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Assessing Coordination of Organic π-Acceptors to Alkali-Metal Nickelates

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Abstract: Nickel olefin complexes have served as ubiquitous precursors in nickel chemistry ever since their discovery. One class of compounds derived from these precursors is low valent nickelate complexes. While their role as key intermediates in challenging cross-coupling reactions has recently been confirmed, knowledge regarding the coordination preferences of these complexes, in particular when extended to π-systems, is still very limited. Herein we present a summary of our most important findings from the investigation of the coordination of a series of organic π-acceptors to low valent alkali-metal nickelate complexes. This includes the coordination of polyaromatic molecules such as anthracene or coronene. Extending these studies to biphenylene has uncovered the ability of these heterobimetallic complexes to mediate C–C bond oxidative addition processes, where the nature of the alkali-metal plays an important role in influencing the rate of these activations.

Keywords: Alkali-metal effects · C-C Bond cleavage · Nickelates · π-Acceptor ligands

Luca Vedani received his BSc (2020) and his MSc in Chemistry and Molecular Sciences (2022) from the University of Bern. During his master's thesis, he worked on developing boron mediated cyclopropanation reactions under the supervision of Prof. Philippe Renaud. He then joined the group of Prof. Eva Hevia as a PhD student where he is currently investigating alkali-metal nickelates and their catalytic applications.

Eva Hevia completed her PhD degree, from the Universidad de Oviedo (Spain) in 2003, under the supervision of the late Victor Riera. In 2006, after a three-year appointment at the University of Strathclyde (UK) as a Marie Curie postdoctoral fellow working with Robert Mulvey, she gained a Lectureship at the same institution. She was then promoted to full Professor in 2013. In 2019, Eva moved to the University of Bern to a Professorship in Inorganic Chemistry. Research in her group focuses on polar organometallic chemistry at the crossroads of inorganic, organic, and green chemistry.

1. Ni(0)-olefin Complexes as Precursor to Low Valent Nickelate Complexes

Nickel sees ever-growing use in synthetic chemistry due to its higher abundance compared to second row transition-metals and the unique reactivity that it can offer.[1] Understanding the coordination chemistry of this metal is therefore important to advance mechanistic understanding and catalyst design. Pioneered by Wilke in the 1960s[2] Ni(0) olefin complexes have become ubiquitous precursors in nickel chemistry. Combination of such Ni(0) precursors with a polar organometallic such as an organolithium or Grignard reagent (R–M in Scheme 1, M = Li, MgX) can enable the transfer of the R group to nickel, giving rise to complexes of the general form [M(solv)$_n$Ni(R)(olefin)], so called nickelates (Scheme 1a).[3] The R group can be viewed as a σ-donating ligand whereas the olefin acts as a π-acceptor, providing stabilization to the low-valent Ni centre through the availability of its antibonding π* orbitals. The secondary metal (often alkali-metal M) balances the charge, and its Lewis acidic character plays an important role in the activation of substrates in catalytic processes. Switching on bimetallic cooperativity between the low-valent Ni centre and the alkali-metal, these heterobimetallic complexes can promote the activation of challenging organic electrophiles such as aromatic ethers or fluorides.[4–6] This reactivity is exemplified in Scheme 1 with the reactivity of Ni(COD)$_2$ (COD = 1,5-cyclooctadiene) in the presence of PhLi and 2-methoxynaphthalene. The C–O bond is cleaved followed by the formation of 2-phenylnaphthalene. Two key intermediates of this reaction are depicted in Scheme 1c. (THF)$_4$Li$_2$(COD)Ph$_2$ (**I**) is formed upon treatment of Ni(COD)$_2$ with PhLi. This nickelate is then able to cleave the C–O bond.[4] Further mechanistic investigations support that the initial π-coordination of the aromatic ether to the Ni(0) centre (intermediate **II**) is essential in order to facilitate the bimetallic cleavage of the C–O bond.[5]

1.1 *Synthetic Strategy to Access Alkali-metal Nickelates with Organic π-Acceptor Ligands*

Building on these results, we have systematically investigated the influence of the π-acceptor and the alkali-metal on the coordination chemistry of nickelates.[7] As a Ni(0) precursor we chose the 16e-complex Ni(CDT) (CDT = *t,t,t*-1,5,9-cyclododecatriene) due to the high lability of the CDT ligand upon co-complexation. The addition of two equivalents of PhLi to Ni(CDT) at –30 °C leads to the formation of Li$_2$(solv)$_n$Ph$_2$Ni(η^2-CDT) (**1**), a thermally unstable complex which decomposes rapidly above –20 °C. The η^2 coordinated CDT ligand in this complex is highly labile and can be displaced by other π-systems.[8–10] This property can be exploited to access diverse Ni(0) π-ligated systems (Scheme 2a). Polyaromatic hydrocarbons such as anthracene and phenanthrene react with **1**, displacing the CDT ligand leading to the formation of complexes Li$_2$(THF)$_4$Ph$_2$Ni(η^2-anthracene) (**2-Li**) and

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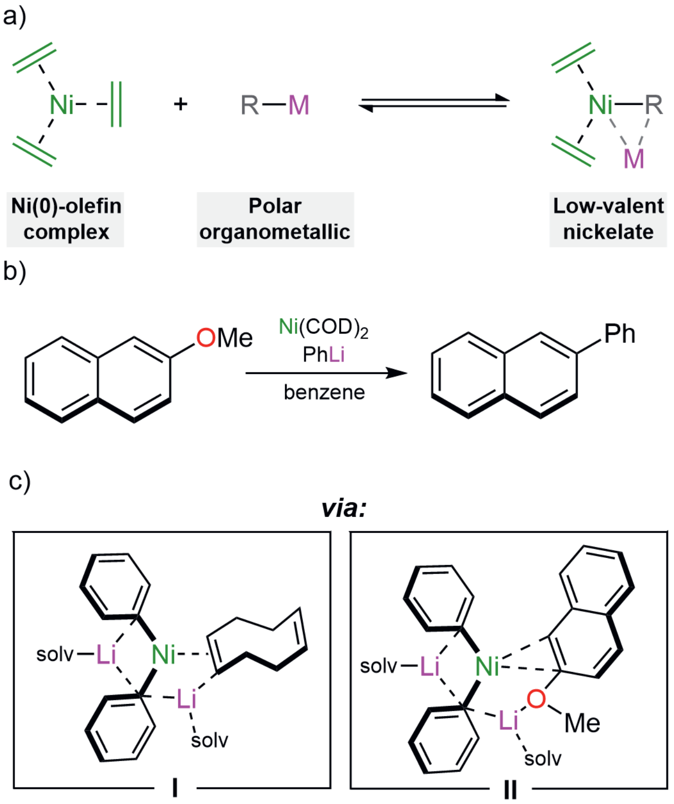
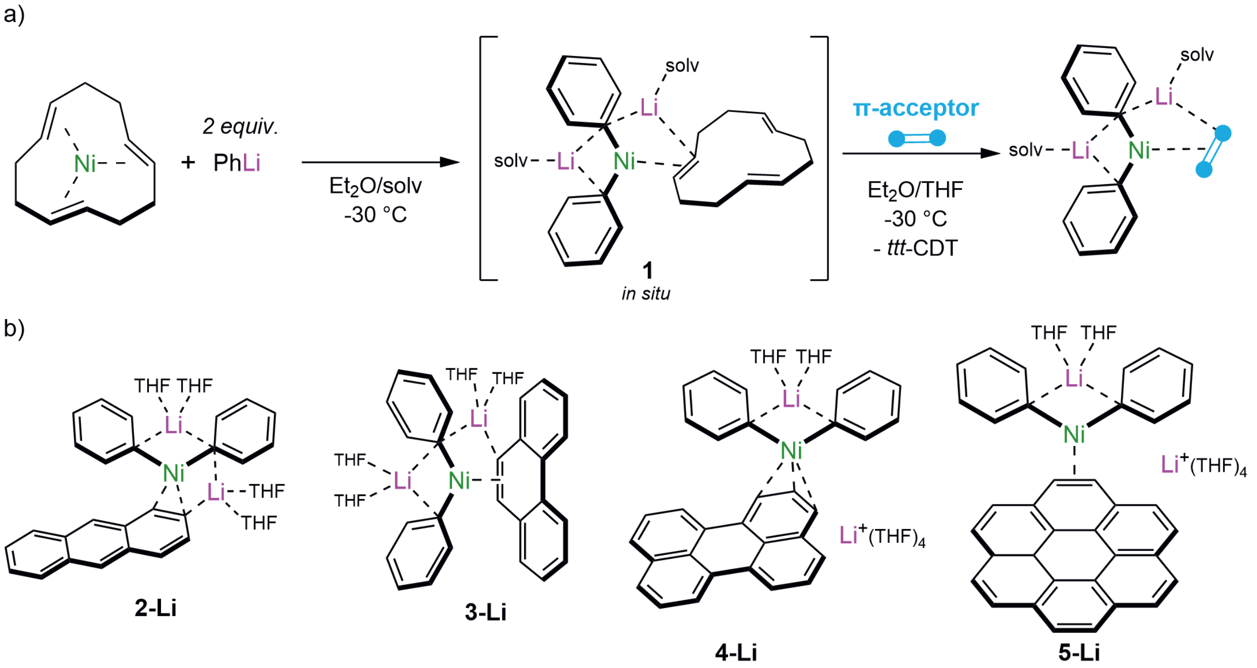


Scheme 1. a) General motif of a nickelate complex. b) Aryl-ether cross-coupling. c) Nickelates identified as intermediates in cross-coupling.

$Li_2(THF)_4Ph_2Ni(\eta^2$-phenanthrene) (**3-Li**) respectively (Scheme 2b). The relevant Na and K analogues can be accessed by salt-metathesis, by preparing the Li complex *in situ* and reacting it with the relevant AMO^{t}Bu (AM = Na, K) (Fig. 1a). Complexes **2-Na-K** and **3-Na-K** could be isolated as crystalline solids and their structures in the solid-state could be established by X-ray crystallographic studies. All three anthracene complexes display monomeric motives in the solid-state, the nickel atom bearing two phenyl ligands is η^2 coordinated to the π-system of anthracene, and the alkali-metals are also in contact. The C=C bond between the Ni-coordinated carbons is strongly elongated (1.462(2) Å Li, 1.449(2) Å Na, 1.397(7) Å K) compared to free anthracene [1.352(3)–1.356(3) Å],[8] as a result of π-backdonation from the electron-rich nickel center, a common feature in Ni(0) olefin complexes. The coordination environment between the alkali-metals differ, with Li being coordinated mainly to the *ipso* carbon of the phenyl groups whereas in **2-Na** and **2-K** one of the alkali-metals displays an additional η^3 interaction towards the central ring of anthracene and the other one is coordinated additionally to the *ortho* carbons of the phenyl rings. This observation is consistent with the increase in cation size and polarizability upon descending group one.[11] In the phenanthrene complexes the nickel atom is η^2 coordinated to the central ring (Fig. 1b), again causing an elongation of the C=C bond. The different alkali-metals cause a change in the solid-state constitution of the complexes. Thus, **3-Li** is monomeric, **3-Na** is dimeric and **3-K** forms a coordination polymer in the solid-state through K···π arene interactions.

The larger π extended systems perylene and coronene were also investigated in the ligand displacement reaction (Scheme 2b). Reacting **1** in an Et_2O/THF mixture at –30 °C leads to an immediate colour change from orange to deep purple. Crystallization resulted in black single crystalline $[Li(THF)_2Ph_2Ni(\eta^3$-perylene)]$[Li(THF)_4]$ (**4-Li**). The solid-state molecular structure displays a pseudo solvent separated motif in which one of the lithium cations is sequestered by four molecules of THF and the other is in contact with the two *ipso* carbons of the phenyl groups. The nickel atom is η^3 coordinated to one of the outer rings of perylene leading to an elongation of the bond between the carbon atoms. A similar behaviour is noted for coronene. From the reaction of **1** with coronene, black crystals of $[Li(THF)_2Ph_2Ni(\eta^2$-coronene)]$[Li(THF)_4]$ (**5-Li**) were isolated and analysed by single crystal X-ray diffraction. Like in **4-Li**, a pseudo solvent separated solid-state structure is noted for **5-Li**, with one lithium cation sequestered by four molecules of THF and the second lithium being coordinated to the two *ipso* carbons. The nickel atom is coordinated to two peripheral carbon atoms resulting in elongation of that peripheral C=C bond. Salt-metathesis using Na/KO^{t}Bu did not allow for the isola-



Scheme 2. a) Synthesis of lithium nickelates containing polyaromatic π-systems. b) Schematic representation of the crystallographically characterized Li-nickelates **2-5-Li**.

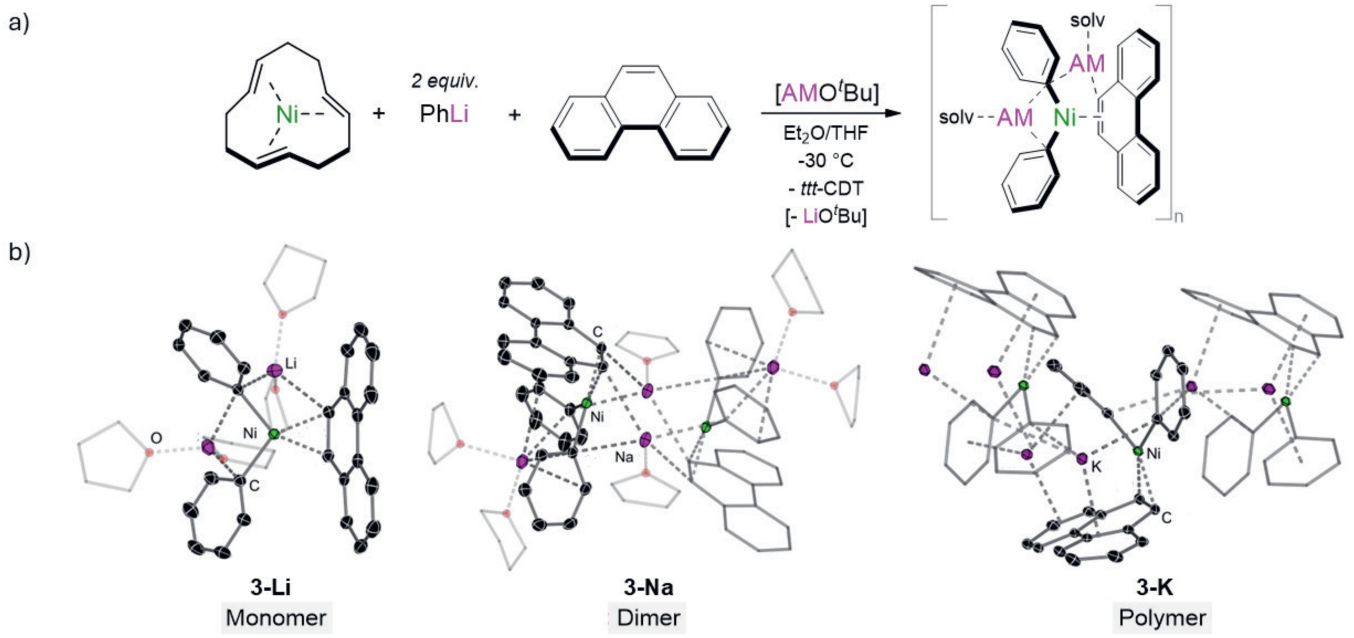


Fig. 1. a) Synthesis of phenanthrene nickelates. b) Solid-state molecular structure of **3-Li**, **3-Na**, and **3-K**. Hydrogen atoms omitted for clarity. Solvents shown as wireframe for clarity.

tion of the other alkali-metal analogues but led to the formation of the perylene radical anion, which could be authenticated by EPR spectroscopy and single crystal X-ray diffraction. It is worthy of note that the potassium coronene nickelate $K_2(DME)_4Ph_2Ni(\eta^2$-coronene) (DME = 1,2-dimethoxyethane) could be isolated without significant formation of the coronene radical anion. This behaviour is reflected in the one electron reduction potential of perylene (–1.98 V)[12] *vs* coronene (–2.36V)[12] and is evidence for the strongly reducing nature of the 2:1 PhAM nickelate complexes, which seems to be influenced by the nature of the alkali-metal.

NMR spectroscopic investigations further confirm the electron-rich nature of the nickel centre. The ^{1}H and ^{13}C chemical shifts corresponding to the sites coordinated to Ni show significant upfield shifts compared to the starting material and the non-coordinated positions. This is consistent with a higher electron density due to partial reduction induced by the back donation from the Ni centre.

2. Extending Coordination Studies to Biphenylene: Applications on C-C Oxidative Bond Cleavage

These studies were extended to biphenylene,[13] a substrate in which its fused ring system offers unique reactivity due to the relatively low bond dissociation energy of the C–C bond of the central ring (65.4 kcal/mol). Furthermore, its central ring does not possess aromaticity.[14] Low valent transition-metal and main group metal complexes can undergo oxidative addition to this C–C bond, resulting in metallacyclopentene complexes.[15] We were therefore curious about the reactivity of our electron- rich nickelates towards biphenylene. Using the approach previously described (Fig. 2a), preparing **1** *in situ* and reacting it with stoichiometric amounts of biphenylene and the Lewis donor DME led to the formation of the coordination adduct [Li(DME)$Ph_2Ni(\eta^4$-biphenylene)][Li(DME)$_3$] (**6-Li**).[14] X-ray crystallographic analysis showed that all C–C bonds in biphenylene remain intact, coordinating in an η^4-fashion to the Ni centre *via* its central four membered ring. This coordination mode introduces a distortion from planarity of the biphenylene ligand. One lithium is sequestered by three DME molecules while the other one is coordinated to the *ipso* carbons of the phenyl groups as previously observed for the lithium nickelates (Fig. 2b). The sodium and potassium analogues were accessed through salt-metathesis from the corresponding *tert*-butoxide (Fig. 2a). Crystallization in the presence of a suitable donor (THF for Na and PMDETA for K) allowed for the isolation of $Na_2(THP)_4Ph_2Ni(\eta^4$-biphenylene) (**6-Na**) (THP = tetrahydropyran) and $K_2(PMDETA)_2Ph_2Ni(\eta^4$-biphenylene) (**6-K**) (PMDETA = N,N,N',N",N"-pentamethyldiethylenetriamine). The Ni atom is η^4-coordinated to the central four membered ring akin to **6-Li**, but unlike in the lithium analogue, both alkali-metals are coordinated in **6-Na** and **6-K**, showing contacts to the *ipso* carbons of the phenyl groups and additional coordination towards the phenyl rings of biphenylene (η^3 for sodium and η^4 for potassium) (Fig. 2b). In the ^{13}C NMR spectra significant shielding of the central carbon atoms of biphenylene are observed in the complexes **6**. These complexes are thermally labile and readily convert to the ring opened products upon warming from –30 °C to room temperature, which can be monitored by ^{1}H-NMR (Figs. 3a and 3b) Interestingly, a pronounced alkali-metal effect was noted concerning the rate of these reactions. While **6-Li** fully reacts within minutes, **6-Na** takes three hours and **6-K** twelve hours (Fig. 3a). This difference in stability might be attributed to the different coordination properties of the alkali-metals and the mechanism involved in this C–C bond cleavage (see section 2.1). The relevant products of these reactions, [Li(DME)Ph_2Ni(2,2-biphenyl)][Li(DME)$_3$] (**7-Li**) (Fig. 3c) and [$Na_2(THP)_3Ph_2$Ni(2,2-biphenyl)]$_2$ (**7-Na**) could be isolated as crystalline products and characterised by single crystal X-ray diffraction. The solid-state molecular structures confirm the formal oxidative addition of the Ni(0) centre to the central C–C bond of biphenylene, resulting in the formation of Ni(II) complexes with a square planar geometry around Ni.

To investigate how the introduction of constraint can influence the coordination chemistry and the reactivity of the biphenylene nickelate, the two equivalents of PhLi were exchanged for one equivalent of 2,2-lithiobiphenyl. Using the previously described approach allowed for the isolation and structural authentication of the relevant coordination adducts, with biphenylene coordinated η^4 to the Ni centre *via* its central ring as described for complexes **6** (see Fig. 4b for $Li_2(THF)_4$(2,2-biphenyl)Ni(η^4-biphenylene) (**8-Li**)).[14] These complexes are significantly more stable in solution but they evolve to the relevant Ni(II) products when heated at 80 °C in THF-d_8 (8 h, 3 days, and 4 days for the Li, Na, and K com-

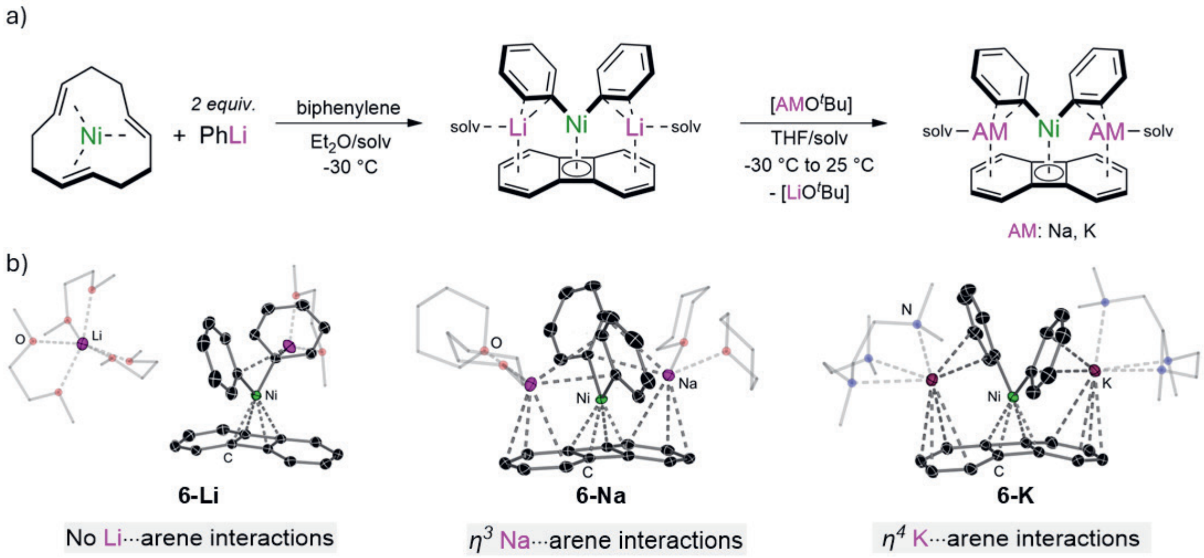


Fig. 2. a) Synthesis of biphenylene nickelates. b) Solid-state molecular structure of **6-Li**, **6-Na**, and **6-K**. Hydrogen atoms omitted for clarity. Solvents shown as wireframe for clarity.

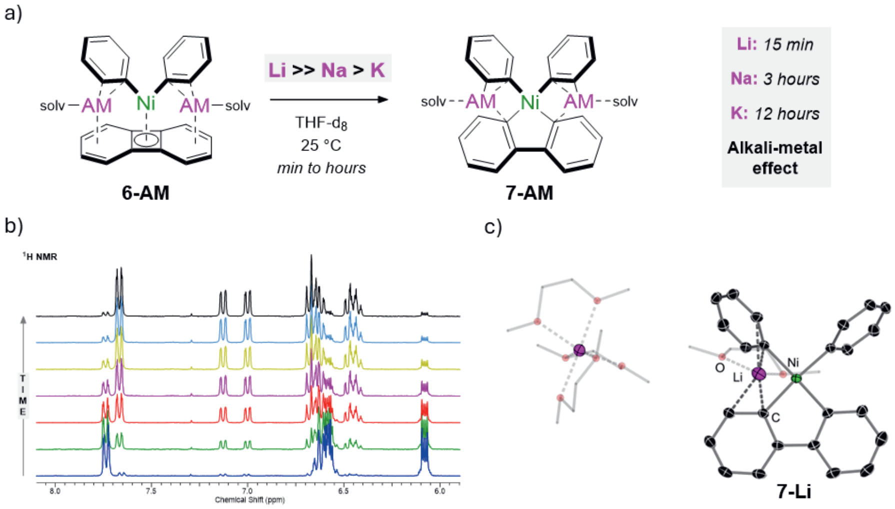


Fig. 3. a) Ring opening of biphenylene nickelates **6**. b) Ring opening of **6-Li** monitored by ^{1}H-NMR in THF-d_8. c) Solid-state molecular structure of **7-Li**. Hydrogen atoms omitted for clarity. Solvents shown as wireframe for clarity.

plexes respectively). In all cases unique spirocyclic alkali-metal nickelates are formed (see Fig. 5b for the lithium nickelate **9-Li**) that are inaccessible by traditional salt-metathesis routes and Ni(II) precursors.

The Ni(II) complexes are stable in solution and do not show signs of reductive elimination even upon prolonged heating. When exposed to dry air however, **7-Li** reacts to give a mixture of biphenyl (62 %) and 2,2-diphenylbiphenyl (49%). The spirocyclic nickelate **9-Li** affords tetraphenylene (94%) as the single product. The formation of biphenylene is not observed in either of the two reactions (Scheme 3).

2.1 *Mechanistic Implications*

To gain further understanding of the coordination chemistry and the reactivity of these unique biphenylene alkali-metal nickelates, quantum chemical calculations were conducted by the Balcells group. Natural bond orbital (NBO) stabilisation energies and 3D non-covalent interaction plots (NCIPLOTs) based on DFT(PBE0/def2SVP) calculations were used to rationalize the different bonding situations in complexes **6-Li**, **6-Na**, and **6-K**.

The interaction between the Ni centre and the biphenylene ligand was studied by NBO analysis and nucleus independent chemical shift (NICS) calculations. The phenyl groups on Ni act as σ-donating ligands, rendering the Ni centre electron-rich. While the central four membered ring of uncoordinated biphenylene is non-aromatic, NICS calculations of the nickelate complex show

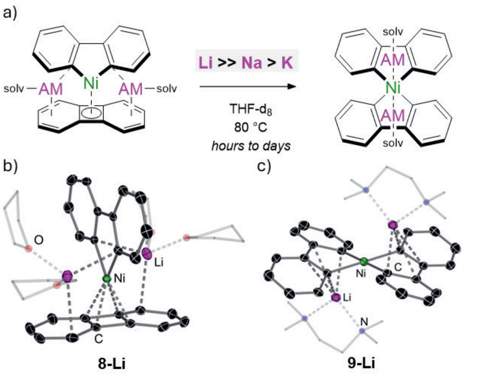
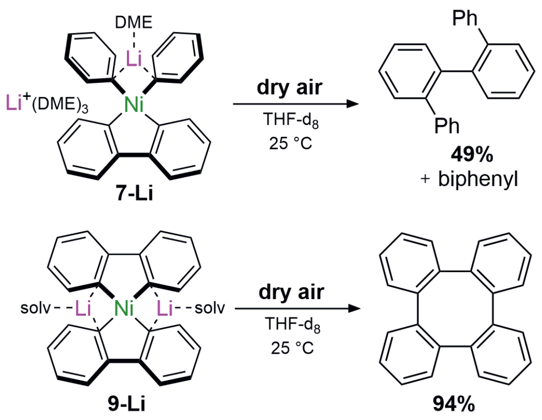


Fig. 4. a) Ring opening of constrained nickelates. b) Solid-state molecular structure of **8-Li** (left) and ring-opened product **9-Li** (right). Hydrogen atoms omitted for clarity. Solvents shown as wireframe for clarity.



Scheme 3. Oxidative coupling of Ni(II) complexes **7-Li** and **9-Li** with dry air.

aromaticity of the central ring. According to Hückel's rule, the central ring should turn aromatic upon two electron reduction, which was confirmed by NICS calculations of the biphenylene dianion. This suggests that the highly electron-rich Ni centre leads to a formal reduction of the biphenylene ligand, rendering the four membered ring aromatic, and thus acting as a π-acceptor.

In all three optimised structures, AM–Ph and AM biphenylene interactions are present. NBO analysis shows a high stabilization energy for Li1–Ph1 interactions, and lower energy for the Li1–Ph2, and η^1 interactions with biphenylene. For K, all AM–Ph (AM = alkali-metal) interactions are similar with an η^4 interaction to biphenylene. Na is in between the two cases. The NBO energies for the AM biphenylene interactions on the other hand do not differ significantly. The NCIPLOTs confirm a larger attractive surface for K compared to Na and Li in decreasing order (Fig. 5). This indicates that the difference in coordination chemistry largely arises from the dispersion forces, not electron delocalisation.

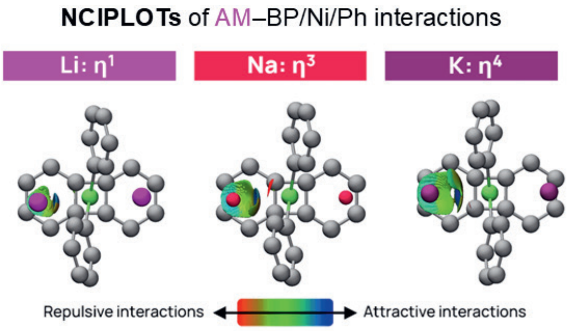


Fig. 5. NCIPLOTs of nickelates **6**.

This greater stabilisation of the heavier alkali-metals manifests itself in the observed reactivity. The pathway for the ring opening, which is proposed based on quantum chemical calculations, involves an initial relocation of one of the alkali-metal cat-ions to the Ni opposing face of the biphenylene. This step is more facile for the small, easily solvated by THF, Li cation compared to Na and K. This causes the decrease in the ring opening reaction rate upon descending group one.

3. Conclusions

In conclusion, this work has uncovered the diverse coordination chemistry of alkali-metal nickelates containing a low valent Ni(0) centre and Ph groups as ligands, towards a variety of organic π-acceptor ligands. The importance of the alkali-metal towards the coordination chemistry in these complexes was demonstrated by synthesising and structurally characterising the homologous series spanning the complexes containing Li, Na, and K as alkali-metal partners. While Li preferentially engages in localised interactions to the *ipso* C of the phenyl groups, Na and K have a greater affinity for electrostatic interactions with the π-systems. In all cases, the coordination of Ni to the π-system is similar and leads to a significant elongation of the C=C bond due to back donation. This is also evident in the case of biphenylene where Ni coordinates η^4 to the central ring and eventually induces the oxidative cleavage of one of the C–C bonds to form a new family of alkali-metal nickelates with Ni in oxidation state (II). With the aid of DFT calculations, it has been shown that the distinct coordination preferences of the alkali-metal have a large impact on the overall stability of the complexes, and on the mediation of the C–C bond activation process. Collectively, these findings shed new light on the heterobimetallic cooperation in nickelate chemistry — an area in which our group is particularly interested, especially in upgrading stoichiometric reactivities to catalytic regimes.

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