

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

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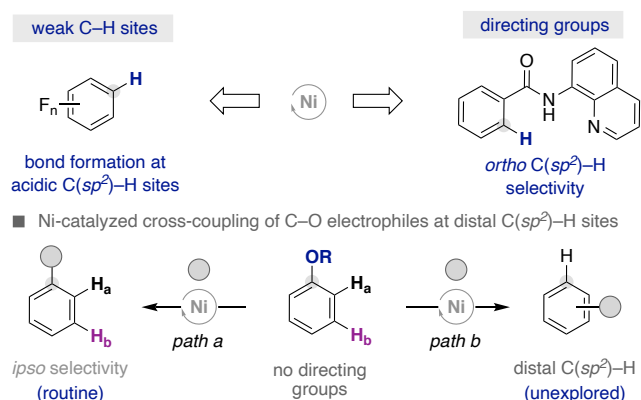
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Supporting Information Placeholder

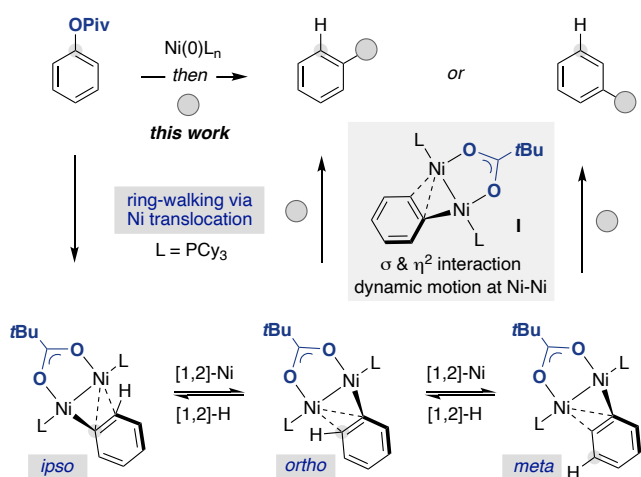
ABSTRACT: Herein, we report the utilization of Ni–Ni species as a manifold for enabling a “ring-walking” event by a dynamic translocation of the metal center over the arene backbone. Experimental and computational studies support a translocation occurring via a 1,2-hydride shift. The synthetic applicability 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 d¹⁰ 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 halides⁵ 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.

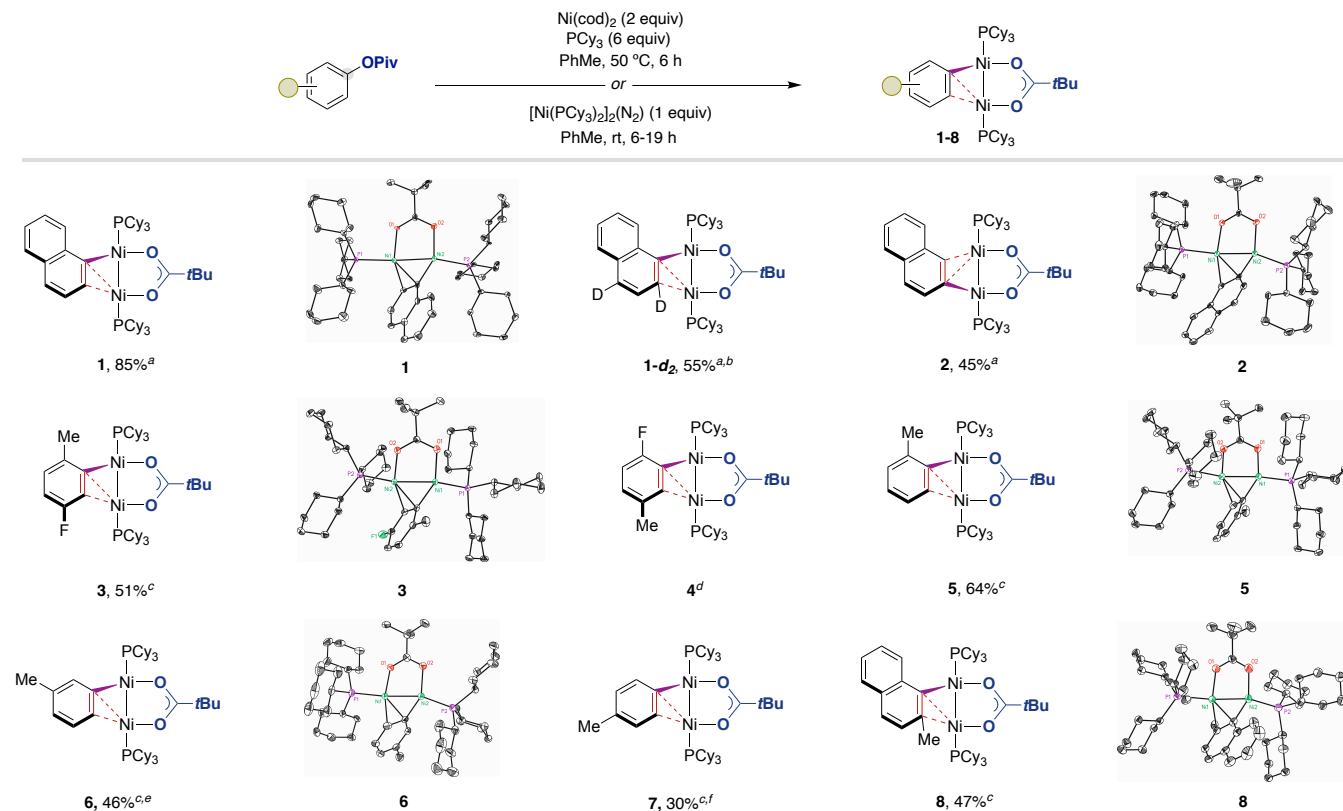


Recently, our group described the involvement of unorthodox dinickel oxidative addition complexes **I** in the C–O bond-cleavage of aryl pivalates (Scheme 2).⁷ The arene fragment interacts with the Ni–Ni core via both a σ -bond and a η^2 -interaction, with a bridging pivalate between the two Ni centers.^{8,9} 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(sp^2) site by forming a new σ -bond and a η^2 -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(sp^2)-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), PCy₃ (6 equiv) in toluene (0.1 M), 50 °C for 6 h. ^b 4 h. ^c Conditions: Aryl pivalate (1.1-1.6 equiv), [Ni(PCy₃)₂]₂(N₂) (1 equiv) in toluene (0.1 M), rt for 6 h. ^d Complex **4** was characterized *in situ* due to its instability. ^e Using *m*-tolyl pivalate at rt for 12 h, resulting in **6**:**7** (86:14 ratio). ^f Utilizing *p*-tolyl pivalate at rt for 19 h, resulting in **6**:**7** (88:12 ratio).

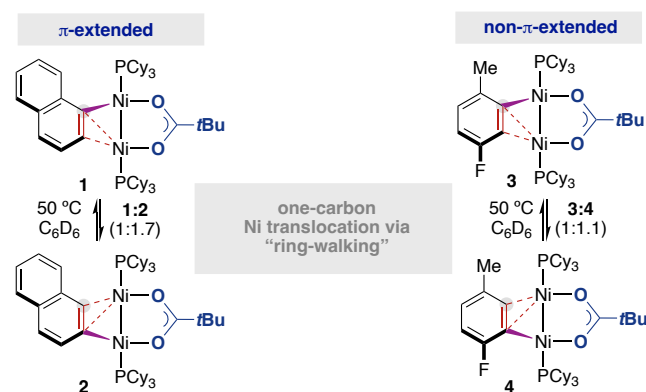
Our study began by preparing a representative set of Ni-Ni complexes by exposure of aryl pivalates to Ni(cod)₂/PCy₃ at 50 °C or [Ni(PCy₃)₂]₂N₂ at rt in toluene (Scheme 3).¹⁴ The choice of **1-8** was not arbitrary; **1** and **2** were designed to study the dynamics on π -extended systems – substrates particularly suited for Ni-catalyzed C-O functionalization⁶ – 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 grounds¹⁵ 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 °C by ³¹P{¹H}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 °C. Intriguingly, an equimolar ratio of **3**:**4** was found when monitoring the isomerization of **3** at 50 °C over 6 h, thus arguing against the positive impact that fluorine atoms might have for stabilizing adjacent σ C(sp^2)–metal bonds.¹⁵ While isomerization of analytically-pure **5** at 50 °C revealed rapid formation of **5**:**6**:**7** in a 1:4.7:1.4 ratio after 4 h, nickel translocation could also be enabled at rt leading to an otherwise identical ratio of **5**:**6**:**7** from pure **5** after 6 days or from **6**:**7** mixtures (86:14) after 24 h (Scheme 5). Notably, **I** was not detected in the crude mixtures. This observation could be interpreted on the basis of the computed energies for the complexes depicted in Scheme 5, corroborating that **I** was the less stable isomer in the Ni–Ni series.¹⁴

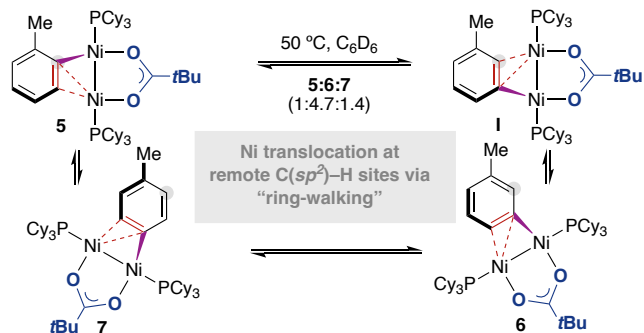
Scheme 4. Ring-Walking of Ni–Ni species **1** & **3**.^a



^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)(PCy₃) and Ni(0)(PCy₃) species,⁷ we wondered whether the presence of additional PCy₃ might destabilize the Ni–Ni core, either facilitating the formation of aryl–Ni(κ^1 -OPiv)(PCy₃)₂ or “ring-walking” by binding Ni(0)(PCy₃)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 PCy₃ resulted in a 1:1.4 ratio of **1**:**2** after 7 days at 50 °C. Similarly, a deleterious effect was observed in the presence of external bases such as CsOPiv or Cs₂CO₃,¹⁴ 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 “ring-walking” event.

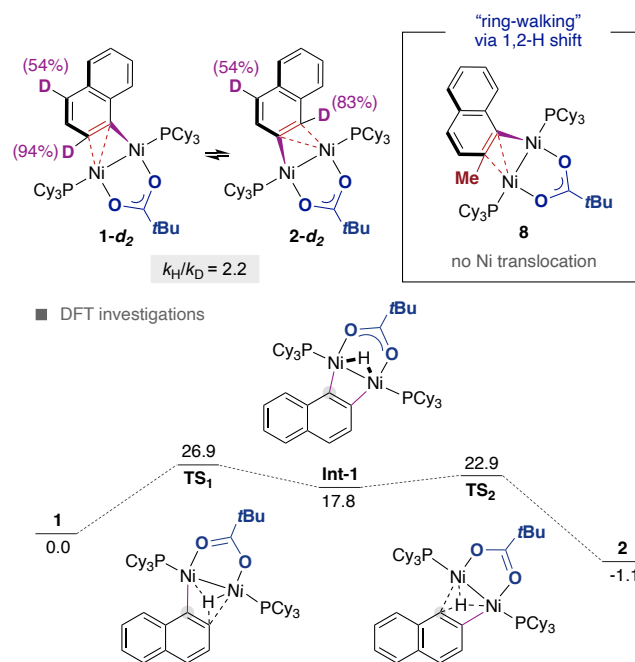
Scheme 5. Ni Translocation at Remote C(sp^2)–H Sites.^a



^a An identical ratio was observed when utilizing **6**:**7** mixtures regardless whether the translocation was effected at rt or 50 °C.

Next, we decided to gather indirect evidence about the ring-walking event by studying the behavior of **1-d**₂ (Scheme 6). As expected, the label at C2 was transferred to the C1 site in **2-d**₂. Notably, no “ring-walking” was observed with **8**, hence reinforcing the notion that Ni translocation is likely driven by a 1,2-hydride shift. In addition, a primary kinetic isotope effect was observed when comparing the initial rates of **1** & **1-d**₂ from parallel experiments ($k_H/k_D = 2.2$). This value was in agreement with our observed computed value ($k_H/k_D = 3.1$), thus suggesting a rate-determining C(sp^2)–H bond-cleavage.

Scheme 6. Isotope-Labeling & DFT Studies.^a

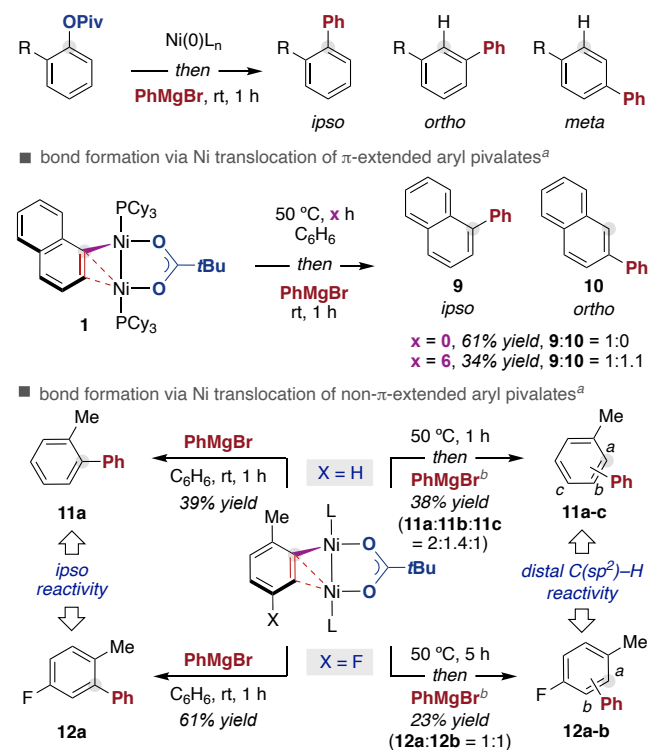


^a Free energy profile. Energies in kcal·mol⁻¹, calculated at the M06/def2-tzvp level with solvent (PhMe) correction.

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-tzvp//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 in **Int-1**.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). It is worth noting that a Ni–Ni bond is observed through the process, maintaining an otherwise similar Ni–Ni linkage of 2.36 Å for **1** and **2**, and 2.38 Å for **Int-1**, thus indirectly suggesting that the bridging hydride and pivalate fragment might not affect the identity of the dinuclear Ni–Ni core in **Int-1**. 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.

Scheme 7. Bond Formation at Distal C(sp²)–H Sites.



^a ipso-Functionalization: **1**, **3** or **5** (0.01–0.03 mmol), PhMgBr (1 equiv) in C₆D₆ (0.06 M), rt, 1 h. GC yields using *n*-decane as internal standard (**9**, **11a**) or ¹⁹F NMR yields using C₆H₅CF₃ as internal standard (**12a**); distal-functionalization: **1**, **3** or **5** (0.01–0.03 mmol) in C₆D₆ (0.06 M), 50 °C for the indicated time, then PhMgBr (1 equiv), rt, 1 h. GC yields using *n*-decane as an internal standard (**10**, **11a–c**) or ¹⁹F NMR yields using C₆H₅CF₃ as internal standard. ^b in C₆H₆ at rt for 1 h.

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(sp²)–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 °C for 6 h,²¹ thus confirming that “ring-walking” might constitute a new vehicle for enabling bond formation at distal C(sp²)–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(sp²)–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(sp²)–H sites initiated via functionalization of strong C–O linkages.²² 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)

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