

New Frontiers in Alkali-Metal Nickelates

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[§]SCS-DSM award for best poster in Inorganic Chemistry

Abstract: Recent advances in heterobimetallic chemistry have revealed the potential for mixed-metal systems to facilitate reactions that are unattainable with their single-metal components. This perspective explores the pairing of nickel(0) complexes with organo-alkali-metal reagents, which yield highly reactive alkali-metal nickelates. These previously underexplored systems have re-emerged as a promising area of research, with recent studies uncovering their unique bonding and structural motifs. Furthermore, the discovery of nickelates as potential intermediates in cross-coupling reactions has provided the foundation for the development and mechanistic understanding of stoichiometric and catalytic transformations.

Keywords: Alkali-Metals · Catalysis · Cross-Coupling · Heterobimetallics · Nickel



Andryj M. Borys received his BSc (2015) and PhD (2018) from the University of Kent (UK), the latter supervised by Dr Ewan Clark. He was a postdoctoral researcher with Dr Michael Cowley at the University of Edinburgh (UK), then with Profs. Thomas Baumgartner and Chris Caputo at York University (Canada) before joining the group of Prof. Eva Hevia at Universität Bern (Switzerland) in 2020. His research explores

the synthesis and catalytic applications of alkali-metal nickelates. Andryj is also the creator of the Schlenk Line Survival Guide.

1. The Origins of Nickelate Chemistry

The chemistry of low-valent organonickel chemistry was serendipitously discovered during the 1960s when Wilke and co-workers investigated the so-called ‘nickel effect’ in the development of Ziegler catalysts.^[11,21] These studies gave birth to ubiquitous Ni(0)-olefin complexes such as Ni(C₂H₄)₃,^[3] Ni(*ttt*-CDT)^[4] (where *ttt*-CDT = *trans,trans,trans*-1,5,9-cyclododecatriene) and Ni(COD)₂^[5] (where COD = 1,5-cyclooctadiene), with the latter recognised as an indispensable Ni(0) precursor with widespread applications across organometallic chemistry.^[6] The reactivity of these Lewis acidic Ni(0)-olefin complexes towards polar organometallics such as organolithium or organoaluminium compounds was documented during the 1970s and 80s, giving rise to highly sensitive low-valent nickelates (Fig. 1).^[17–15] These species had limited synthetic utility at the time, but the ability for these complexes to activate N₂ hint at the latent reactivity and structural diversity of these heterobimetallic systems.^[16–18]

Although these early studies into low-valent nickelates uncovered a wealth of unique chemistry, they remained largely unexplored for decades and were overshadowed by parallel developments in nickel catalysis (*i.e.* Kumada-Corriu cross-coupling reactions).^[19–21] Recent discoveries, however, have revealed that these overlooked species may actually be crucial intermediates in a variety of Ni-catalysed reactions involving polar organometallics,^[22–27] sparking a renaissance of both experimental and theoretical interest into low-valent nickelates.

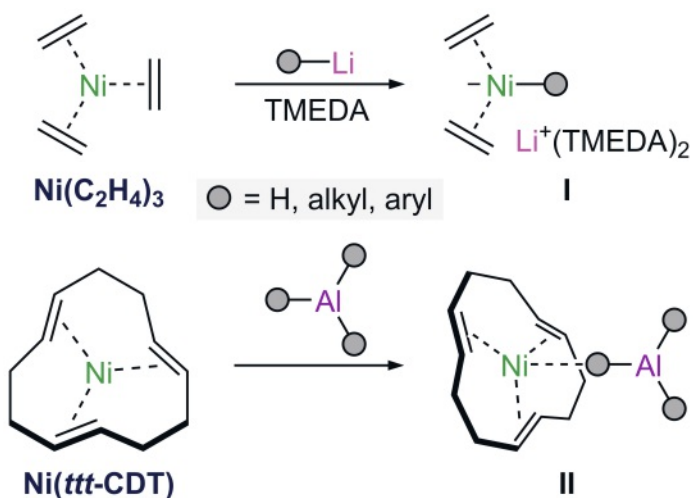


Fig. 1. Examples of low-valent nickelates derived from Ni(0)-olefin complexes and polar organometallics.

2. Nickelate Intermediates in Cross-Coupling

Nickel catalysis has the unique ability to functionalise substrates that are typically out of scope for palladium catalysis, with the cross-coupling of phenol-derived electrophiles being a prime example.^[22,28–30] First discovered by Wenkert in 1979,^[31] this process allows the cross-coupling of inert aryl ethers with Grignard or organolithium reagents under mild conditions, often without the need for supporting ligands or additives.^[32,33]

Theoretical studies by Wang and Uchiyama have proposed that these transformations occur *via* an alternative anionic mechanism which involve nickelate intermediates derived from Ni(0) complexes combined with the organometallic nucleophile;^[23,24] this contrasts with traditional Ni(0)/Ni(II) mechanisms that invoke direct oxidative addition of the C–OMe bond to Ni(0).^[34,35] While low-valent nickelates were reported in the 1970s and 80s, they were almost exclusively derived from Ni(C₂H₄)₃ or Ni(*ttt*-CDT) (see Fig. 1),^[8] which are not representative of catalytic reactions using commonly employed Ni(0) complexes. In contrast, Ni(COD)₂ is widely used as a pre-catalyst or catalyst

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itself,^[6] making the isolation of nickelates derived from Ni(COD)₂ and polar organometallics crucial for understanding and assessing potential catalytic intermediates.

Using the cross-coupling between 2-methoxynaphthalene (**1**) and PhLi catalysed by Ni(COD)₂ as the model reaction^[32] (Fig. 2), we systematically evaluated the co-complexation chemistry of Ni(COD)₂ with PhLi.^[36] Remarkably, a diverse family of lithium nickelates with varying lithium to nickel ratios (**3–5**) could be isolated or structurally characterised depending on the stoichiometry and reaction conditions. Interestingly, the simplest 1:1 species [**3**, Li(solv)_nPhNiCOD] only exists as a minor species in concentrated THF solutions and readily dissociates to the favoured 2:1 species [**4**, Li₂(solv)_nPh₂NiCOD], which could be isolated in high yields and authenticated by X-ray crystallography with either terminal or bridging COD ligands.^[36] This contrasts with the 1:1 lithium nickelate derived from Ni(C₂H₄)₃, PhLi and TMEDA reported by Cornella,^[25] demonstrating how the olefin ligand can influence the constitution of low-valent nickelates. Stoichiometric, catalytic and kinetic studies demonstrate that the isolated lithium nickelates facilitate the cross-coupling of 2-methoxynaphthalene (**1**) to give 2-phenylnaphthalene (**2**), supporting their involvement as on-cycle reaction intermediates.^[35,36] Most notably, the choice of solvent or presence of donor additives was found to play a key role in the success of the reaction, suggesting that the two metals work cooperatively to facilitate the transformation. Thus, the aryl ether substrate can coordinate to the Lewis acid lithium cation which primes it for C–OMe bond cleavage by the nucleophilic nickel centre. Structural assessment of the lithium nickelates reveals that the phenyl-carbanion acts as a strong σ -donating ligand, akin to classically employed phosphine or *N*-heterocyclic carbene ligands,^[37] and demonstrates how these challenging transformations can operate under mild conditions without external ligands.

3. Unique Bonding and Structural Motifs in Nickelate Chemistry

3.1 Unmasking the True Constitution of the Lithium-rich Nickelate, 'Li₃NiPh₃(solv)₃'

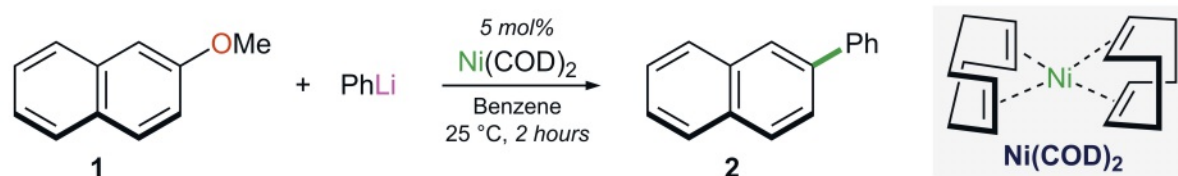
The renewed interest into low-valent nickelates has prompted a re-evaluation of previously documented systems to gain more fundamental insights into the structure and bonding present in these

unique heterobimetallic complexes. In 1979, Taube reported that the treatment of Ni(COD)₂ with excess PhLi under reflux conditions affords the homoleptic tri-lithium nickelate 'Li₃NiPh₃(THF)₃' (Fig. 3).^[38] This species was proposed to adopt a planar geometry based on NMR spectroscopy, but the lack of a solid-state structure raised doubts on its true constitution. By continuing to assess the co-complexation of Ni(COD)₂ with PhLi, our group in collaboration with the group of Jesús Campos at IIQ Sevilla instead found that excess PhLi results in the formation of Li₆(Et₂O)₄Ph₆Ni₂(μ_2 - η^2 : η^2 -C₆H₄) (**6**).^[39] This compound displays matching NMR spectroscopic features to the proposed 'Li₃NiPh₃(THF)₃' species,^[38] indicating that it had been misassigned. X-ray crystallographic analysis of **6** reveals a complex octanuclear cluster which contains a benzyne-type ligand bridging between two Ni centres.^[39] Interestingly, this compound displays similar structural features to the side-on N₂ alkali-metal nickelate complexes obtained by treating Ni(*ttt*-CDT) with excess PhLi or PhNa under an N₂ atmosphere.^[16–18]

The C–C bond length in the coordinated C₆H₄ moiety measures 1.449(6) Å, which is considerably longer than other Ni-aryne complexes.^[40,41] Theoretical bonding analysis reveals extreme back-bonding from the electron-rich Ni-centres with a stabilisation energy of 474.1 kcal mol⁻¹ resulting in a C–C bond order of 1.12. Compound **6** is therefore best described as a Ni(I) complex containing a formally reduced [C₆H₄]²⁻ ligand.^[39] The formation of **6** suggests that the homoleptic tri-lithium nickelate 'Li₃NiPh₃(solv)₃'^[38] is too electron-rich and reactive to form a stable compound, leading to intramolecular C–H activation of a phenyl substituent to form the π -accepting benzyne-type ligand. Sodium nickelates could also be obtained by treating Ni(COD)₂ with two or three equivalents of PhNa, but the competing deprotonation of COD with PhNa meant that the isolation of a sodium analogue of **6** was not possible.^[39]

3.2 Hexagonal vs. Trigonal Planar Tri-Lithium Nickelates

The requirement for π -accepting ligands to stabilise low-valent nickelates indicates that the formation of homoleptic species such as 'Li₃NiPh₃(solv)₃' is not possible when employing electron-rich alkyl or aryl organometallics.^[39] By switching to lithium aryl acetylides, which possess a nucleophilic *sp*-carbanion whilst also serving as a π -acceptor, we could readily access homoleptic tri-lithium nickelates [**7**, Li₃(TMEDA)₃Ni(C \equiv C–Ph)₃] in high yields (Fig. 4).^[42]



Characterised lithium nickelates

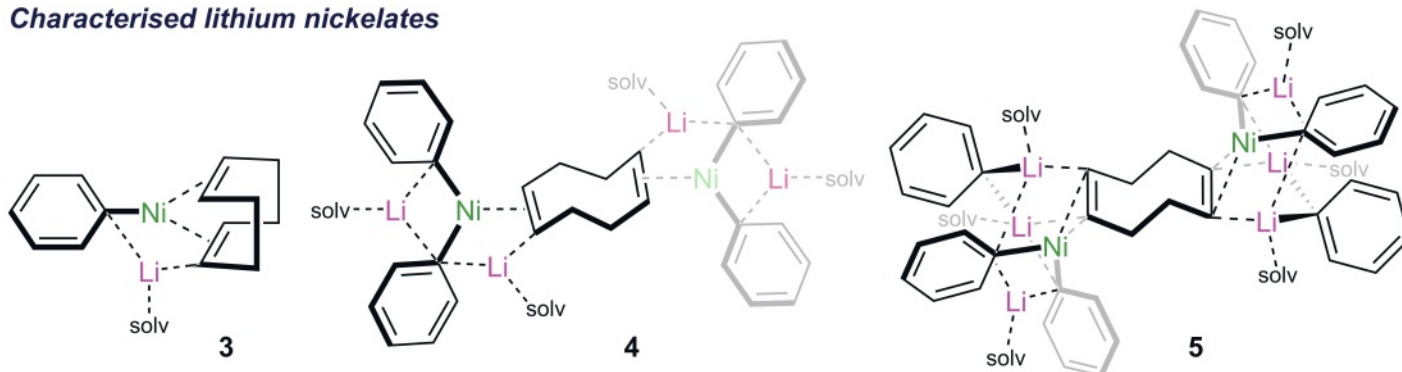


Fig. 2. Lithium nickelates (**3–5**) derived from Ni(COD)₂ and PhLi which are potential intermediates in the Ni(COD)₂-catalysed cross-coupling of 2-methoxynaphthalene (**1**).^[36]

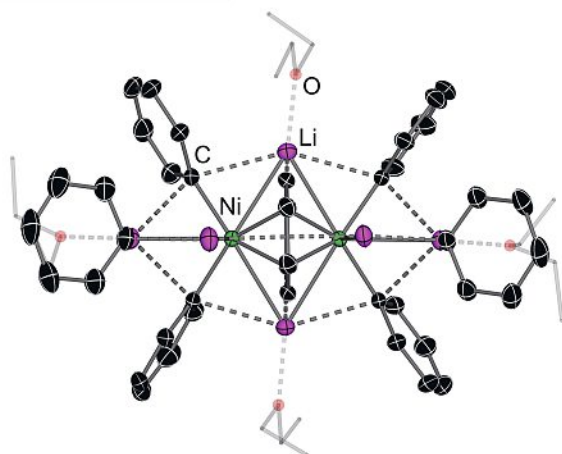
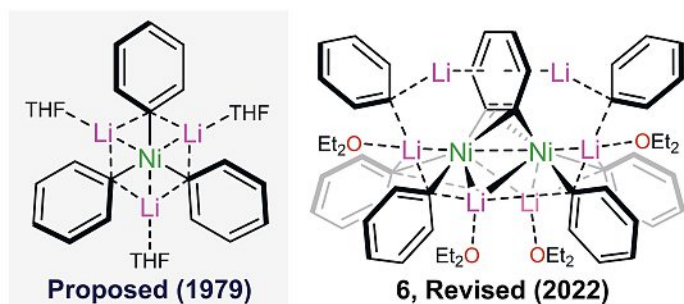
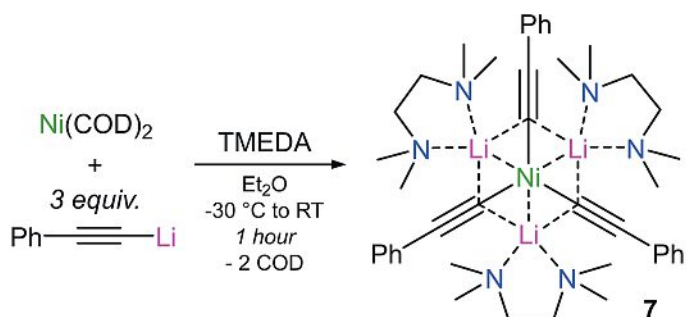


Fig. 3. Taube's proposed homoleptic tri-lithium nickelate ' $\text{Li}_3\text{NiPh}_3(\text{THF})_3$ '^[38] and the revised structure, **6**.^[39]

The solid-state structure of **7** reveals an apparent hexagonal planar geometry around Ni, with Ni...Li distances within the sum of the covalent radii. Since geometrical proximity is not necessarily an indicator of a bonding interaction, however, complementary bonding analysis^[43] was performed to evaluate the structure and bonding. Assessment of the non-covalent interactions (NCI) reveals that the forces along the Ni...Li axes are actually repulsive in nature, indicating there is no bonding interaction, as further supported by QTAIM analysis.^[42] Surprisingly, however, the NCI plot also shows green areas of weakly attractive interactions between the TMEDA donor ligand and the C=C bond of the acetylide substituents. These correspond to London dispersion (van der Waals) interactions,^[44,45] and whilst weak in nature, can contribute to significant stabilisation when summed up over an entire molecule. Experimentally, the bidentate donor ligand TMEDA was crucial to facilitate the isolation of **7**, characterising this compound as a dispersion-stabilised molecule.^[42] Hence despite the close proximity of Li and Ni in these compounds, they are best described as trigonal planar homoleptic tri-lithium nickelates. When treating $\text{Ni}(\text{COD})_2$ with more electron-rich aliphatic lithium acetylides such as $\text{Me}_3\text{Si}-\text{C}\equiv\text{C}-\text{Li}$, a dinickelate cluster (similar to **6**) in which an acetylide coordinates side-on between two Ni centres was isolated, illustrating the fine balance between σ -donating and π -accepting properties of the organolithium reagent employed.^[42] Compound **7** reacts stoichiometrically with iodobenzene to give the C-C coupled product diphenylacetylene which coordinates side-on between two Ni centres akin to the benzyne-type ligand in **6**.^[39]

3.3 Diphenylacetylene Stabilised Alkali-Metal Nickelates

The isolation of compound **6** and related dinickelate clusters containing bridging side-on acetylide or acetylene ligands^[39,42] prompted a deeper study into these heterobimetallic systems containing triply-bonded π -accepting ligands. By combining $\text{Ni}(\text{COD})_2$, diphenylacetylene and alkali-metal aryl species in a 2:1:4 ratio (Fig. 5), we could isolate a series of dinickelate



NCI Plot

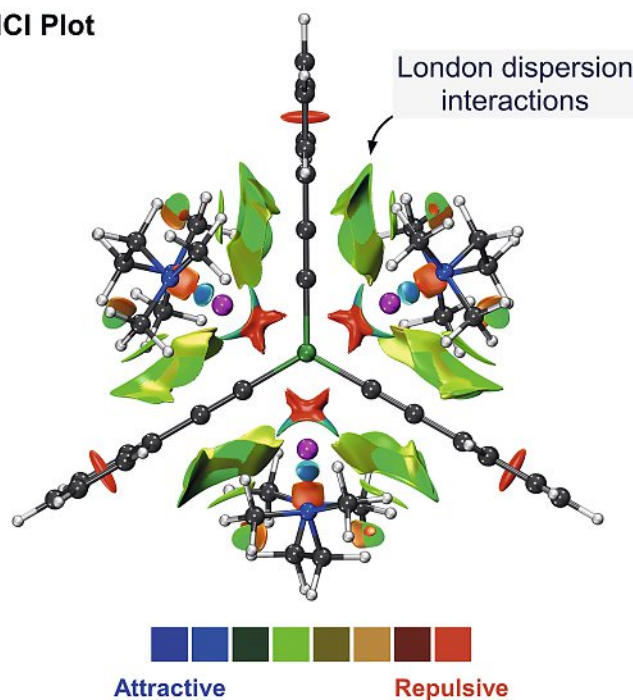


Fig. 4. Synthesis and NCI analysis of homoleptic tri-lithium nickelate (**7**).^[42]

complexes [**8**, $\text{Li}_4(\text{solvent})_n(\text{Ar})_4\text{Ni}_2\{\mu_2-\eta^2-\eta^2-\text{Ph}-\text{C}\equiv\text{C}-\text{Ph}\}$].^[46] This versatile methodology was compatible with PhNa to give the analogous sodium nickelate, whilst alkali-metal exchange using KO^tBu granted access to the potassium congener, to provide the first homologous series of alkali-metal nickelates. When employing sterically demanding or structurally constrained aryl-lithiums, mononickelate complexes [**9**, $\text{Li}_2(\text{solvent})_n(\text{Ar})_2\text{Ni}\{\eta^2-\text{Ph}-\text{C}\equiv\text{C}-\text{Ph}\}$] were instead obtained. Complexes **8** and **9** provide a rich platform to evaluate the unique structural and spectroscopic features of alkali-metal nickelates. In addition, compounds **8** and **9** are competent catalysts for the [2+2+2] cyclotrimerisation of diphenylacetylene to hexaphenylbenzene (Fig. 5), with mononickelate complexes bearing electron-rich aryl-substituents displaying the best catalytic performance.^[46]

4. Outlook

New investigations of heterobimetallic complexes derived from Ni(0) sources and alkali-metal organometallics have unlocked a wealth of unique and diverse structural motifs, intriguing bonding scenarios, and catalytic potential. Through a combination of theoretical and experimental studies, evidence supporting the crucial role of nickelate intermediates in catalytic cross-coupling reactions have been uncovered. In particular, these findings demonstrate how the synergistic cooperation between the two metals facilitates challenging transformations under mild conditions. It is hoped that this perspective serves as a catalyst for the continued innovation and advancement in this evolving field of research.

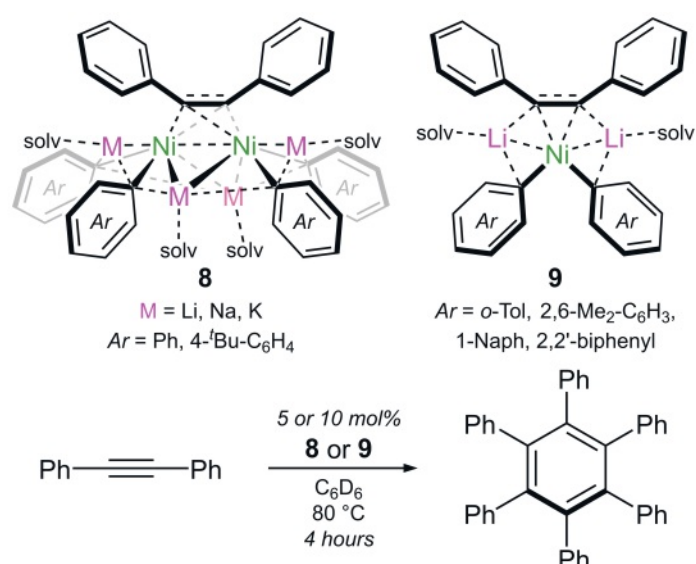


Fig. 5. Synthesis and catalytic applications of diphenylacetylene stabilised alkali-metal dinickelate (**8**) and mononickelate (**9**) complexes.^[46]

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