Ring-Walking Mediated by Ni–Ni Species as a Vehicle for Enabling Distal C(sp²)–H Functionalization of Aryl Pivalates

Carlota Odena,[†¶] Enrique Gómez-Bengoa,*[§] and Ruben Martin*[†£]

[†] Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology, Av. Països Catalans 16, 43007 Tarragona, Spain

[¶] Universitat Rovira i Virgili, Departament de Química Orgànica, c/ Marcel·lí Domingo, 1, 43007 Tarragona, Spain

[§] Department of Organic Chemistry I, Universidad País Vasco, UPV/EHU, Apdo. 1072, 20080 San Sebastian, Spain

[£] ICREA, Passeig Lluís Companys, 23, 08010, Barcelona, Spain

Supporting Information Placeholder

ABSTRACT: Herein, we report the utilization of Ni-Ni species as a manifold for enabling a "ring-walking" event by a dynamic translocation of the metal center over the arene backbone. Experimental and computational studies support a translocation occurring via a 1,2-hydride shift. The synthetic applicability of the method is illustrated in a series of C–C bond formations that occur at distal C(sp²)–H sites of simple aryl pivalates.

Prompted by the seminal stoichiometric work of Kleiman and Dubeck,[1] the recent years have witnessed significant progress in Ni-catalyzed C(sp²)–H functionalization reactions.[2,3] Unlike other metals in the d[10] series, the reactivity of nickel catalysts in C(sp²)–H functionalization remain predominantly confined to the utilization of proximal, yet strongly-coordinating, directing groups, with bond formation occurring at the *ortho* position (Scheme 1, *top*).[3] Despite the advances realized, particularly in Catellani-type reactions,[4] the means to enable distal C(sp²)–H functionalization aided by Ni species without recourse to directing groups, acidic C(sp²)–H bonds or aryl halides[5] still remains an unexplored cartography, particularly with phenol C–O derivatives as traceless entities (*path b*).[6]

**Scheme 1**. **Ni-catalyzed C(sp²)–H Functionalization**.
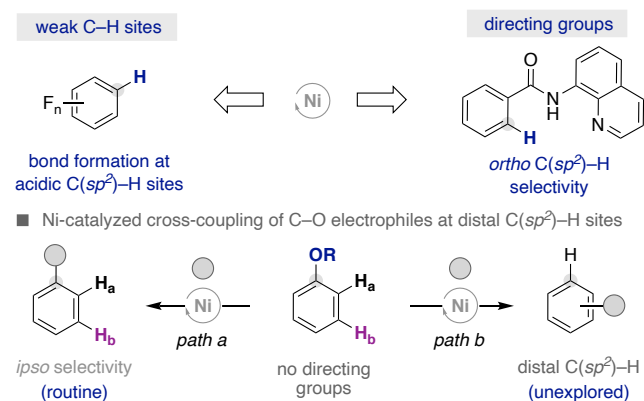
Scheme 2. **Ring-Walking from ArOPiv by Ni-Ni Complexes.**
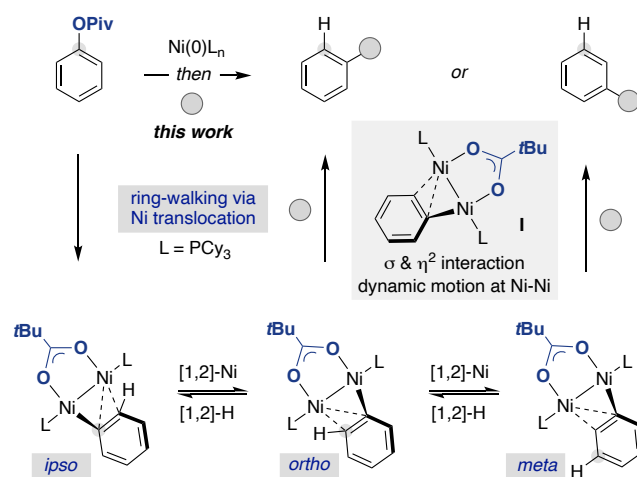
Recently, our group described the involvement of unorthodox dinickel oxidative addition complexes **I** in the C–O bond-cleavage of aryl pivalates (Scheme 2).[7] The arene fragment interacts with the Ni–Ni core via both a σ-bond and a η²-interaction, with a bridging pivalate between the two Ni centers.[8,9] Given that NBO analysis of **I** showed a symmetrical distribution of charge at the Ni–Ni core,[7] we wondered whether a dynamic motion between the Ni–Ni core might enable a formal translocation of the Ni center at a proximal C(sp²) site by forming a new σ-bond and a η²-interaction with the arene backbone. If successful, such a process might constitute a formal metal translocation over the arene backbone,[10,11] thus setting the basis for establishing a new rationale for enabling Ni-catalyzed C(sp²)–H functionalization of C–O electrophiles via "ring-walking" in the absence of directing groups or metalation events.[12] Prompted by our interest in Ni-catalyzed C–H functionalization,[5,13] we report herein the successful realization of this goal. Experimental and DFT studies demonstrate the viability for enabling a "ring-walking" prior to C–C bond formation, with a mechanism likely arising from an abnormal 1,2-hydride shift.

**Scheme 3. Synthesis of Ni-Ni Species from π-Extended and non-π-Extended Aryl Pivalates**.
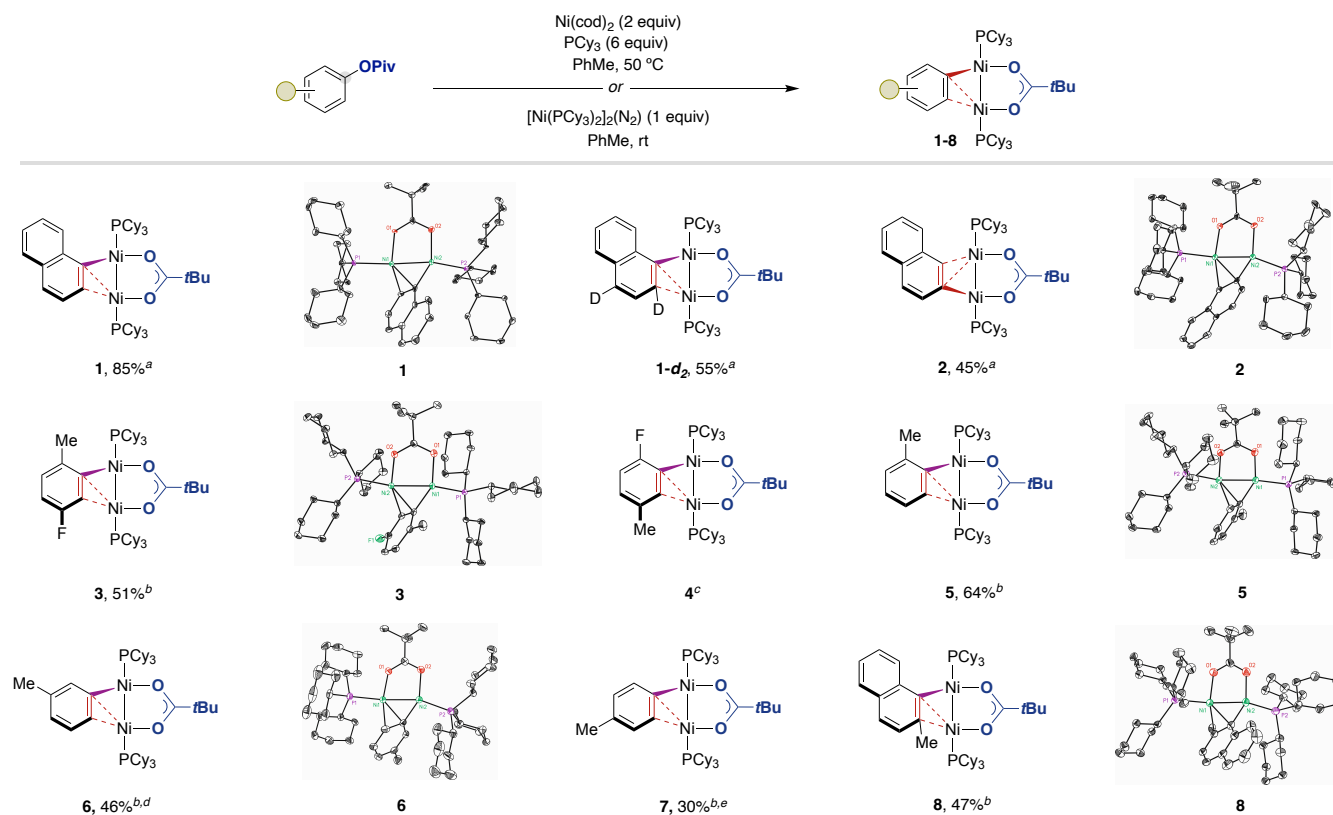
a Conditions: Aryl pivalate (1 equiv), Ni(cod)$_2$ (2 equiv), PCy$_3$ (6 equiv) in toluene (0.1 M), 50 ºC. *b* Conditions: Aryl pivalate (1.1-1.6 equiv), [Ni(PCy$_3$)$_2$]$_2$(N$_2$) (1 equiv) in toluene (0.1 M), rt. *c* Complex **4** was characterized *in situ* due to its instability. *d* Using *m*-tolyl pivalate at rt, resulting in **6:7** (86:14 ratio). *e* Utilizing *p*-tolyl pivalate at rt, resulting in **6:7** (88:12 ratio).

Our study began by preparing a representative set of Ni-Ni complexes by exposure of aryl pivalates to Ni(cod)$_2$/PCy$_3$ at 50 ºC or [Ni(PCy$_3$)$_2$]$_2$N$_2$ at rt in toluene (Scheme 3).[14] The choice of **1-8** was not arbitrary; **1** and **2** were designed to study the dynamics on π−extended systems – substrates particularly suited for Ni-catalyzed C–O functionalization[6] – whereas **3-7** would provide an opportunity to extend the "ring-walking" event to non-π-extended arenes. Moreover, **3** and **4** would allow to rationalize whether the nickel translocation might be affected by proximal fluorine atoms on electronic grounds[15] whereas the study of **5-7** could offer an opportunity to rationalize the extension at which "ring-walking" might occur at remote C(sp^2)–H sites. The preparation of **3-7** is particularly noteworthy, representing the first examples of isolation of dinuclear oxidative addition species from non-π-extended aryl pivalates.[16] While these complexes could unambiguously be characterized by NMR spectroscopy, x-ray crystallography of **1**, **2**, **3**, **5**, **6** and **8** univocally confirmed the interaction of the arene with the Ni–Ni core by both a σ-bond and a η^2-interaction.[17] In line with these observations, **1-8** show a representative δ$_p$ of 22.5-27.5 ppm with a Ni–Ni bond ranging from 2.3855(4)-2.433(3) Å.[8] The dinuclear structure is completed by a bridging pivalate ligand having identical Ni–O bond distances.[18]

With a series of well-defined Ni-Ni complexes in hand, we turned our attention to study the viability for triggering a "ring-walking" throughout the arene backbone. We anticipated that the motion required for enabling a nickel translocation might be facilitated by a subtle temperature control or stereoelectronic effects. To this end, we monitored the stability of **1** at 50 ºC by ^{31}P{^{1}H}NMR spectroscopy (Scheme 4). A ratio of **1:2** (1:1.2 ratio) was observed after 6 h, thus confirming the viability for nickel translocation over a π-extended backbone. This ratio reached a thermodynamic equilibrium at 1:1.7 ratio of **1:2** that could not be improved regardless of the temperature utilized due to the inherent instability of these complexes in solution. Notably, an otherwise identical **1:2** ratio was found by exposure of **2** after 6 h at 50 ºC. Intriguingly, an equimolar ratio of **3:4** was found when monitoring the isomerization of **3** at 50 ºC over 6 h, thus arguing against the positive impact that fluorine atoms might have in ring-walking for stabilizing adjacent σ C(sp^2)–metal bonds.[15] While isomerization of analytically-pure **5** at 50 ºC revealed rapid formation of **5:6:7** in a 1:4.7:1.4 ratio after 4 h, it is worth mentioning that nickel translocation could also be enabled at room temperature leading to an otherwise identical ratio of **5:6:7** from either pure **5** after 6 days or from **6:7** mixtures (86:14) after 24 h (Scheme 5).

Scheme 4. Ring-Walking of Ni-Ni species 1 & 3.[a]
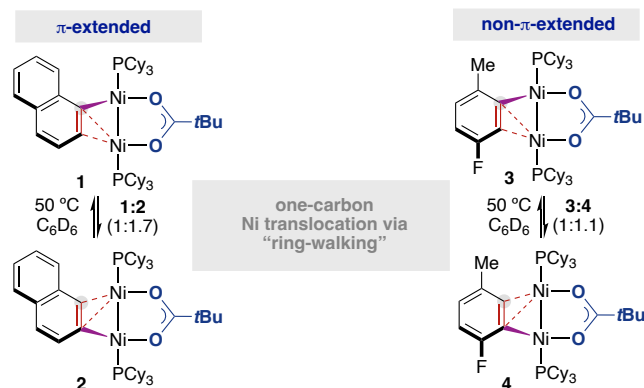
[a] An otherwise identical **1:2** ratio was reached independently on whether the study was conducted with analytically pure **1** or **2**.

Given that Ni-Ni species have shown to act as reservoirs of monovalent aryl-Ni(κ^2-OPiv)(PCy$_3$) and Ni(0)(PCy$_3$) species,[7] we wondered whether the presence of additional PCy$_3$ might destabilize the Ni–Ni core, either facilitating the formation of aryl-Ni(κ^1-OPiv)(PCy$_3$)$_2$ or "ring-walking" by binding Ni(0)(PCy$_3$)$_2$ to the arene backbone in a η^2-manner. Unfortunately, this was not the case and nickel translocation of **1** in the presence of additional PCy$_3$ resulted in a 1:1.4 ratio of **1:2** after 7 days at 50 ºC. Similarly, a deleterious effect was observed in the presence of external bases such as CsOPiv or Cs$_2$CO$_3$,[14] thus arguing against the intervention of concerted metalation-deprotonation pathways.[19] Taken together, these observations reinforce the importance that the Ni-Ni dinuclear core might have in the targeted "ring-walking" event.

Scheme 5. Ni Translocation at Remote C(sp^2)–H Sites.[a]
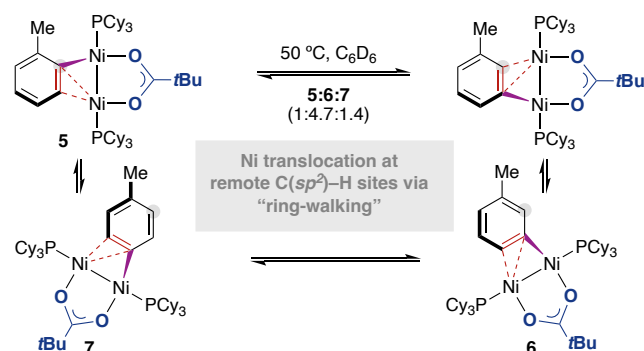
[a] An identical ratio was observed when utilizing **6:7** mixtures regardless whether the translocation was effected at rt or 50 ºC.

Next, we decided to gather indirect evidence about the mechanism of the ring-walking by studying the behavior of **1-d$_2$** (Scheme 6). As expected, 76% deuterium incorporation was observed at C1 in **2-d$_2$**. Notably, no "ring-walking" was observed with **8**, hence reinforcing the notion that metal translocation might only be accomplished via 1,2-hydride shift. In addition, a primary kinetic isotope effect was observed when comparing the rates of **1** & **1-d$_2$** (k_H / k_D = 2.2), suggesting that C(sp^2)–H cleavage might be involved in the rate-determining step.

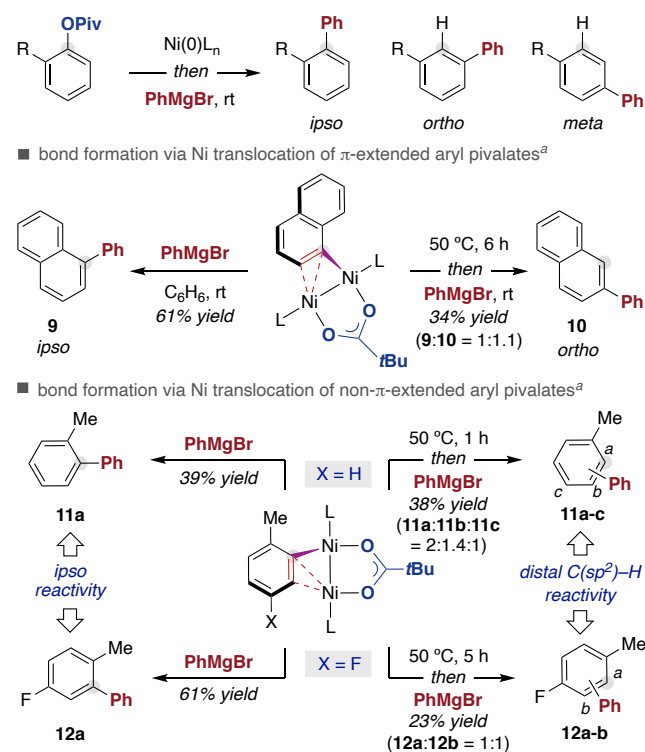**Scheme 6. Isotope-Labelling & DFT Studies.**[a]
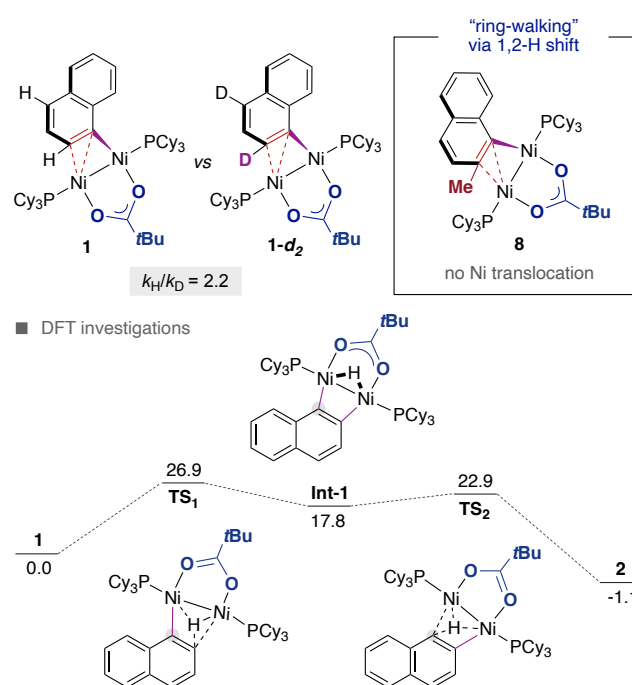
[a] Free energy profile. Energies in kcal·mol^{-1}, calculated at the M06/def2-tzvpp level with solvent (PhMe) correction.

Aiming at understanding the "ring-walking" of **1** and **2** at the molecular level, we turned our attention to DFT calculations [Gaussian 16, M06/def2-tzvpp//B3LYP/6-31G(d,p) + SDD for Ni with toluene as solvent (IEF-PCM)] (Scheme 6, *bottom*).[14] Interestingly, dinuclear species **2** bearing a C–Ni σ-bond at C2 of the naphthalene ring was slightly lower in energy (1.1 kcal/mol) than its C1–Ni analogue **1**. However, the energy difference between **1** and **2** was not significant enough to ensure exclusive formation of the latter, thus reinforcing the results illustrated in Scheme 4. DFT calculations revealed that "ring-walking" of **1** en route to **2** might occur via 1,2-hydride shift via an energetically-favorable transition state **TS1** (26.9 kcal·mol^{-1}) in which C–H bond-cleavage is enabled by formation of a Ni–H bond.[20] Interestingly, the shifting hydrogen atom is shared by the two Ni centers at unsymmetrical distances of 1.5 and 1.9 Å and by the C2 carbon atom (1.6 Å). An otherwise similar **TS2** was located by starting with **2** as precursor instead with an activation barrier of 22.9 kcal·mol^{-1}. Putting these results into perspective, the 1,2-hydride shift might not occur directly from carbon to carbon, but rather in a two-step process via the intermediacy of **Int-1** possessing a μ-hydride bridge between the two Ni centers. Unfortunately, all our attempts at either isolating **Int-1** or detect the formation of the highly shielded bridging μ-hydride by NMR spectroscopy were unsuccessful, suggesting that these species might not be particularly stable in solution. This notion gains credence by the kinetically instability found for **Int-1,** possessing a higher energy when compared to both **1** and **2** (>17.0 kcal·mol^{-1}), thus precluding its isolation or detection by conventional analytical techniques.

The results compiled in Schemes 4 and 5 suggest that a nickel translocation throughout the arene backbone might hold promise to establish a new rationale for enabling C–C bond formations of aryl pivalates at remote C(sp^2)–H sites. Thus, we turned our attention to study the reactivity of Ni-Ni species with an appropriate nucleophilic counterpart (Scheme 7). As anticipated, 1-phenylnaphthalene **9** (61%) was exclusively obtained upon exposure of **1** to PhMgBr at rt after 1 h. Under the limits of detection, not even traces of 2-phenylnaphthalene **10** were detected in the crude mixtures. Interestingly, however, statistical mixtures of **9**:**10** were found by addition of PhMgBr after exposure of **1** to 50 ºC for 6 h, thus confirming that "ring-walking" might constitute a new vehicle for enabling bond formation at distal C(sp^2)–H bonds of aryl pivalates. An otherwise similar scenario was observed when conducting the Kumada-Corriu reaction of **3** and **5** (Scheme 7). While these results require stoichiometric amounts of Ni, our data should be assessed against the challenge that is addressed. Indeed, our protocol represents the first time that distal C(sp^2)–H functionalizations can be enabled by "ring-walking" aided by Ni complexes, thus paving the way for designing future Ni-catalyzed endeavors triggered by a dynamic translocation of the metal center throughout the arene backbone.

In summary, we have shown that Ni-Ni species can be utilized as a manifold for promoting a formal "ring-walking" events in aryl pivalates, thus establishing a new rationale for enabling C–C bond formation at distal C(sp^2)–H sites initiated via functionalization of strong C–O linkages. Our study demonstrates that the substituents on the arene backbone and the temperature might have a non-negligible influence on the nickel translocation. Preliminary mechanistic studies suggest that a 1,2-hydride shift might come into play. Further studies into the exploitation of "ring-walking" events are currently underway in our laboratories.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website. Experimental procedures, spectral and crystallographic data (PDF)

Data for **2** (CCDC-2306072) (CIF)
Data for **3** (CCDC-2306073) (CIF)
Data for **6** (CCDC-2306074) (CIF)
Data for **8** (CCDC-2306071) (CIF)

AUTHOR INFORMATION

Corresponding Author

* rmartinromo@iciq.es

Scheme 7. Bond Formation at Distal C(sp^2)–H Sites.

^{a} *ipso*-Functionalization: **1, 3** or **5** (0.01-0.03 mmol), PhMgBr (1 equiv) in C_6D_6 (0.06 M), rt, 1 h. GC yields using *n*-decane as internal standard (**9, 11a**) or ^{19}F NMR yields using (trifluoromethyl)benzene as internal standard (**12a**); *distal*-functionalization: **1, 3** or **5** (0.01-0.03 mmol) in C_6D_6 (0.06 M), 50 ºC for the indicated time, then PhMgBr (1 equiv), rt, 1 h. GC yields using *n*-decane as an internal standard (**10, 11a-c**) or ^{19}F NMR yields using (trifluoromethyl)benzene as internal standard.

REFERENCES

(1) Kleiman, J. P.; Dubeck, M. The Preparation of Cyclopentadienyl [*o*-(Phenylazo)Phenyl]Nickel. *J. Am. Chem. Soc.* **1963**, *85*, 1544–1545.

(2) For selected reviews on metal-catalyzed C(sp^2)–H functionalization: (a) Davies, H. M. L.; Morton, D. Recent Advances in C–H Functionalization. *J. Org. Chem.* **2016**, *81*, 343–350. (b) Niu, B.; Yang, K.; Lawrence, B.; Ge, H. Transient Ligand-Enabled Transition Metal-Catalyzed C–H Functionalization. *ChemSusChem* **2019**, *12*, 2955–2969. (c) Rogge, T.; Kaplaneris, N.; Chatani, N.; Kim, J.; Chang, S.; Punji, B.; Schafer, L. L.; Musaev, D. G.; Wencel-Delord, J.; Roberts, C. A.; Sarpong, R.; Wilson, Z. E.; Brimble, M. A.; Johansson, M. J.; Ackermann, L. C–H activation. *Nat. Rev. Methods Primers* **2021**, *1*, 43. (d) Dutta, U.; Maiti, S.; Bhattacharya, T.; Maiti, D. Arene diversification through distal C(sp^2)–H functionalization. *Science* **2021**, *372*, 6543. (e) Sinha, S. K.; Guin, S.; Maiti, S.; Biswas, J.

P.; Porey, S.; Maiti, D. Toolbox for Distal C–H Bond Functionalizations in Organic Molecules. *Chem. Rev.* **2022**, *122*, 5682–5841. (f) Giri, R.; Shi, B. -F.; Engle, K. M.; Maugel, N.; Yu, J. -Q. Transition metal-catalyzed C–H activation reactions: diastereoselectivity and enantioselectivity. *Chem. Soc. Rev.* **2009**, *38*, 3242–3272. (g) Yamaguchi, J.; Yamaguchi, A. D.; Itami, K. C–H bond functionalization: emerging synthetic tools for natural products and pharmaceuticals. *Angew. Chem. Int. Ed.* **2012**, *51*, 8960–9009. (h) Baudoin, O. Multiple catalytic C–H bond-functionalization for natural product synthesis. *Angew. Chem. Int. Ed.* **2020**, *59*, 17798–17809. (i) Labinger, J. A.; Bercaw, J. E. Understanding and exploiting C–H bond activation. *Nature* **2002**, *417*, 507–514, and references therein.

(3) For selected reviews on Ni-catalyzed C–H functionalization: (a) Cai, X.-H.; Xie, B. Recent advances on nickel-catalyzed C–H bonds functionalized reactions. *Arkivoc* **2015**, 184–211. (b) Khake, S. M.; Chatani, N. Chelation-Assisted Nickel-Catalyzed C–H Functionalization. *Trends Chem.* **2019**, *1*, 524–539. (c) Liu, Y.-H.; Xia, Y.-N.; Shi, B.-F. Ni-Catalyzed Chelation-Assisted Direct Functionalization of Inert C–H Bonds. *Chin. J. Chem.* **2020**, *38*, 635–662. (d) Shrikant, M. K.; Chatani, N. Nickel-Catalyzed C–H Functionalization Using a Non-directed Strategy. *Chem* **2020**, *6*, 1056–1081. (e) Yang, K.; Li, Z.; Hu, Q.; Elsaid, M.; Liu, C.; Chen, J.; Ge, H. Recent Strategies in Nickel-Catalyzed C–H Bond Functionalization for Nitrogen-Containing Heterocycles. *Catalysts* **2022**, *12*, 1163–1184, and references therein.

(4) Huo, J.; Fu, Y.; Tang, M. J.; Liu, P.; Dong, G. Escape from Palladium: Nickel-Catalyzed Catellani Annulation. *J. Am. Chem. Soc.* **2023**, *145*, 11005–11011.

(5) For recent Ni-catalyzed C(sp^2)–H reactions of aryl halides enabled by [1,4]-Ni shift: (a) Börjesson, M.; Janssen-Müller, D.; Sahoo, B.; Duan, Y.; Wang, X.; Martin, R. Remote sp² C–H Carboxylation via Catalytic 1,4-Ni Migration with CO₂. *J. Am. Chem. Soc.* **2020**, *142*, 16234–16239. (b) He, Y.; Börjesson, M.; Song, H.; Xue, Y.; Zeng, D.; Martin, R.; Zhu, S. Nickel-Catalyzed *Ipso/Ortho* Difunctionalization of Aryl Bromides with Alkynes and Alkyl Bromides via a Vinyl-to-Aryl 1,4-Hydride Shift. *J. Am. Chem. Soc.* **2021**, *143*, 20064–20070. (c) Wang, C.-T.; Liang, P.-Y.; Li, M.; Wang, B.; Wang, Y.-Z.; Li, X.-S.; Wei, W.-X.; Gou, X.-Y.; Ding, Y.-N.; Zhang, Z.; Li, Y.-K.; Liu, X.-Y.; Liang, Y.-M. Aryl-to-Vinyl 1,4-Nickel Migration/Reductive Cross-Coupling Reaction for the Stereoselective Synthesis of Multisubstituted Olefins. *Angew. Chem. Int. Ed.* **2023**, *62*, e202304447. (d) Yang, J.; Gui, Z.; He, Y.; Zhu, S. Functionalization of Olefinic C–H Bonds by an Aryl-to-Vinyl 1,4-Nickel Migration/Reductive Coupling Sequence. *Angew. Chem. Int. Ed.* **2023**, *135*, e202304713. (e) Zhang, H.; Rodrigalvarez, J. Martin, R. C(sp²)–H Hydroxylation via Catalytic 1,4-Ni Migration with N₂O. *J. Am. Chem. Soc.* **2023**, *145*, 17564–17569.

(6) For selected reviews on Ni-catalyzed C(sp^2)–O bond-cleavage: (a) Rosen, B. M.; Quasdorf, K. W.; Wilson, D. A.; Zhang, N.; Resmerita, A.-M.; Garg, N. K.; Percec, V. Nickel-Catalyzed Cross-Couplings Involving Carbon–Oxygen Bonds. *Chem. Rev.* **2011**, *111*, 1346–1416. (b) Cornella, J.; Zarate, C.; Martin, R. Metal-catalyzed activation of ethers *via* C–O bond cleavage: a new strategy for molecular diversity. *Chem. Soc. Rev.* **2014**, *43*, 8081–8097. (c) Tobisu, M.; Chatani, N. Cross-Couplings Using Aryl Ethers via C–O Bond Activation Enabled by Nickel Catalysts. *Acc. Chem. Res.* **2015**, *48*, 1717–1726. (d) Su, B.;

Cao, Z.-C.; Shi, Z.-J. Exploration of Earth-Abundant Transition Metals (Fe, Co, and Ni) as Catalysts in Unreactive Chemical Bond Activations. *Acc. Chem. Res.* **2015**, *48*, 886–896. (e) Zarate, C.; van Gemmeren, M.; Somerville, R. J.; Martin, R. Chapter Four – Phenol Derivatives: Modern Electrophiles in Cross-Coupling Reactions. *Adv. Organomet. Chem.* **2016**, *66*, 143–222. (f) Guo, L.; Rueping, M. Decarbonylative Cross-Couplings: Nickel Catalyzed Functional Group Interconversion Strategies for the Construction of Complex Organic Molecules. *Acc. Chem. Res.* **2018**, *51*, 1185–1195. (g) Tobisu, M. C–O Bond Transformations. In *Nickel Catalysis in Organic Synthesis: Methods and Reactions.*; Wiley, 2019; pp 123–149. (h) Boit, T. B.; Bulger, A. S.; Dander, J. E.; Garg, N. K. Activation of C–O and C–N Bonds Using Non-Precious-Metal Catalysis. *ACS Catal.* **2020**, *10*, 12109–12126.

(7) Somerville, R. J.; Hale, L. V. A.; Gómez-Bengoa, E.; Burés, J.; Martin, R. Intermediacy of Ni–Ni Species in sp² C–O Bond Cleavage of Aryl Esters: Relevance in Catalytic C–Si Bond Formation. *J. Am. Chem. Soc.* **2018**, *140*, 8771–8780.

(8) For related Ni-Ni complexes supported by phosphine ligands, *N*-heterocyclic carbenes or diimine ligands, see: (a) Velian, A.; Lin, S.; Miller, A. J. M.; Day, M. W.; Agapie, T. Synthesis and C–C Coupling Reactivity of a Dinuclear Ni^I–Ni^I Complex Supported by a Terphenyl Diphosphine. *J. Am. Chem. Soc.* **2010**, *132*, 6296–6297. (b) Beck, R.; Johnson, S. A. Structural Similarities in Dinuclear, Tetranuclear, and Pentanuclear Nickel Silyl and Silylene Complexes Obtained via Si–H and Si–C Activation. *Organometallics* **2012**, *31*, 3599–3609. (c) Zhou, Y.-Y.; Hartline, D. R.; Steiman, T. J.; Fanwick, P. E.; Uyeda, C. Dinuclear Nickel Complexes in Five States of Oxidation Using a Redox-Active Ligand. *Inorg. Chem.* **2014**, *53*, 11770–11777. (d) Matsubara, K.; Yamamoto, H.; Miyazaki, S.; Inatomi, T.; Nonaka, K.; Koga, Y.; Yamada, Y.; Veiros, L. F.; Kirchner, K. Dinuclear Systems in the Efficient Nickel-Catalyzed Kumada-Tamao-Corriu Cross-Coupling of Aryl Halides. *Organometallics* **2017**, *36*, 255–265. (e) Powers, I. G.; Andjaba, J. M.; Zeller, M.; Uyeda, C. Catalytic C(sp²)–H Amination Reactions Using Dinickel Imides. *Organometallics* **2020**, *39*, 3794–3801.

(9) For selected reviews of metal-metal bonds, see: (a) Inatomi, T.; Koga, Y.; Matsubara, K. Dinuclear Nickel(I) and Palladium(I) Complexes for Highly Active Transformations of Organic Compounds. *Molecules* **2018**, *23*, 140–161. (b) Powers, I. G.; Uyeda, C. Metal–Metal Bonds in Catalysis. *ACS Catal.* **2017**, *7*, 936–958. (c) Xu, W.; Li, M.; Qiao, L.; Xie, J. Recent advances of dinuclear nickel- and palladium-complexes in homogeneous catalysis. *Chem. Commun.* **2020**, *56*, 8524–8536. (d) Xiong, N.; Zhang, G.; Sun, X.; Zeng, R. Metal-Metal Cooperation in Dinucleating Complexes Involving Late Transition Metals Directed towards Organic Catalysis. *Chin. J. Chem.* **2020**, *38*, 185–201. (e) Uyeda, C.; Farley, C. M. Dinickel Active Sites Supported by Redox-Active Ligands. *Acc. Chem. Res.* **2021**, *54*, 3710–3719.

(10) For an elegant aromatic rearrangement enabled by Pd catalysts via aryne intermediates: (a) Matsushita, K.; Takise, R.; Muto, K.; Yamaguchi, J. Ester dance reaction on the aromatic ring. *Sci. Adv.* **2020**, *6*, eaba7614. (b) Kubo, M.; Inayama, N.; Ota, E.; Yamaguchi, J. Palladium-catalyzed tandem ester dance/decarbonylative coupling reactions. *Org. Lett.* **2022**, *24*, 3855–3860.

(11) For base-promoted halogen dance reactions: (a) Bunnett, J. F. Base-catalyzed halogen dance, and other reactions or

aryl halides. *Acc. Chem. Res.* **1972**, *5*, 139–147. For an Ir-catalyzed boron translocation, see: (b) Eliseeva, M. N.; Scott, L. T. Pushing the Ir-catalyzed C–H polyborylation of aromatic compounds to maximum capacity by exploiting reversibility. *J. Am. Chem. Soc.* **2012**, *134*, 15169–15172.

(12) For selected references of *ortho* C(sp^2)–H functionalization of C–O electrophiles driven by metalation techniques, see: (a) Sibi, M. P.; Snieckus, V. The Directed Ortho Lithiation of *O*-Aryl Carbamates. An Anionic Equivalent of the Fries Rearrangement. *J. Org. Chem.* **1983**, *48*, 1935–1937. (b) Vabre, B.; Deschamps, F.; Zargarian, D. Ortho Derivatization of Phenols through C–H Nickelation: Synthesis, Characterization, and Reactivities of Ortho-Nickelated Phosphinite Complexes. *Organometallics* **2014**, *33*, 6623–6632. (c) Mangin, L. P.; Zargarian, D. C–H nickellation of phenol-derived phosphinites: regioselectivity and structures of cyclonickellated complexes. *Dalton Trans.* **2017**, *46*, 16159–16170. (d) Jalil Miah, M. A.; Sibi, M. P.; Chattopadhyay, S.; Familoni, O. B.; Snieckus, V. Directed *ortho*-Metalation of Aryl Amides, *O*-Carbamates, and Methoxymethoxy Systems: Directed Metalation Group Competition and Cooperation. *Eur. J. Org. Chem.* **2018**, 447–454.

(13) For selected references: (a) Gaydou, M.; Moragas, T.; Juliá-Hernández, F.; Martin, R. Site-Selective Catalytic Carboxylation of Unsaturated Hydrocarbons with CO_2 and Water. *J. Am. Chem. Soc.* **2017**, *139*, 12161–12164. (b) Juliá-Hernández, F.; Moragas, T.; Cornella, J.; Martin, R. Remote carboxylation of halogenated aliphatic hydrocarbons with carbon dioxide. *Nature* **2017**, *545*, 84–88. (c) Sun, S.-Z.; Börjesson, M.; Martin-Montero, R.: Martin, R. Site-Selective Ni-Catalyzed Reductive Coupling of alpha-Haloboranes with Unactivated Olefins. *J. Am. Chem. Soc.* **2018**, *140*, 12765–12769. (d) Sun, S.-Z.; Romano, C.; Martin, R. Site-Selective Catalytic Deaminative Alkylation of Unactivated Olefins. *J. Am. Chem. Soc.* **2019**, *141*, 16197–16201. (e) Yue, W.-J.; Martin, R. Ni-Catalyzed Site-Selective Hydrofluoroalkylation of Terminal and Internal Olefins. *ACS Catal.* **2022**, *12*, 12132–12137. (f) Buendia, M. K.; Higginson, B.; Kegnaes, S.; Kramer, S.; Martin, R. Redox-Neutral Ni-Catalyzed sp^3 C–H Alkylation of α-Olefins with Unactivated Alkyl Bromides. *ACS Catal.* **2022**, *12*, 3815–3820. (g) Rodrigalvarez, J.; Wang, H.; Martin, R. Native Amides as Enabling Vehicles for Forging sp^3–sp^3 Architectures via Interrupted Deaminative Ni-Catalyzed Chain-Walking. *J. Am. Chem. Soc.* **2023**, *145*, 3869–3874.

(14) See Supporting Information for details.

(15) Selected examples: (a) Selmeczy, A. D.; Jones, W. D. Partridge, M. G.; Perutz, R. N. Selectivity in the activation of fluorinated aromatic hydrocarbons by rhodium complexes [(C5H5)Rh(PMe3)] and [(C5Me5)Rh(PMe3)]. *Organometallics* **1994**, *13*, 522–532. (b) Evans, M. E.; Burke, C. L.; Yaibuathes, S.; Clot, E.; Eisenstein, O.; Jones, W. D. Energetics of C–H Bond Activation of Fluorinated Aromatic Hydrocarbons Using a [Tp'Rh(CNneopentyl)] Complex. *J. Am. Chem. Soc.* **2009**, *131*, 13464–13473. (c) Obligacion, J. V.; Bezdek, M. J.; Chirik, P. J. C(sp^2)–H Borylation of Fluorinated Arenes Using an Air-Stable Cobalt Precatalyst: Electronically Enhanced Site Selectivity Enables Synthetic Opportunities. *J. Am. Chem. Soc.* **2017**, *139*, 2825–2832. (d) Shi, X.; Mao, S.; Soulé, J.-F.; Doucet, H. Reactivity of 1,2,3- and 1,2,4-Trifluorobenzenes in Palladium-Catalyzed Direct Arylation. *J. Org. Chem.* **2018**, *83*, 4015–4023. (e) Pabst, T. P.; Obligacion, J. V.; Rochette, É.; Pappas, I.; Chirik, P. J. Cobalt-Catalyzed Borylation of Fluorinated Arenes: Thermodynamic Control of C(sp^2)–H Oxidative Addition Results in *ortho*-to-Fluorine Selectivity. *J. Am. Chem. Soc.* **2019**, *141*, 15378–15389.

(16) Unfortunately, all our attempts to prepare analytically-pure **4** and **7** were unsuccessful due to their inherent instability. Therefore, their formation was monitored *in situ*.

(17) Day, C. S.; Somerville, R. J.; Martin, R. Deciphering the dichotomy exerted by Zn(II) in the catalytic sp^2 C–O bond functionalization of aryl esters at the molecular level. *Nat. Cat.* **2021**, *4*, 124–133.

(18) Consistent with their well-resolved NMR spectra, magnetic measurements of these complexes confirmed that these structures are diamagnetic with a single ground state. See ref. 12.

(19) For selected reviews on concerted metalation-deprotonation in C–H functionalization reactions, see: (a) Lapointe, D.; Fagnou, K. Overview of the Mechanistic Work on the Concerted Metallation-Deprotonation Pathway. *Chem. Lett.* **2010**, *39*, 1118–1126. (b) Gorelsky, S. I. Origins of regioselectivity of the palladium-catalyzed (aromatic)C–H bond metalation-deprotonation. *Coord. Chem. Rev.* **2013**, *257*, 153–164. (c) Kapdi, A. R. Organometallic aspects of transition-metal catalysed regioselective C–H bond functionalization of arenes and heteroarenes. *Dalton Trans.* **2014**, *43*, 3021–3034.

(20) For a formal C–H functionalization enabled by 1,2-addition, see ref. 8e.