenyl sulfoximines, (b) acyclic metalloalkenyl sulfoximines, and (c) axially chiral lithioalkenyl sulfoximines.

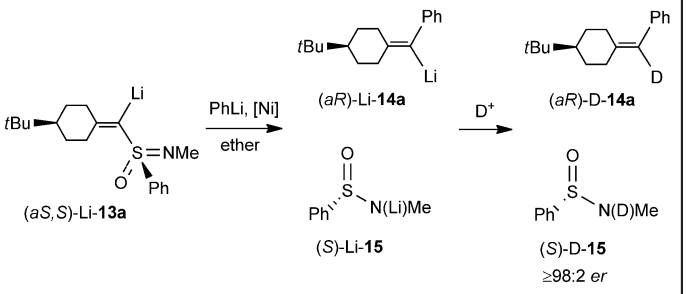
The axially chiral lithioalkenyl (*N*-methyl)sulfoximines (*aS*,*S*)-Li-**13a** and (*aR*,*S*)-Li-**13a**, which are accessible through metalation of the corresponding alkenyl sulfoximines (*aS*,*S*)-H-**13a** and (*aR*,*S*)-H-**13a**[23] with MeLi, exist as equilibrium mixtures in which the composition 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 °C (95:5 at 0 °C) and 97:3 in dimethoxyethane (DME) at −50 °C, it is 33:67 in THF at −70 °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-sulfonyl O atom, most likely involves a solvent-assisted cleavage of the C–Li bond and formation of N,Li or O,Li contact ion pairs, which undergo inversion at the anionic C atom and rotation around the C–S bond followed by the formation of the C–Li bond to give the corresponding diastereomer.[15] 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*-silyl)sulfoximine (*aR*,*S*)-Li-**13c** is configurationally stable at −70 °C in diethyl ether, but forms a 1:1 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*-sulfonyl)sulfoximine (*aR*,*S*)-Li-**13b** experiences even at −70 °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*-sulfonyl)alkenyllithiums is unknown.

The axially chiral metalloalkenyl sulfoximine (*aS*,*S*)-Li-**13a** was considered to be a good stereochemical probe, because it carries diastereotopic 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 (*aR*,*S*)-Li-**13c** should also serve to explore the substrate specificity of the ACCR. Finally, the axially chiral metalloalkenyl sulfoximines, which carry sulfonimidoyl groups of different nucleofugacity and Lewis basicity,[15,29] 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, sulfonimidoyl 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 $Ni(COD)_2$[30] (5 mol%) and salt-free PhLi (2 equiv)[31] at −60 °C to −55 °C for 3 h followed by quenching the mixture with CF_3CO_2D 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 ^1H NMR spectroscopy in the presence of AgFOD (FOD = 7,7-dimethyl-1,1,1,2,2,3,3-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 chirotropic 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 (*S*)-H-**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.

Table 1. Ni-catalyzed ACCR of lithioalkenyl sulfoximine (*aS*,*S*)-Li-**13a** using PhLi.



Entry	Catalyst/Precatalyst	Yield [%]	D [%]	*er*
1	$Ni(COD)_2$	82	97	84:16
2	$Ni(PPh_3)_2(COD)$	93	[a]	85:15
3	$Ni(COD)_2/2PiPr_3$	88	95	83:17
4	$Ni(COD)_2/2P(OMe)_3$	94	[a]	82:18
5	$Ni(PPh_3)_2Cl_2$	91	97	85:15
6[b]	$Ni(acac)_2$	80	[a]	82:18
7	$NiCl_2$/(+)-DIOP	87	[a]	82:18
8[c]	$Ni(PPh_3)_2Cl_2$	82	98	64:36[c]

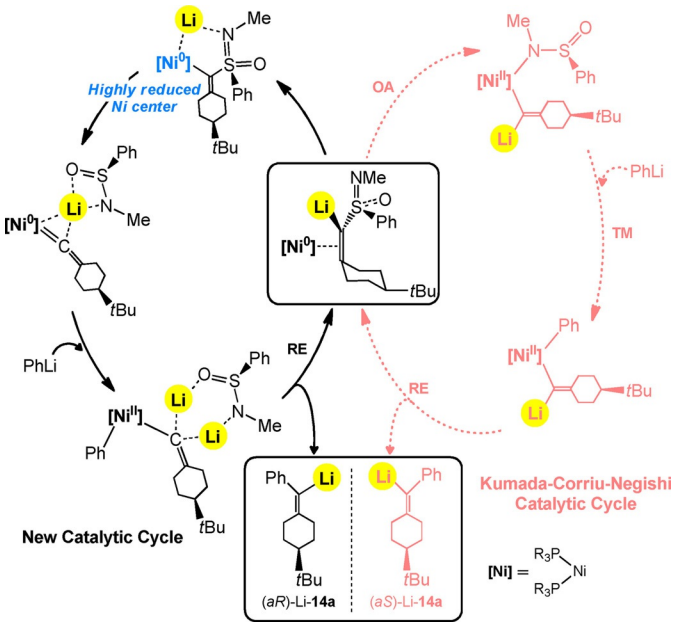
Reaction conditions: (*aS*,*S*)-Li-**13a**, catalyst/precatalyst (5 mol%), PhLi (2 equiv), 3 h, −65 °C to −50 °C. [a] Not determined. [b] 1.5 h. [c] Reaction was conducted with (*aR*,*S*)-Li-**13a** for 4 h at −65 °C, and *er* represents the ratio of (*aS*)-D-**14a** to (*aR*)-D-**14a**.

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 °C to −55 °C. First, the reaction mixture was quenched after 1.5 h and the alkenyl sulfoximine (*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 *dr*) with PhLi was conducted with in situ prepared $Ni(PPh_3)_2(COD)$[36] (5 mol%) in diethyl ether at −60 to −55 °C for 3 h followed by quenching the mixture with CF_3CO_2D, 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 *dr*) with PhLi and $Ni(COD)_2$ (entries 3 and 4), and different Ni^{II}-precatalysts were tested (entries 5–7). Complex $Ni(PPh_3)_2Cl_2$

proved to be an excellent precatalyst (entry 5), which is converted by PhLi to a Ni^0-complex.[37] Alkenes (*aR*)-H(D)-**14a** and (*aS*)-H(D)-**14a** were isolated in 80–94% yield and 82:18 to 85:15 *er*. ACCR of (*aS*,*S*)-Li-**13a** (97:3 *dr*) with PhLi and $Ni(PPh_3)_2Cl_2$ in diethyl ether at 0 °C was less selective. After a reaction time of only 2 min (*aR*)-D-**14a** and (*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 (*aR*,*S*)-Li-**13a**, which is configurationally less stable than (*aS*,*S*)-Li-**13a**. ACCR of (*aR*,*S*)-Li-**9a** of approximately 95:5 *dr* with PhLi in ether in the presence of $Ni(PPh_3)_2Cl_2$ at −65 °C for 4 h followed by quenching the mixture with CF_3CO_2D gave alkenes (*aS*)-D-**10a** and (*aR*)-D-**10a** (98% D) in 64:36 *er* and 82% yield (entry 8). The selectivity of the ACCR of (*aR*,*S*)-Li-**13a** is lower than that of diastereomer (*aS*,*S*)-Li-**13a**. Responsible for the lower selectivity is most likely the competing isomerization of (*aR*,*S*)-Li-**13a** to the more stable diastereomer (*aS*,*S*)-Li-**13a** and its respective ACCR.

Previously, alkenyl sulfoximines (*E*)-H-**6** and (*aS*,*S*)-H-**13a** were found to be subject to a highly stereoselective Ni^0-catalyzed and Lewis acid-promoted cross-coupling reaction with diorganozincs,[6,23,38,39] which most likely proceeds by a KCN catalytic cycle.[3,23] The adaption of this cycle to the ACCR involved (i) an oxidative addition of (*aS*,*S*)-Li-**13a** to the Ni^0-catalyst to afford a Ni^{II}-complex, (ii) a transmetalation with PhLi, and (iii) a reductive elimination to furnish alkenyllithium (*aS*)-Li-**14a** as described in Scheme 5 with the dotted red line. Although the KCN cycle leads, under retention of configuration, to alkenyllithium (*aS*)-Li-**14a**, the alkenyllithium obtained experimentally in ACCR had the (*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^{-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^0-vinylidene complex that is stabilized by lithium sulfinamide 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^0-vinylidene to form a Ni^{II}-intermediate with carbanionic character, which requires stabilization by two Li^+. Finally, reductive elimination of the Ni^{II}-intermediate extrudes alkenyllithium (*aR*)-Li-**14a**.



Scheme 5. Solid lines represent the newly proposed reaction pathway of the Ni-catalyzed ACCR. Dotted lines represent the oxidative addition pathway, which is of opposite stereoselectivity (OA, oxidative addition; TM, transmetalation; RE, reductive elimination).

Figure 1 illustrates the computed free-energy profile for the proposed mechanism. In our computer model, $Ni(PMe_3)_2Cl_2$ was used as the precatalyst and (*aS*,*S*)-Li-**13a** was employed as representative substrate. Notably, the electron-rich Ni-center in the anionic Ni^0-ate intermediate **A1** is stabilized by π-back-donation 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 dianionic Ni^0-ate complex **A10** at 25.1 kcal mol^{-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_3 could act as an effective electron acceptor. Our calculations indicate that compared with the model ligand PMe_3, the PPh_3-analogue of **A10** is indeed lower, but still too high in energy at 20.6 kcal mol^{-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^0 intermediate **A2** located at 4.2 kcal mol^{-1}, which can form the anionic Ni^0-ate intermediate **A3** through a nucleophilic attack of the carbanion substrate mediated by Li^+. We found that this process only requires the passage through the transition state **A2-TS** at 16.3 kcal mol^{-1}. Subsequently, the transient intermediate **A3** must undergo an α-elimination via **A3-TS** at 20.4 kcal mol^{-1} to form intermediate **A4**. And again, the presence of Li^+ is important for this step, as the barrier would be nearly 6 kcal mol^{-1} higher in energy without it (see Supporting Information for details). Intriguingly, Li^+ also plays a critical role in determining the stereoselectivity. Lithium sulfinamide-coordinated Ni^0-vinylidene **A4** is energetically preferred over the noncoordinated Ni^0-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-

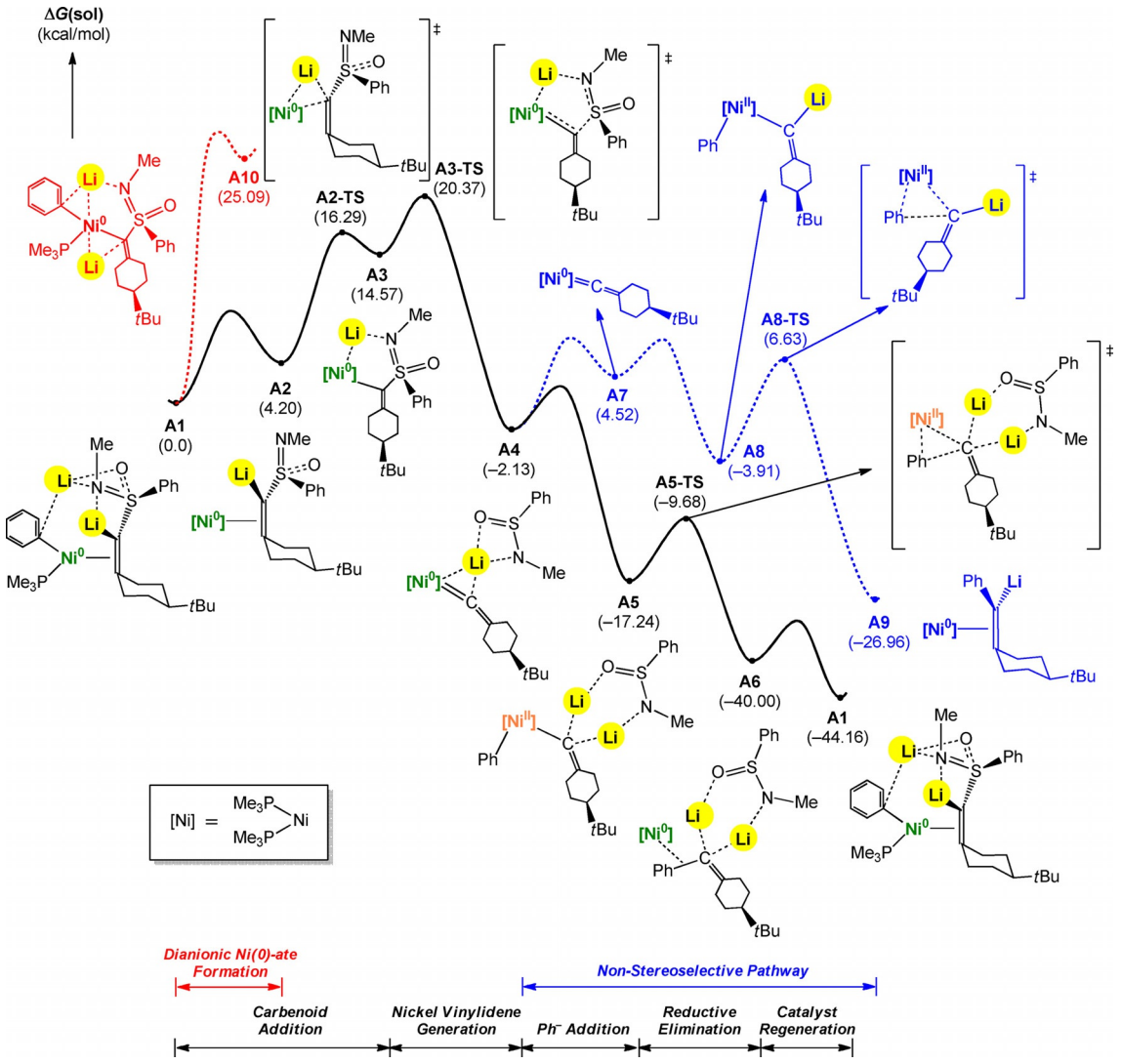


Figure 1. Free energy profile for stereoselective ACCR via lithium coordinated Ni^0-vinylidene intermediate. Black and blue traces represent the stereoselective and non-stereoselective pathway, respectively.

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^0-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 $\Delta G \approx -17$ 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^0-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.[40] 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-

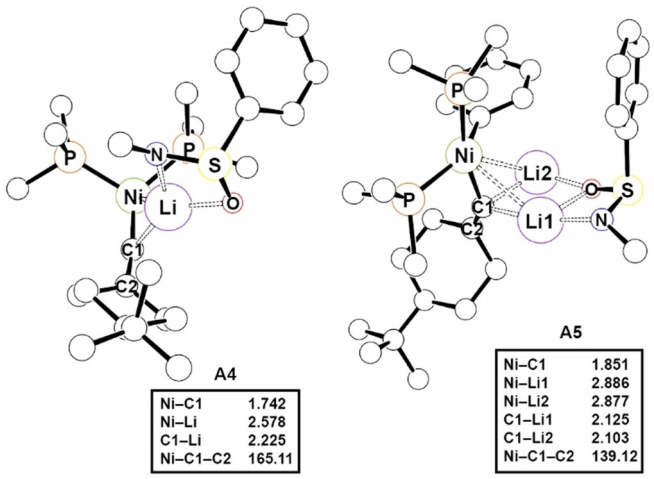
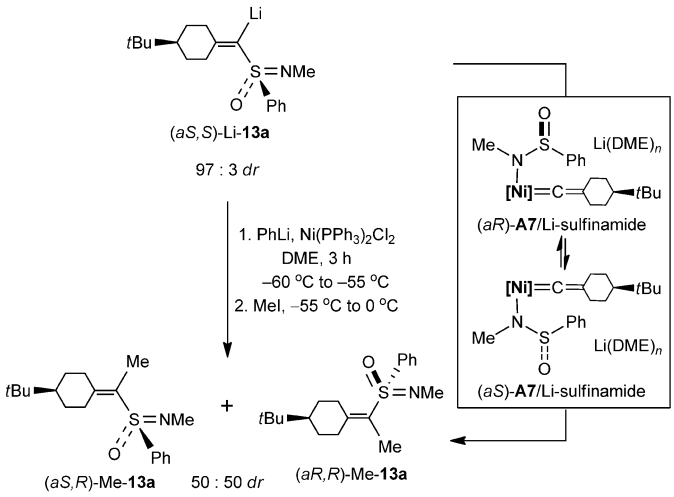


Figure 2. Optimized structures of Ni-complexes **A4** and **A5** (bond lengths are represented in Å, and hydrogen atoms have been omitted for clarity).

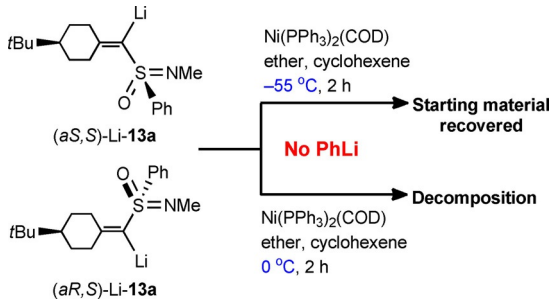
bene complexes stabilized by alkali metals.[41] Taken together, this structural pattern demonstrates why the three-center interaction of Ni–Li–C1 cannot be easily overcome to afford the free Ni^0-vinylidene intermediate **A7**. Moreover, the two Li^+ interact covalently with C1 as shown in **A5** with 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 Ni^{II}. 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, alkenyllithium (*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 Ni^{II}-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 $Ni(PPh_3)_2Cl_2$ (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 alkenyl 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 alkenyllithium (*aR*)-Li-**14a** (see below, Scheme 6). Formation of the mixture of the diastereomeric methylated alkenyl sulfoximines in 50:50 *dr* indicates that the Ni^0-vinylidene intermediate **A7** and two different isomers of **A7**/Li-sulfinamide (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 Ni^{II} 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 Ni^{II} intermediate **A5** from **A7** or (*aR*)- and (*aS*)-**A7**/Li-sulfinamide intermediates, which might be generated because of the different reaction conditions with DME as solvent.



Scheme 6. Attempted Ni-catalyzed ACCR of lithioalkenyl sulfoximine (*aS*,*S*)-Li-**13a** with PhLi in DME using PPh_3 as ligand.

The anionic Ni^0-ate mediated catalytic pathway was established with $Ni(PPh_3)Cl_2$ as precatalyst. However, we also obtained experimental results when employing $Ni(PPh_3)_2(COD)$ as the precatalyst that were inconsistent with the aforementioned mechanism. Scheme 7 represents a control experiment with



Scheme 7. Control experiment of (*aS*,*S*)-Li-**13a** with $Ni(PPh_3)_2(COD)$ in the absence of PhLi.

(*aS*,*S*)-Li-**13a** (96:4 *dr*) and stoichiometric amounts of $Ni(PPh_3)_2(COD)$[36] 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,[43] indicating that the reaction pathway of **A2**→**A3**→**A3-TS** does not occur when COD is present as 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 $Ni(PPh_3)_2Cl_2$ system in which the dianionic Ni^0 intermediate **A10** is located at high energy of 25.1 kcal mol^{-1}, whereas in the $Ni(COD)_2$ system the dianionic Ni^0 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 Ni^0 complexes has been described when COD was employed as innocent ligand.[5] In these complexes, which display an intriguing catalytic activity, the highly reduced Ni^0 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 $Ni(PPh_3)_2Cl_2$, we decided to further examine the elusive

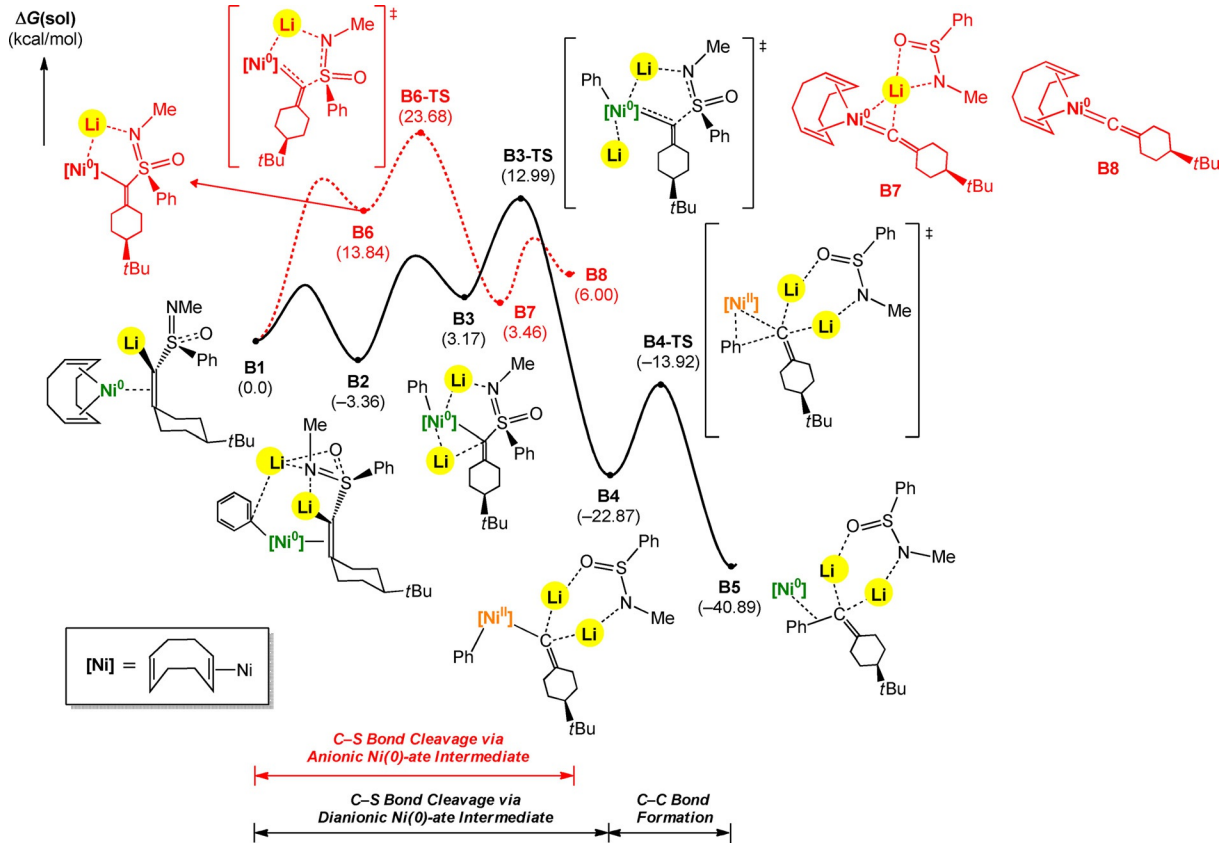


Figure 3. Free-energy profile for the stereoselective ACCR via dianionic Ni^0-ate intermediate. Black and red traces represent the reaction pathway via dianionic Ni^0-ate and anionic Ni^0-ate intermediates.

mechanism of the ACCR via dianionic Ni^0-ate intermediates with theoretical methods.

DFT calculations of the ACCR of (*aS*,*S*)-Li-**13a** with PhLi in the presence of $Ni(COD)_2$ represented in Figure 3 began with the neutral Ni^0 intermediate **B1** that coordinates the lithioalkenyl sulfoximine. 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^{-1}. This barrier suggests that the decomposition of the lithioalkenyl sulfoximine via Ni^0-vinylidenes **B7** 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^0-ate 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^0-ate complex **B3** at 1.5 kcal mol^{-1}.

Optimized structures of **B2** and **B3** are shown in Figure 4. Although the anionic Ni^0-ate complex could be stabilized by the C=C bond of the lithioalkenyl sulfoximine for both ligands PMe_3 (**A1**) and COD (**B2**), only the dianionic Ni^0-ate 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^0-ate **A10** is associated with a high barrier. Electron-rich $[Ni^0]^{-1}$ in **B2** engages in π-backdonation to the C=C bond of the lithioalkenyl sulfoximine that displays

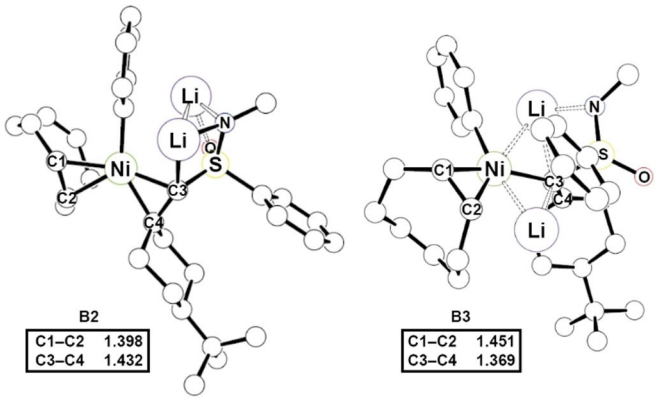


Figure 4. Optimized structures of Ni-complexes **B2** and **B3** (bond lengths are represented in Å, and hydrogen atoms have been omitted for clarity).

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^0-ate complex **B3**, the interaction between the Ni atom and C=C bond of the lithioalkenyl sulfoximine is resolved and instead the Ni–C3 σ-bond is formed. The other olefinic ligand, COD, accepts an electron from the highly reduced $[Ni^0]^{2-}$ metal center, which is indicated by the elongated bond length of

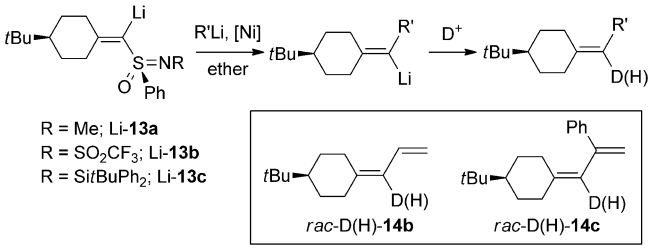
C1–C2 (1.45 Å) in **B3**, whereas there is no more proper electron acceptor in the PMe_3 coordinated system (**A10**). The proposed formation of the Ni^0-ate complexes **B2** and **B3** is supported by the synthesis of lithium and dilithium Ni^0-ate complexes from Ni^0 complexes including $Ni(COD)_2$ and organolithiums.[44] Furthermore, the highly electron-rich $[Ni^0]^{2-}$ metal center of **B3** can easily push some electron density to the alkenyl 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 Ni^{II} complex **B4** is mediated by two Li^+ in an exogenic process. Finally, reductive elimination of **B4** via transition state **B4-TS** affords alkenyllithium (*aR*)-Li-**14a**, as observed when $Ni(PPh_3)_2Cl_2$ was used as precatalyst.

To gain information about the observed lack of a competing ACCR of the lithioalkenyl sulfoximine with alkenyllithium (*aR*)-Li-**14a**, ACCRs of (*aS*,*S*)-Li-**13a** (97:3 *dr*) with vinyllithium and α-phenyl vinyllithium as model compounds for (*aR*)-Li-**14a** were performed (Table 2, entries 1–4). ACCR of (*aS*,*S*)-Li-**13a** (96:4 *dr*) with vinyllithium in the presence of $Ni(PPh_3)_2Cl_2$ (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 CF_3CO_2D diene *rac*-D-**14b** (83% D) in 86% yield (entry 3). A similar ACCR of (*aS*,*S*)-Li-**13a** (96:4 *dr*) with α-phenyl vinyllithium in the presence of $Ni(PPh_3)_2Cl_2$ (5 mol%) at 0 °C in diethyl ether for 1.5 h followed by treatment of the reaction mixture with CF_3CO_2D afforded diene *rac*-D-**14c** (42% D) in only 30% yield (entry 4). The rate of the ACCR of (*aS*,*S*)-Li-**13a** with the sp^2-organolithiums strongly decreases in the order PhLi ≫ vinyllithium > α-phenyl vinyllithium. These data suggest that the ACCR of (*aS*,*S*)-Li-**13a** with alkenyllithium (*aR*)-Li-**14a** should be even slower than with α-phenyl vinyllithium. 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 from a vinyl–allyl isomerization of (*aS*,*S*)-Li-**13a**, by the dienyllithium under formation of the corresponding dilithioallyl sulfoximine and the protonated diene (see the Supporting Information for details). In contrast, attempts to achieve a Ni-catalyzed ACCR of (*aS*,*S*)-Li-**13a** with alkyllithiums, including MeLi, *n*BuLi, and $LiCH_2SiMe_3$, 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 (*aS*,*S*)-Li-**13a**, the (*N*-sulfonyl)sulfoximines (*aR*,*S*)-Li-**13b** and (*aS*,*S*)-Li-**13b** (50:50 *dr*), which were synthesized through metalation of alkenyl sulfoximine (*aR*,*S*)-H-**13b**[23] with *n*BuLi, did not undergo an ACCR with PhLi at −75 °C in diethyl ether for 1 h in the presence of $Ni(PPh_3)_2Cl_2$ (5 mol%) (Table 2, entry 5). Quenching the reaction mixture with CF_3CO_2D led to a recovery of the deuterated sulfoximines (*aR*,*S*)-D-**13b** and (*aS*,*S*)-D-**13b** (95% D) in 50:50 *dr*. Under these conditions, already 30% of the (*N*-methyl)sulfoximine (*aS*,*S*)-Li-**13a** had been converted to alkenyllithium (*aR*,*S*)-Li-**14a** (see above). Correspondingly, no ACCR was observed between the (*N*-silyl)sulfoximine (*aR*,*S*)-Li-**13c**, which was obtained from alkenyl sulfoximine (*aR*,*S*)-H-**13c** on reaction with MeLi, and PhLi in the presence of $Ni(PPh_3)_2Cl_2$ (5 mol%) at −75 °C (entry 6). After the temperature of the reaction mixture was raised to −5 °C and the mixture quenched with CF_3CO_2D, alkene *rac*-D-**14a** (77% D) was isolated in only 12% yield. Alkenyl sulfoximines (*aR*,*S*)-D-**13c** and (*aS*,*S*)-D-**13c** (98% D) were recovered in 73% yield and 50:50 *dr* (entry 7).

So far the phenyl-substituted alkenyllithiums (*aS*,*S*)-Li-**14a** and (*aR*,*S*)-Li-**14a** were trapped by protonation and/or deuteriation. It was of interest to see, however, whether the alkenyl-

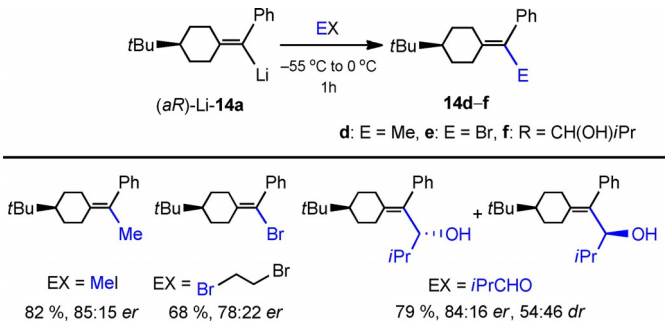
Table 2. Ni-catalyzed ACCR based on different lithioalkenyl sulfoximines and alkenyllithiums.



Entry	Alkenyl sulfoximine	R'Li	*T* [°C]	*t* [h]	Yield [%]	D [%]	*er*
1	(*aS*,*S*)-Li-**13a**	CH_2=CHLi	−30	3.5	39[a]	41	50:50
2	(*aS*,*S*)-Li-**13a**	CH_2=CHLi	−20	3.5	68[b]	79	50:50
3	(*aS*,*S*)-Li-**13a**	CH_2=CHLi	0	1	86	83	50:50
4	(*aS*,*S*)-Li-**13a**	CH_2=C(Ph)Li	0	1.5	30[c]	42	50:50
5	(*aR*,*S*)-Li-**13b** (*aS*,*S*)-Li-**13b**	PhLi	−75	1	–	–	–
6	(*aS*,*S*)-Li-**13c**	PhLi	−75	1	–	–	–
7	(*aR*,*S*)-Li-**13c** (*aS*,*S*)-Li-**13c**	PhLi	−5	5	12	77	50:50

[a] A mixture of (*aS*,*S*)-D-**13a** and (*aR*,*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 (*aS*,*S*)-D-**13a** and (*aR*,*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.

First, the ACCR of (*aS*,*S*)-Li-**13a** (97:3 *dr*) with PhLi was run in the presence of $Ni(PPh_3)_2Cl_2$ or $Ni(PPh_3)_2(COD)$[36] (5 mol%). Treatment of thus obtained alkenyllithiums (*aR*)-Li-**14a** and (*aS*)-Li-**14a** (85:15 *er*) with MeI 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 $Pr(tfc)_3$.[32] The absolute configuration of (*aR*)-**14d** was assigned based on its chirotropic 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 bromoalkenes (*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 $Pr(tfc)_3$.[32] The absolute configuration of (*aR*)-**14e** was assigned based on its chiroptical 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 in 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 $Pr(tfc)_3$.[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 precatalyst 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-vinylidene 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 ethers[8c,d,22] and Cu mediated ACCR of litthioalkenyl sulfoximines,[13] which has been postulated as key step a 1,2-metalate shift[8] of higher-order cuprates under displacement of the nucleofuge at the sp^2 C atom.

Acknowledgements

Financial support of this research by the Deutsche Forschungsgemeinschaft, VW Foundation and Fonds der Chemischen Industrie is gratefully acknowledged. The analytic and spectroscopic laboratories of the institutes of organic chemistry of Technische Universität Darmstadt, Albert-Ludwigs Universität Freiburg and RWTH Aachen University are gratefully acknowledged for support of this work. We thank Cornelia Vermeeren for GC analysis and Professors Dr. Helmut Vorbrüggen and Dr. Werner Skuballa for generous support and helpful discussions. This research was supported by the Institute for Basic Science (IBS-R010-A1) in South Korea.

Conflict of interest

The authors declare no conflict of interest.

Keywords: carbenoids · diastereoselectivity · nickel · nickel–vinylidene · organolithium

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Manuscript received: October 25, 2019
Accepted manuscript online: October 30, 2019
Version of record online: February 20, 2020

