

Tuning NaCo(II) Bimetallic Cooperativity to Perform Co–H Exchange / C–F Bond Activation Processes in Polyfluoroarenes

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Abstract: Recent advances in cooperative chemistry have shown the potential of heterobimetallic complexes combining an alkali-metal with an earth abundant divalent transition metal for the functionalisation of synthetically relevant aromatic molecules *via* deprotonative metalation. Pairing sodium with cobalt (II), here we provide an overview of the reactivity of bimetallic [NaCo(HMDS)₂] [HMDS = N(SiMe₃)₂] towards C–H and C–F functionalisation of a wide range of perfluorinated molecules. These studies also uncover the enormous potential of this heterobimetallic base to perform Co–H exchanges with excellent selectivity and exceptional stoichiometric control as well as shedding light on the key role played by the alkali-metal.

Keywords: Alkali metals · Amides · Ate complexes · Cobalt · Cooperativity



Dr. Alessandra Logallo was born in Matera (Italy) and moved to Bari to obtain her master's degree in Medicinal Chemistry at the University of Bari in 2019. During this time, she also worked on asymmetric autocatalytic reactions at the University of Oslo under the supervision of Prof. M. Amedjkouh and then moved to Strathclyde University in Glasgow where she investigated the reactivity of zincate complexes in the group

of Prof. Eva Hevia. She finally moved to the University of Bern where, in the same group, she explored the synthesis and reactivity of cobalt bimetallic complexes, obtaining her PhD in January 2024.

1. Transition Metal (ates) in Deprotonative Metalation Reactions

Deprotonative metalation, where a non-polar C–H σ -bond is regioselectively transformed into a more polar and reactive, C–M bond, is arguably one of the most powerful methodologies for the functionalisation of aromatic molecules.^[1] The resulting metalated products can be used for various synthetic methods, such as electrophilic quenching, cross-coupling processes, or nucleophilic additions.

Above all, regioselective functionalisation of fluoroarenes molecules is highly sought due to their ever-growing importance in numerous fields of chemistry, including agrochemicals, biochemistry, and pharmaceuticals.^[2–4]

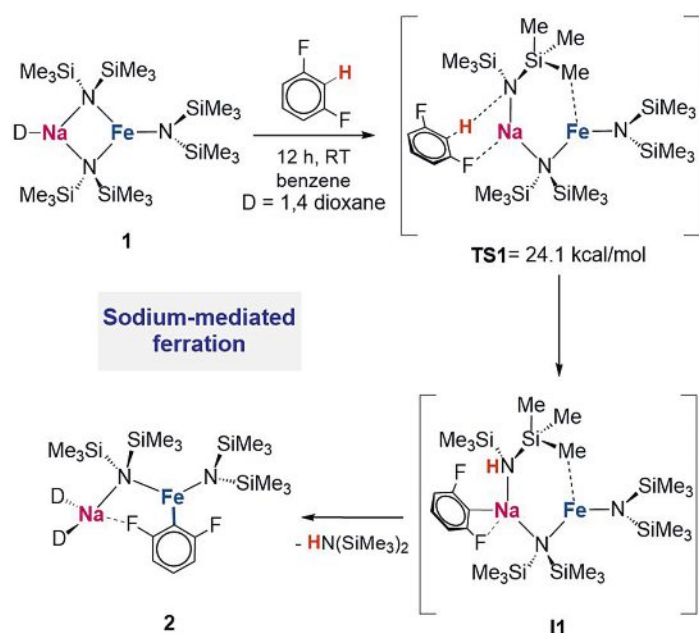
Over the last decade, the applications of earth-abundant 3d transition metals for this type of reaction^[5–9] have gained significant attention, as a more sustainable alternative to those approaches that require the use of noble transition metals, such as Rh, Ru, Pt, and Pd, which pose health and environmental challenges due to their toxicity and higher costs. Within this context, recent advances in this field have uncovered the excellent stoichiometric

and catalytic abilities of cobalt complexes to promote C–F bond activation of fluoroarenes, allowing for their regioselective functionalisation.^[10–14]

Taking fluorobenzene as a model substrate, Chirik has elegantly shown how this substrate undergoes regioselective *ortho*-C–H bond activation using a low valent bis(phosphino)pyridine Co(I) catalyst.^[15–17] Contrastingly, Holland has developed low coordinate Co(I) complexes supported by a sterically demanding β -diketiminate ligand which can be used for the chemoselective C–F bond activation of fluorobenzene.^[18,19] This binuclear oxidative addition, previously observed in other aryl halides, is a rare phenomenon when it comes to the strong C–F bond found in fluoroarenes.^[20] Interestingly, it should be noted that in both examples, reactions take place with a concomitant change in the oxidation state of the cobalt centers.

Exploring the power of bimetallic cooperation between transition metals and alkali metals, our group has recently uncovered the potential of these systems to promote low polarity C–H deprotonative metalations. This type of reactivity has been previously studied in alkali-metal zincate chemistry and for other related bimetallic mixtures containing main group metals such as gallium or aluminium.^[21–25] Breaking new ground in this area, recently our group reported that combining equimolar amounts of sodium amides with Fe(II) bis(amide) Fe(HMDS)₂ [HMDS = N(SiMe₃)₂] allows for the regioselective functionalisation of a range of aromatic substrates including fluoroarenes *via* direct Fe–H exchange.^[26–28] This special reactivity is thought to arise from the cooperative behaviour that is inherent in these heterobimetallic bases. Mechanistic investigations, which included DFT calculations, have proposed that initially sodium coordinates the substrate, activating the fluoroarene towards its sodiation, followed by a fast transmetalation step to iron which allows for the stabilisation of the delicate aryl anion by the formation of a less polar (or more covalent) Fe–C bond (Scheme 1).^[27]

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Scheme 1. Proposed mechanism by DFT calculations for the reaction of $[(D)NaFe(HMDS)_3]$ (**1**) with 1,3-difluorobenzene [D = 1,4 dioxane, TMEDA, or toluene].

2. NaCo(II)-ates in Deprotonative Metalation of Fluoroarenes

Building on these studies we next pondered whether alkali-metal cobaltates could also engage in fluoroarene functionalisation processes *via* direct Co(II)-H exchange processes. Here we present an overview of our main findings assessing the ability of sodium cobaltate $[NaCo(HMDS)_3]$ (**3**) as a synergic base for chemo- and regio-selective cobaltation of fluoroarenes.^[29]

2.1 Mono-cobaltation of Polyfluorinated Molecules

We started our investigations focussing on pentafluorobenzene as a model substrate. Featuring a relatively activated C-H bond in terms of its pK_a value, pentafluorobenzene has also shown a great tendency to undergo C-F bond activation processes when reacted with low valent transition metal complexes.^[30,31] Furthermore it should be noted that this substrate is inert towards metalation when using 1 equiv. of $Co(HMDS)_2$, and reacts unselectively with $Na(HMDS)$, yielding a mixture of decomposition products.

Nevertheless, when 1 equiv. of pentafluorobenzene was added to a benzene solution of $[NaCo(HMDS)_3]$ (**3**), the immediate formation of a light green precipitate was apparent, which upon recrystallisation in THF allowed for the isolation of a rare disodium tetra(aryl)cobaltate $[(THF)_4Na_2Co(C_6F_5)_4]$ (**4**) in a 21% yield (Fig. 1a). The isolation of **4** supported the unprecedented ability of the sodium cobaltate base to perform alkali metal cobaltation, forming a rare square planar Co(II) complex by selectively metalating *ortho*- to the fluorine substituent and leaving the remaining C-F bonds intact. Interestingly, changing the coordination sphere around the Na atom by using the macrocyclic donor 15-crown-5 and therefore forming solvent-separated ion-pair $[\{Na(15-crown-5)_2\}^+ \{Co(HMDS)_3\}^-]$,^[32] we found that the cobaltation process was entirely inhibited. This result further emphasizes the cooperativity between sodium and cobalt in successfully performing the metalation.

Intrigued by these findings, and in order to shed some light on the unexpected formation of **4**, we performed the same reaction of $[NaCo(HMDS)_3]$ (**3**) with pentafluorobenzene in benzene but this time at 0 °C. Under these conditions we could spectroscopically detect the selective formation of bis(amide)aryl sodium cobaltate $[NaCo(HMDS)_2(C_6F_5)]$ (**5**) which could be isolated in an 86% yield and structurally authenticated by X-ray crystallographic analysis (Fig. 1a).^[29] Featuring a contacted-ion pair structure where both metals are connected by two bridging amide groups and the C_6F_5 group binds terminally to the Co(II) center, **5** displays a structural motif which is reminiscent to that reported for the ferration of pentafluorobenzene by $[NaFe(HMDS)_3]$ (**1**).^[27] Interestingly while **5** is stable in benzene solutions at 0 °C, at room temperature it readily undergoes a ligand redistribution process to form sodium tetra(aryl) **4**, that precipitates as a green solid, along with $Co(HMDS)_2$ and $[NaCo(HMDS)_3]$ (**3**) which remain in solution and can be detected by 1H NMR spectroscopy (Fig. 1a). This behavior contrasts with our previous studies where sodium ferrate $[NaFe(HMDS)_2(C_6F_5)]$ is perfectly stable in arene solution at room temperature over several days without observing any signs of decomposition.^[27] Finally, an optimised yield of 90% of the tetra(aryl)cobaltate product **4** was obtained by using a 2:1 mixture of $Na(HMDS)$ and $Co(HMDS)_2$ with four equivalents of C_6F_5H , making this reaction atom economical, generating four equivalents of $HMDS(H)$ as the byproduct of the reaction.

To advance the understanding on these intriguing experimental findings, we next performed computational studies using DFT calculations. Taking **3** as the starting point to model the Co-H exchange when using a 1:1 ratio of the Na and Co(II) amide

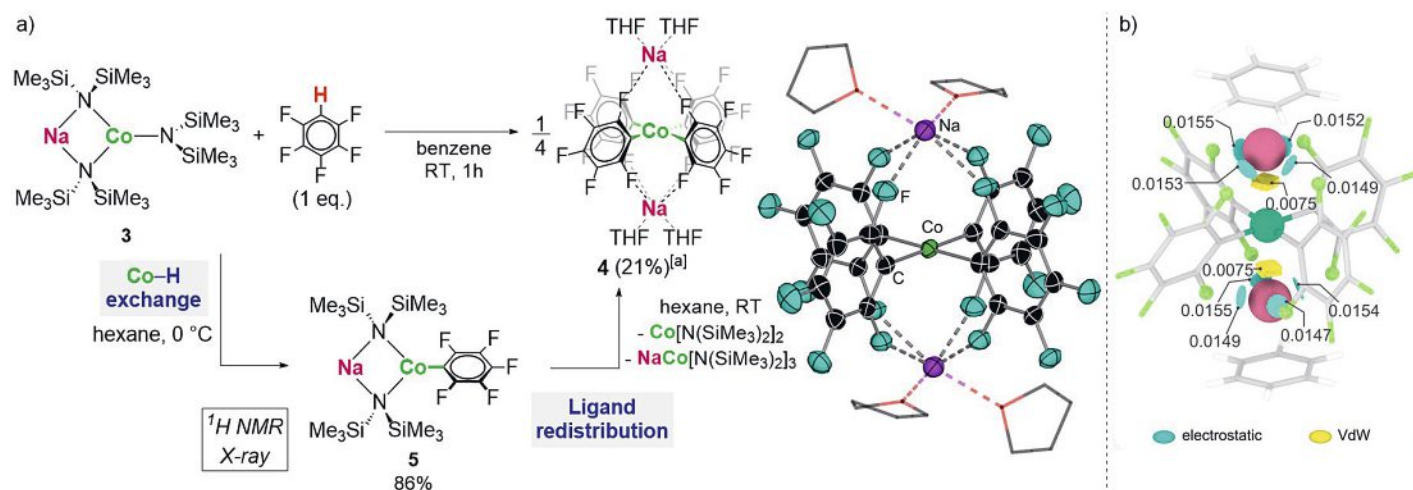


Fig. 1. a) Metallation studies for the cobaltation of pentafluorobenzene using a 1:1 Na:Co ratio of the starting reagents; [a]: an increased 90% yield was obtained using a 2:1:4 Na:Co: C_6F_5H stoichiometry; inset: crystallographic structure of $[(THF)_4Na_2Co(C_6F_5)_4]$ (**4**) with displacement ellipsoids at 50% probability. H atoms are omitted for clarity; b) NCI (Non-Covalent Interactions) analysis performed on complex **4**.

precursors, a stepwise mechanism, similar to the one previously discussed for sodium ferrates (Scheme 1) was proposed. Thus, sodium coordinates the substrate by forming two Na \cdots F dative interactions with C₆F₅H and performs the initial metalation *via* Na-H exchange. The hypersensitive fluoroaryl anion immediately undergoes fast intramolecular transmetalation to the cobalt centre, which aids its stabilisation. Similarly, when a 2:1 Na:Co ratio was used, the Co-H exchange mechanism proceeds *via* the initial sodiation of pentafluorobenzene by the excess Na(HMDS), followed by rapid intermolecular transmetalation of the newly formed pentafluorophenyl anion from Na to the Co centre. In both scenarios the formation of the heteroleptic sodium cobaltate [NaCo(HMDS)₂(C₆F₅)] (**5**) was found to be energetically favoured with the intermolecular transmetalation process having a lower energetic barrier (16.1 kcalmol⁻¹) than the intramolecular transmetalation (21.8 kcalmol⁻¹).

Encouraged by these findings, we next explored how far this reactivity could be applied to other perfluorinated substrates. Strikingly, even though the optimised reaction conditions (*i.e.* 2:1:4 ratio of Na(HMDS):Co(HMDS)₂:Ar_FH) were used in all cases, our studies showed markedly different results depending on the substitution pattern of the substrate. 1,3-disubstituted fluoroarenes such as 1,3-difluoro, 1,2,4-trifluoro, 1,3,5-trifluoro, 1,2,3,5-tetrafluoro, and 1,2,4,5-tetrafluorobenzenes behaved similarly to pentafluorobenzene, yielding square planar complexes with the general formula [Na₂CoAr_{F_n}]. On the other hand, substrates that lack the presence of fluorine substituents in the 1,3-positions (*e.g.* 1,2,3,4-tetrafluorobenzene, fluorobenzene and 2-fluoroanisole), allowed for the isolation of thermally stable [NaCo(HMDS)₂(Ar_F)] complexes, structural analogues to **5**, as only reaction products. These findings suggest that the formation of tetra(aryl) sodium cobaltates *via* ligand redistribution is only favoured in those cases where the substrate possesses two *meta*-disposed F-substituents on the aromatic ring. This scenario allows to maximise the number of Na \cdots F interactions (Fig. 1b). This interpretation is consistent with the different reactivities observed for 1,2,3,4-tetrafluorobenzene and 1,3,5-trifluorobenzene which exhibit similar acidities in terms of pK_a values (30.6 vs 31.5).^[33] To advance the understanding on the influence of the arene substitution pattern on favouring the formation of [Na₂CoAr_n] complexes, the NCIs (non-covalent interactions) in complex **4** were also investigated. As shown in Fig. 1b, two sets of four strong attractive electrostatic Na \cdots F interactions (highlighted in blue) can be identified. The combination of these interactions together with the van der Waals (vdW) interactions between the Co centre and the two peripheric Na atoms, are believed to be the reason for the stability of the disodium tetra(aryl)cobaltate complexes. Finally, further in-depth DFT calculations, electronic structure and energy decomposition analyses were carried out on these bimetallic NaCo(II) square planar [Na₂CoAr_n] species.^[34] By selectively changing the substituents and/or its position on the aromatic ring, we advanced the understanding of the critical role that Na \cdots X (X = F, Cl, Br) interactions and X \cdots X repulsions play in the stabilisation or de-stabilisation of these bimetallic NaCo(II) square planar [Na₂CoAr_n] complexes. The overall balance of these forces ultimately dictates the fate of the [NaCoAr(HMDS)₂] intermediates, which are first generated during the formal Co(II)-H exchange process.

2.2 Di-cobaltation and C-F Bond Activation of Polyfluorinated Molecules

Intrigued by our initial results that proved the ability of the heterobimetallic sodium cobaltate [NaCo(HMDS)₃] (**3**) to selectively perform mono-cobaltations, we next investigated the possibility of performing multi-metalation on these substrates as well as the activation of their C-F bonds.^[35]

We commenced our studies with 1,3,5-trifluorobenzene (pK_a = 31.5),^[33] which we have seen can undergo mono-cobaltation

yielding the respective tetra(aryl) product when 1 equiv. of the bimetallic base [NaCo(HMDS)₃] (**3**) was used. Remarkably, when the reaction was carried out in the presence of a 2 molar excess of **3**, at room temperature and within just 1 h, selective 1,3-di-cobaltation was observed furnishing [Na₂Co₂(C₆F₃H)(HMDS)₄] (**6**) in a 67% yield (Fig. 2a and 2b). Similarly, di-cobaltation can be achieved with other activated substrates such as 1,2,4,5-tetrafluorobenzene (pK_a = 23.1),^[33] where full conversion to the 1,5-di-cobaltated product can be obtained at room temperature within 5 minutes.

It is important to mention that both these double-metalated products are stable at room temperature for a long time in C₆D₆. This is strikingly different with what was observed for the heteroleptic mono-cobaltation products such as **5**, where ligand redistribution occurred at temperatures higher than 0 °C. This unexpected stability can be attributed to the bulky HMDS groups offering excellent steric protection for the otherwise reactive Co-C bonds. Next, we attempted the three-fold cobaltation of 1,3,5-trifluorobenzene using a three molar excess of **3**, allowing the reaction mixture to stir at 80 °C for 16 hours. Remarkably, under these conditions homometallic cobalt (II) complex [1,3-bis(CoHMDS)-2,4,6-tris(HMDS)-C₆H] (**7**) could be isolated as a crystalline solid in a 78% isolated yield (Fig. 2a, ii). X-ray crystallographic analysis revealed that **7** is the result of a unique Co(II)-H exchange, 3-fold C-F bond activation process. Remarkably every original C-F bond in the substrate has been selectively replaced by a C-N(SiMe₃)₂ bond. This is particularly remarkable when considering that C-F bonds are typically described as the strongest bonds in organic chemistry (diatomic bond dissociation energy of 513.8 kJmol⁻¹).^[36] Although another factor that should also be taken into account is the fact that metal-mediated C-F bond activation processes are usually more exothermic due to the formation of a new M-F bond, which sometimes can act as a thermodynamic drive for this type of reactivity.^[31,37] In the case of **7** it should be noted that the oxidation state (II) remains constant and its formation takes place with the subsequent elimination of NaF. While this reactivity is entirely new in cobalt chemistry,^[18–20,38] previous studies reported by our group have revealed a similar behavior for [NaFe(HMDS)₃] (**1**) under similar harsh reaction conditions (excess of **1**, longer reaction times and elevated temperatures).^[26]

Further reactivity studies also showed that alternatively, **7** can be obtained from the addition of an extra equivalent of Na(HMDS) to the di-cobaltated product **6** upon heating at 80 °C for 16 h. Preliminary mechanistic studies suggest that formation of **7** takes place *via* a fast sequence of reactions, initiated by the elimination of NaF and Co(HMDS)₂ from **6**, with the concomitant formation of a benzyne intermediate that can subsequently undergo addition with the cobalt amide. Attempts to isolate any intermediate species in the formation of **7** were unsuccessful, although when the reaction was carried out in the presence of 15-crown-5 the C-F bond activation process was inhibited.

This study also evaluated the importance of the alkali-metal, and the possible effects in the reactivity of the bimetallic base if Na was replaced by Li or K (Fig. 2d). Interestingly when 1,3,5-trifluorobenzene was treated with three molar equivalents of [MCo(HMDS)₃] (M = Li, K), we found completely different results than when using **3**. Independent of the stoichiometry or conditions employed (16 h, 80 °C), the lithium cobaltate can only promote the mono-cobaltation of the fluoroarene to furnish [LiCo(HMDS)₂(C₆F₃H₂)] (**8**). Contrastingly the potassium cobaltate was shown to be completely inert towards 1,3,5-trifluorobenzene metalation. This Li < Na > K trend contradicts the commonly found trend in Group 1 metal organometallics where reactivity tends to increase according to the size of the alkali-metal, Li < Na < K.^[39]

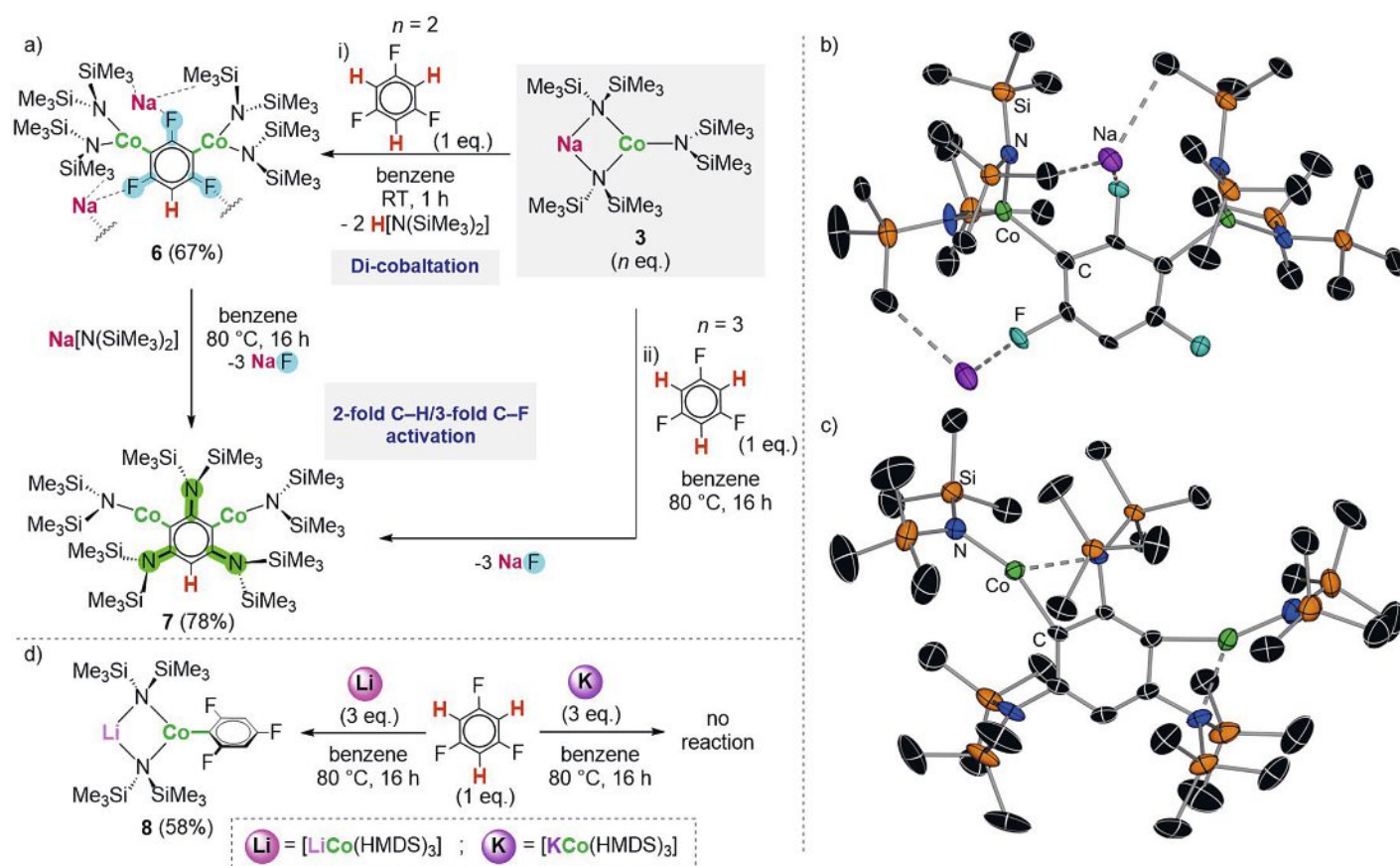


Fig. 2. a) i) Reaction of 1,3,5-trifluorobenzene with 2 equiv. of **3** to form the 1,4-di-cobaltation product **6**. ii) Reaction of 1,3,5-trifluorobenzene with 3 equiv. of **3** to form the two-fold Co-H exchange, 3-fold C-F bond activation product **7**; b and c) Polymeric structures of [Na₂Co₂(C₆F₃H)(HMDS)₂] (**6**) and [1,3-bis(CoHMDS-2,4,6-tris(HMDS)-C₆H)] (**7**), respectively, with displacement ellipsoids at 50% probability. H atoms are omitted for clarity; d) Reactivity of 1,3,5-trifluorobenzene with [MCo(HMDS)₃] (M = Li, K).

3. Conclusions and Outlook

Shedding light on how bimetallic cooperation can be established in transition metal(ate) systems, we have presented an overview of our work regarding the use of a mixed Na/Co(II) heterobimetallic base to promote Co-H exchanges and C-F bond activation of fluoroarenes. By exploiting the bimetallic cooperation in [NaCo(HMDS)₃], mono- or dimetalation of a wide range of different perfluorinated molecules was achieved. Mono-metalation of 1,3-disubstituted fluoroarenes yielded rare square planar Co(II) complexes, selectively metalated *ortho*- to the fluorine substituents. A thorough investigation into the formation and stability of these complexes showed a true synergistic behaviour between the Na and the Co centres in the formation and stability of such complexes. Moreover, proving an exceptional stoichiometric control, double-cobaltation was observed when a two molar excess of [NaCo(HMDS)₃] was reacted with tetra- and tri-fluorobenzene. Interestingly, studies on the reaction of 1,3,5-trifluorobenzene revealed a unique reactivity occurring under harsh reaction conditions, where the substrate undergoes two-fold metalation and three-fold C-F activation *via* what is believed to be a cascade reaction. Overall, *via* the isolation of key reaction intermediates, detailed NMR analysis, X-ray crystallography and computational calculations, our work provided fundamental insights into the potential of alkali metal cobaltate systems in performing metalation reactions, therefore opening new ground to numerous potentially interesting paths for further research to be explored including the development of new bimetallic partnerships.

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- [1] G. Dyker, 'Handbook of C-H Transformations: Applications in Organic Synthesis', Wiley-VCH Verlag GmbH: Weinheim, Germany, **2005**.
- [2] D. O'Hagan, *Chem. Rev.* **2008**, *37*, 308, <https://doi.org/10.1039/B711844A>
- [3] H. Amii, K. Uneyama, *Chem. Rev.* **2009**, *109*, 2119, <https://doi.org/10.1021/cr800388c>
- [4] J. Weaver, S. Senaweera, *Tetrahedron* **2014**, *70*, 7413, <https://doi.org/10.1016/j.tet.2014.06.004>
- [5] P. Gandeepan, T. Müller, D. Zell, G. Cera, S. Warratz and L. Ackermann, *Chem. Rev.* **2019**, *119*, 2192, <https://doi.org/10.1021/acs.chemrev.8b00507>
- [6] U. Dhawa, N. Kaplaneris, L. Ackermann, *Org. Chem. Front.* **2021**, *8*, 4886, <https://doi.org/10.1039/D1QO00727K>
- [7] Ł. Woźniak, N. Cramer, *Trends Chem.* **2019**, *1*, 471, <https://doi.org/10.1016/j.trechm.2019.03.013>
- [8] R. L. Carvalho, A. S. De Miranda, M. P. Nunes, R. S. Gomes, G. A. M. Jardim, E. N. Da Silva, *Beilstein J. Org. Chem.* **2021**, *17*, 1849, <https://doi.org/10.3762/bjoc.17.126>
- [9] L. Ackermann, R. Vicente, A. R. Kapdi, *Angew. Chem. Int. Ed.* **2009**, *48*, 9792, <https://doi.org/10.1002/anie.200902996>
- [10] B. J. Fallon, E. Derat, M. Amatore, C. Aubert, F. Chemla, F. Ferreira, A. Perez-Luna, M. Petit, *J. Am. Chem. Soc.* **2015**, *137*, 2448, <https://doi.org/10.1021/ja512728f>
- [11] J. Sanjosé-Orduna, D. Gallego, A. Garcia-Roca, E. Martin, J. Benet-Buchholz, M. H. Pérez-Temprano, *Angew. Chem. Int. Ed.* **2017**, *56*, 12137, <https://doi.org/10.1002/anie.201704744>
- [12] A. Reckziegel, C. Pietzonka, F. Kraus, C. G. Werncke, *Angew. Chem. Int. Ed.* **2020**, *59*, 8527, <https://doi.org/10.1002/anie.201914718>
- [13] M. H. Li, X. J. Si, H. Zhang, D. Yang, J. L. Niu, M. P. Song, *Org. Lett.* **2021**, *23*, 914, <https://doi.org/10.1021/acs.orglett.0c04122>
- [14] P. Ghosh, R. Schoch, M. Bauer, A. J. von Wangelin, *Angew. Chem. Int. Ed.* **2022**, *134*, e202110821, <https://doi.org/10.1002/ange.202110821>

- [15] T. P. Pabst, J. V. Obligacion, É. Rochette, I. Pappas, P. J. Chirik, *J. Am. Chem. Soc.* **2019**, *141*, 15378, <https://doi.org/10.1021/jacs.9b07984>
- [16] J. V. Obligacion, M. J. Bezdek, P. J. Chirik, *J. Am. Chem. Soc.* **2017**, *139*, 2825, <https://doi.org/10.1021/jacs.6b13346>
- [17] J. V. Obligacion, H. Zhong, P. J. Chirik, *Isr. J. Chem.* **2017**, *57*, 1032, <https://doi.org/10.1002/ijch.201700072>
- [18] T. R. Dugan, X. Sun, E. V. Rybak-Akimova, O. Olatunji-Ojo, T. R. Cundari, P. L. Holland, *J. Am. Chem. Soc.* **2011**, *133*, 12418, <https://doi.org/10.1021/ja2052914>
- [19] T. R. Dugan, J. M. Goldberg, W. W. Brennessel, P. L. Holland, *Organometallics* **2012**, *31*, 1349, <https://doi.org/10.1021/om200991k>
- [20] D. Zhu, P. H. M. Budzelaar, *Organometallics* **2010**, *29*, 5759, <https://doi.org/10.1021/om100811f>
- [21] M. Uchiyama, T. Miyoshi, Y. Kajihara, T. Sakamoto, Y. Otani, T. Ohwada, Y. Kondo, *J. Am. Chem. Soc.* **2002**, *124*, 8514, <https://doi.org/10.1021/ja0202199>
- [22] S. H. Wunderlich, P. Knochel, *Angew. Chem. Int. Ed.* **2007**, *46*, 7685, <https://doi.org/10.1002/anie.200701984>
- [23] M. Mosrin, P. Knochel, *Org. Lett.* **2009**, *11*, 1837, <https://doi.org/10.1021/ol900342a>
- [24] P. Mastropierro, A. R. Kennedy, E. Hevia, *Chem. Commun.* **2022**, *58*, 5292, <https://doi.org/10.1039/d2cc00979j>
- [25] R. McLellan, M. Uzelac, A. R. Kennedy, E. Hevia, R. E. Mulvey, *Angew. Chem. Int. Ed.* **2017**, *56*, 9566, <https://doi.org/10.1002/anie.201706064>
- [26] L. C. H. Maddock, T. Nixon, A. R. Kennedy, M. R. Probert, W. Clegg, E. Hevia, *Angew. Chem. Int. Ed.* **2018**, *57*, 187, <https://doi.org/10.1002/anie.201709750>
- [27] L. C. H. Maddock, M. Mu, A. R. Kennedy, M. García-Melchor, E. Hevia, *Angew. Chem. Int. Ed.* **2021**, *60*, 15296, <https://doi.org/10.1002/anie.202104275>
- [28] L. C. H. Maddock, A. R. Kennedy, E. Hevia, *Helv. Chim. Acta* **2021**, *104*, e2021002, <https://doi.org/10.1002/hlca.202100206>
- [29] A. Logallo, M. Mu, M. García-Melchor, E. Hevia, *Angew. Chem. Int. Ed.* **2022**, *61*, <https://doi.org/10.1002/anie.202213246>
- [30] E. Clot, O. Eisenstein, N. Jasim, S. A. MacGregor, J. E. McGrady, R. N. Perutz, *Acc. Chem. Res.* **2011**, *44*, 333, <https://doi.org/10.1021/ar100136x>
- [31] O. Eisenstein, J. Milani, R. N. Perutz, *Chem. Rev.* **2017**, *117*, 8710, <https://doi.org/10.1021/acs.chemrev.7b00163>
- [32] T. X. Gentner, R. E. Mulvey, *Angew. Chem. Int. Ed.* **2021**, *60*, 9247, <https://doi.org/10.1002/anie.202010963>
- [33] K. Shen, Y. Fu, J. N. Li, L. Liu, Q. X. Guo, *Tetrahedron* **2007**, *63*, 1568, <https://doi.org/10.1016/j.tet.2006.12.032>
- [34] M. Mu, A. Logallo, E. Hevia, M. García-Melchor, *ChemCatChem* **2023**, *15*, <https://doi.org/10.1002/cctc.202300769>
- [35] A. Logallo, E. Hevia, *Chem. Commun.* **2023**, *59*, 5383, <https://doi.org/10.1039/d3cc01216f>
- [36] D. R. Lide, 'Handbook of Chemistry and Physics', CRC Press: Boca Raton, 89th Editi., **2008**.
- [37] S. D. Pike, M. R. Crimmin, A. B. Chaplin, *Chem. Commun.* **2017**, *53*, 3615, <https://doi.org/10.1039/C6CC09575E>
- [38] H. Lei, J. C. Fettinger, P. P. Power, *Inorg. Chem.* **2012**, *51*, 1821, <https://doi.org/10.1021/ic202116s>
- [39] S. D. Robertson, M. Uzelac, R. E. Mulvey, *Chem. Rev.* **2019**, *119*, 8332, <https://doi.org/10.1021/acs.chemrev.9b00047>

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