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Carbonylative Coupling of Alkyl Zinc Reagents with Benzyl Bromides Catalyzed by an NN_2 Pincer Ligand Nickel Complex

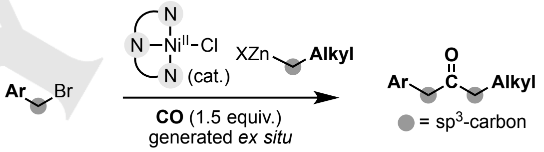
Thomas L. Andersen,[a] Aske S. Donslund,[a] Karoline T. Neumann[a] and Troels Skrydstrup[a]*

Abstract: An efficient catalytic protocol for the three-component assembly of benzyl bromides, carbon monoxide and alkyl zinc reagents to benzyl alkyl ketones is described, representing the first Ni-catalyzed carbonylative coupling of two sp^3-carbon fragments. The method, which relies on the application of NN_2-type pincer ligand nickel complexes and a controlled release of CO gas from a solid precursor, works well with a range of benzylic bromides. Mechanistic studies suggest the intermediacy of carbon-centered radicals.

Over 40 years ago, Richard Heck and coworkers reported their pioneering work on the Pd-catalyzed carbonylation reaction of aryl halides with N- and O-nucleophiles.[1] Since then, these carbonylation reactions have been expanded to the use of C-nucleophiles as well, and today three-component versions of the Negishi, Suzuki, Sonogashira, Stille and Hiyama couplings with carbon monoxide have become common-use.[2] In contrast to palladium, carbonylation reactions mediated by nickel catalysts are far less prominent, which is surprising considering the current and high focus from the chemical community to develop catalysts based on earth abundant transition metals.

The underdeveloped state of Ni-catalyzed carbonylative cross-coupling is undoubtedly related to the strong binding affinity of CO to nickel leading to toxic Ni-carbonyl complexes (e.g. $Ni(CO)_4$).[3] A number of early examples on the use of stoichiometric $Ni(CO)_4$ in carbonylation reactions do exist,[4] but the use of this and related species for catalytic purposes is limited.[5] Recently, a few groups have relied on the use of CO surrogates for the slow release of this diatomic gas as a means to counteract the formation of inactive Ni-carbonyl species.[6] For example, Ogoshi and coworkers successfully applied phenylformate in a Ni(0)-catalyzed aza-Pausen-Khand reaction for accessing γ-lactams, whereas direct exposure to CO gas hampered the carbonylative cycloaddition.[7] Similarly, the groups of Troupel and Weix relied on $Fe(CO)_5$ as the CO-source for demonstrating the concept of Ni(0)-catalyzed carbonylative cross-electrophile coupling between aryl and alkyl halides.[8]

In an effort to identify suitable conditions for the first Ni-catalyzed carbonylative coupling between a C(sp^3)-nucleophile and C(sp^3)-electrophile, we examined an alternative approach for carrying out such catalytic carbonylations with Ni-complexes that would be less sensitive to the concentration of CO. We reasoned that Ni(II) pincer complexes may be suitable due to the strong and three-point binding of the pincer ligand to the metal center, thereby possibly preventing multiple CO binding on some of the reactive intermediates. Herein, we report the application of such a Ni(II) pincer complex for the successful carbonylative Negishi coupling between alkyl zinc reagents with benzyl bromides in a CO atmosphere applying our two-chamber technology (Scheme 1).[9] Many of these fast coupling reactions prove to be high yielding and function at near ambient temperature. A prominent feature of these reactions is the viability of sp^3-derived building blocks, which are problematic components in the analogous plethora of Pd-catalyzed carbonylation reactions, due to the inherent tendency of palladium alkyl complexes to undergo β-hydride elimination.[10,11]



Scheme 1. General strategy for Ni-catalyzed carbonylative coupling of sp^3-carbon fragments.

We started our work, by investigating a set of nickel(II) pincer complexes (**NiL1**–**NiL3**)[12–15] by ^1H and ^{13}C NMR spectroscopy for their ability to mediate a sequence of discrete reaction steps (Scheme 2). These steps consisted of transmetallation with an organometallic reagent (e.g. propyl zinc bromide) followed by migratory insertion with ^{13}CO to produce a Ni-acyl species (Scheme 2). Efficient transmetallation was observed in all three cases, but only the use of **NiL3** led to the formation of a stable acyl species, as indicated by a singlet resonating at $\delta = 270.5$ ppm in ^{13}C NMR spectrum. Both **NiL3** and the acyl species were found to be stable over a prolonged period of exposure to excess ^{13}CO in THF (1 h, 30−50 °C). Furthermore, we found that the *in situ* generated acyl species was consumed by the addition of benzyl bromide, with concomitant formation of **^{13}C-2a** as the major species as determined by ^{13}C NMR spectroscopy. Without optimization, **^{13}C-2a** could be isolated in a 40% yield by this approach.

To convert these stoichiometric experiments to a catalytic protocol, we commenced optimization studies with **NiL3** in the carbonylative coupling between BnBr and *n*Pr-ZnBr. For this purpose, a two-chamber setup was employed, where CO gas could be generated in a controlled rate from a solid precursor in order to limit the exposure of the catalytic system to excess CO (see Supporting Information). Conducting the reaction at 50 °C in butyronitrile and THF, employing **NiL3** (5 mol%) and 1.5

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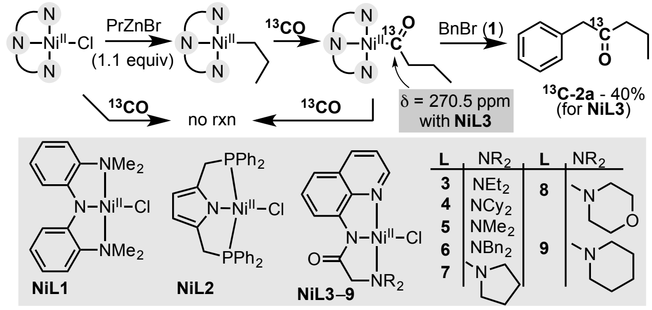
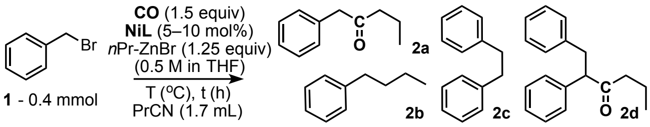


Scheme 2. Stoichiometric reaction sequence and pincer complexes.

equivalents of CO with stirring for 5 h, led to the formation of **2a** in a 13% yield (Table 1, entry 1). Performing the reaction solely in THF afforded only trace amounts of the product (entry 2). In both cases considerable amounts of side products were observed including direct coupling to **2b** and homocoupling to **2c**. In most reactions, minor quantities of the product **2d** could also be observed along with traces of dibenzylketone.

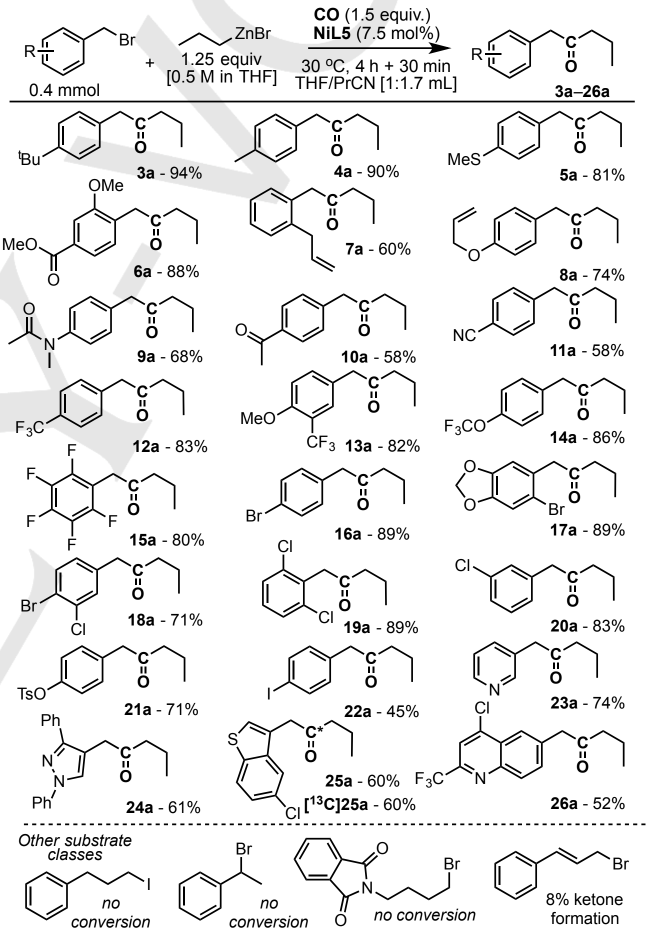
Table 1. Initial results and optimization.[a]



#	Deviations from std. conditions	t [h]	T [°C]	NiL [mol%]	2a/2b/2c/2d [%][b]
1	none	5	50	**NiL3**[5]	**13**/38/10/3
2	in THF	5	50	**NiL3**[5]	**2**/17/29/1
3	none	5	30	**NiL3**[5]	**35**/2/2/16
4	none	5	25	**NiL3**[5]	**22**/1/1/18
5	none	5	30	**NiL3**[10]	**36**/21/6/4
6	slow add. of 1	2	30	**NiL3**[10]	**40**/1/1/4
7	slow add. of 1	2	30	**NiL4**[10]	**0**/13/2/0
8	slow add. of 1	2	30	**NiL5**[10]	**56**/11/2/1
9	slow add. of 1	2	30	**NiL6**[10]	**50**/10/6/1
10	slow add. of 1	2	30	**NiL7**[10]	**45**/12/1/0
11	slow add. of 1	2	30	**NiL8**[10]	**44**/22/1/0
12	slow add. of 1	2	30	**NiL9**[10]	**56**/15/2/0
13	slow add. of 1	4+½	30	**NiL5**[7.5]	**92**[c]/1/0/0

[a] All reactions were conducted in a two-chamber setup, in which CO was released from a solid precursor in one chamber; see Supporting Information for full detail. [b] Yields determined by GC using dodecane as internal standard. [c] Isolated yield.

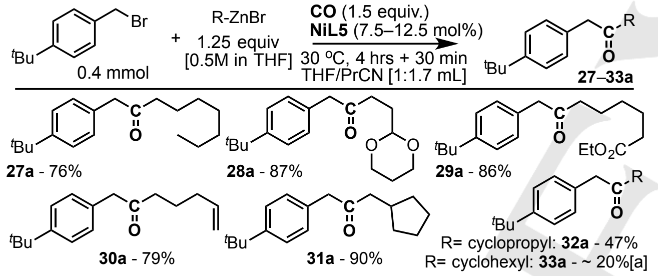
The selectivity and yield for **2a** could be increased considerably (35% yield) by lowering the reaction temperature to 30–35 °C (entry 3). Attempts at lower reaction temperatures (entry 4) or increasing the amount of catalyst (entry 5) were not beneficial. As compound **2c**[16] was suspected to be derived from a side reaction involving unreacted BnBr, we attempted to diminish this pathway by maintaining a low concentration of the starting benzyl bromide. Thus, by adding a stock solution of **1** to a stirred solution of **NiL3** and *n*Pr-ZnBr over 2 h, **2a** was formed in a 40% yield while side product formation was minimal (entry 6). Next, the effect of the substitution pattern on the pincer ligand amine moiety was investigated (entries 7–12). The best results were obtained by applying the *N*,*N*-dimethyl analog **NiL5** (7.5 mol%), which in combination with the addition of BnBr over a 4 h period, furnished the desired ketone **2a** in an isolated yield of 92% (entry 13). Remarkably, when **NiL5** was employed in the reaction sequence depicted in Scheme 2, it was possible to isolate ^{13}**C-2a** in 99% yield (see Supporting Information). Control experiments revealed that the absence of a Ni-based catalyst leads to no product formation. Moreover, the use of NiCl$_2$•DME as a Ni(0)-precursor did not result in any conversion of the starting bromide. The latter finding supports the suggestion that low valent Ni-carbonyl species are not involved in the transformation.



Scheme 3. Scope of benzyl bromides. All reactions were conducted in a two-chamber setup, in which CO was released from a solid precursor in one chamber; see Supporting Information for full detail. Yields are isolated and are an average of two separate reactions.

The substrate scope for the catalytic reaction is illustrated in Scheme 3. In general, many functionalities on the aromatic ring of benzyl bromide are well-tolerated under unaltered reaction conditions providing the desired ketones in good to excellent yields. This includes alkyl (**3a** and **4a**), sulfur and oxygen (**5a**, **6a** and **8a**) substituents, as well as 2-allyl, ester, acetamide, ketone and cyano groups (**7a**, **9a**–**11a**). In contrast, neither a nitro group nor a *N*-Boc protected amine were compatible with the developed conditions (not shown). A range of polyfluorinated benzylic bromides proved to be excellent substrates in the carbonylative transformation, affording the desired products **12a**–**15a**. Halides on the aromatic ring such as bromide and chloride were untouched (compounds **16a**–**20a)**, thereby allowing for the possibility of sequential cross-coupling reactions. An aryl tosylate could also be employed to furnish the corresponding ketone **21a**. On the other hand, the use of a substrate with an aryl iodide proved less optimal, but nevertheless provided the carbonylative product **22a** in a reproducible fashion and an acceptable yield. Finally, the feasibility of bromomethylated heteroaromatics as coupling partners was tested affording ketones **23a**–**26a** in satisfactory yields. As demonstrated by the synthesis of compound **[^{13}C]25a**, the use of a two-chamber system for *ex situ* generation of carbon monoxide provides a convenient platform for isotope labeling, by simply substituting the CO releasing molecule for a ^{13}C-labeled analog.

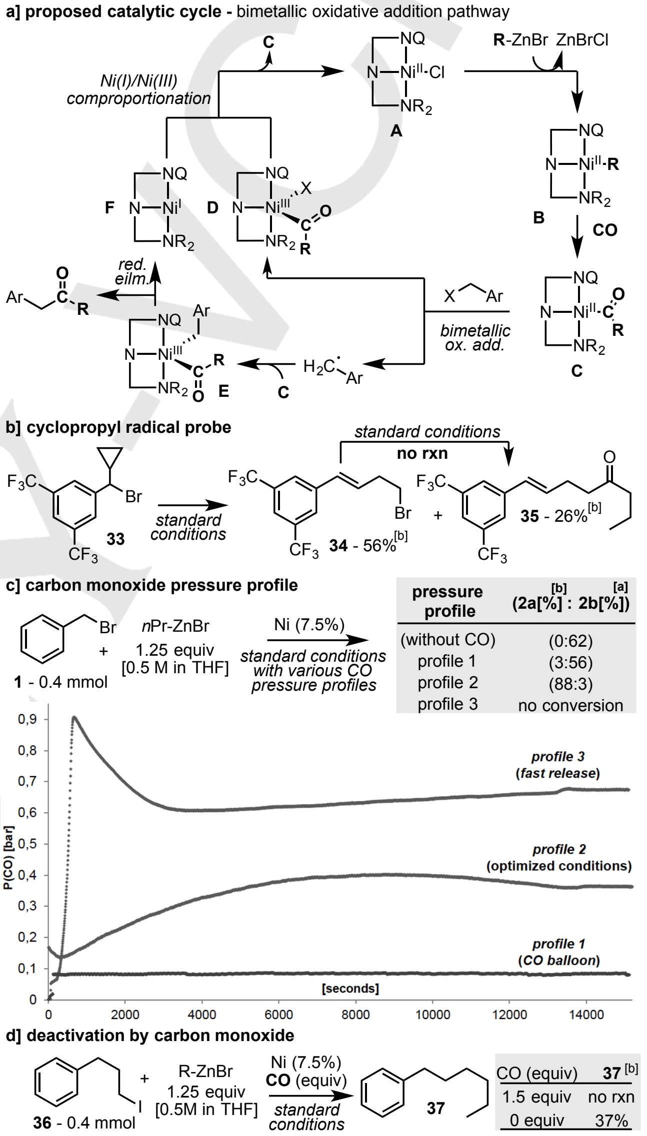
Attempts to employ (1-bromoethyl)benzene in the catalytic coupling led to no overall conversion. Presumably the increased bulk of this secondary bromide is not viable. Similarly, no reactivity was observed with a primary alkyl iodide or bromide. Cinnamyl bromide provided the linear carbonylation product in 8% isolated yield, while the corresponding alkylation product was formed in 16%, suggesting that this substrate class may be suitable, with further optimization.



Scheme 4. Scope of alkyl zinc reagents. All reactions were conducted in a two-chamber setup, in which CO was released from a solid precursor in one chamber; see Supporting Information for full detail. Yields are isolated and are an average of two separate reactions. [a] Compound not isolated.

A selection of alkyl zinc reagents was also tested in the coupling with 4-*tert*-butylbenzyl bromide under unaltered conditions (Scheme 4). Pleasingly, all of the primary alkyl zinc reagents examined proved to be efficient coupling partners, whereby the best results could be obtained with a small increase in the catalytic loading of **NiL5**. This afforded the ketones **27a**–**30a** bearing substituents such as an ethyl carboxylate, an acetal and a terminal olefin in good to excellent yields. We also found that increased sterical hindrance on the C2-position of the alkyl zinc reagent is tolerated as demonstrated in the synthesis of **31a** in 90% yield. Nevertheless, with secondary alkyl zinc reagents the scope becomes more limited. For instance, the cyclopropyl benzyl ketone **32a** could be prepared in a 47% isolated yield, but the use of a cyclohexyl zinc reagent led to less than 20% of **33a**. Stoichiometric experiments have shown that the main issue for this compound is a non-optimal transmetallation step.[17]

The mechanism of a related nickel(II) pincer complex catalyzed Kumada coupling has been investigated thoroughly by the group of Xile Hu.[18] They propose a bimetallic oxidative addition pathway[19] where single electron transfer from a nickel(II) alkyl complex to organic halides occurs to form two distinct nickel(III) species. A similar mechanistic scenario could operate in the present case (Scheme 5a). Here, the catalytic cycle would be initiated by transmetallation of the starting nickel(II) complex **A** to give a nickel(II) alkyl complex **B** that inserts CO to yield the corresponding nickel(II) acyl complex **C**.



Scheme 5. Mechanistic assays and proposed mechanism. See Supporting Information for full detail. [a] Yield determined by GC using dodecane as internal standard. [b] Isolated yield.

Single electron transfer from this species to the electrophile leads to the nickel(III) complex **D** and a benzylic radical. Recombination of the radical with a second nickel(II) acyl species **C** provides a formal nickel(III) acyl-alkyl complex **E**, which undergoes reductive elimination to expel the product while forming a nickel(I) species **F**. Comproportionation with **D** generates the two nickel(II) complexes **A** and **C**, which can reenter the catalytic cycle.[20]

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Several experiments were performed to support the involvement of radical intermediates. The carbonylative coupling between benzyl bromide and *n*Pr-ZnBr was inhibited by the addition of 1,4-dinitrobenzene (20 mol%), which serves as a reversible electron acceptor (See Supporting Information).[21] Furthermore, employing **33** as the electrophile, led to ring opening of the cyclopropyl moiety to form **35** in a 26% yield, being consistent with the proposed intermediacy of a benzylic radical (Scheme 5b).[22] The main product from this reaction was the primary bromide **34**, however, control reactions confirmed that this structure is not a viable precursor for **35** under the employed conditions.

The role of carbon monoxide in the proposed mechanism was examined by analyzing the effect of the reaction pressure profile in bar on the outcome of the coupling between benzyl bromide and *n*Pr-ZnBr (Scheme 5c). As expected, the only major outcome observed in the absence of CO was direct alkylation to give **2b** in a 62% yield. Curiously, we found that a very similar product distribution was formed when CO (approx. 5 mmol) was applied from a balloon, giving rise to only trace amounts of the carbonylation product under such low pressure conditions (profile 1). In contrast to these results, the slow release of CO, which are employed under the optimized conditions, lead to near perfect selectivity between **2a** and **2b**, the former of which could be isolated in this case in 88% yield (profile 2). Modulating the conditions to ensure rapid CO-release leads to catalyst inactivation, and no overall conversion of the starting bromide is observed (profile 3). Thus, it seems that although the starting nickel(II) halide (**A**) and the proposed nickel(II) acyl species (**C**) are stable to excess CO gas, the system remains vulnerable to high concentrations CO. We suggest that the proposed Ni(I) and Ni(III) intermediates react with CO to generate inactive off-cycle species. On the other hand, when the partial pressure of CO is too low, direct alkylation becomes the dominant pathway.

Finally, we found that no conversion of 3-iodo-1-phenyl propane (**36**) occurred under standard carbonylation conditions (Scheme 5d), but in the absence of CO, the corresponding alkylation took place in 37% yield. This suggests that the nickel(II) alkyl complex **B**, being generated upon transmetallation, is capable of activating both alkyl and benzyl halides, whereas the corresponding nickel(II) acyl complex **C**, is only reactive in presence of more activated benzylic substrates. Most likely, this is a consequence of the electronic differences between the two complexes invoked by the binding of CO.

In conclusion, a NN_2-type pincer ligand nickel(II) complex has been employed along with a controlled release of CO gas, in order to facilitate Ni-catalyzed carbonylation to produce a range of benzyl alkyl ketones. The method represents the first carbonylative assembly of two sp^3-hybridized carbon fragments, which is catalyzed by nickel. Further studies are underway to identify other nickel based pincer complexes for expanding the scope of this reaction to other alkyl halides.

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Keywords: • Carbonylation • nickel catalysis • Pincer ligand

[1] a) A. Schoenberg, R. F. Heck, *J. Am. Chem. Soc.* **1974**, *96*, 7761–1764. b) A. Schoenberg, R. F. Heck, *J. Org. Chem.* **1974**, *39*, 3327–3331. c) A. Schoenberg, I. Bartoletti, R. F. Heck, *J. Org. Chem.* **1974**, *39*, 3318–3326.

[2] a) A. Brennführer, H. Neumann, M. Beller, *Angew. Chem. Int. Edit.* **2009**, *48*, 4114–4133. b) X. F. Wu, H. Neumann, M. Beller, *Chem. Soc. Rev.* **2011**, *40*, 4986–5009.

[3] a) M. F. Semmelhack, P. M. Helquist, *Org. Synth.* **1972**, *52*, 115–121. b) *The Merck Index. 10th ed.* Rahway, New Jersey: Merck Co., Inc., **1983**, 93.

[4] a) N. L. Bauld, *Tetrahedron Lett.* **1963**, *27*, 1841–1845. b) G. P. Chiusoli, L. Cassar, *Angew. Chem. Int. Edit.* **1967**, *6*, 124–133. c) E. Yoshisato. S. Tsutsumi, *J. Org. Chem.* **1968**, *33*, 869–871. d) I. Rhee, M. Ryang, T. Watanabe, H. Omura, S. Murai, N. Sonoda, *Synthesis*, **1977**, *11*, 776–777. e) E. R. H. Jones, G. H. Whitham, M. C. Whiting, *J. Chem. Soc.* **1957**, *0*, 4628–4633.

[5] a) Q. L. Wang, C. Chen, *Tetrahedron Lett.* **2008**, *49*, 2916–2922. b) L. Cassar, M. Foa, *J. Organomet. Chem.* **1973**, *51*, 381–393. c) I. Amer, H. Alper, *J. Org. Chem.* **1988**, *53*, 5147–5148. d) H. Arzoumanian, F. Cochini, D. Nuel, N. Rosas, *Organometallics* **1993**, *12*, 1871–1875. e) H. Arzoumanian, M. Jean, D. Nuel, A. Cabrera, J. L. G. Gutierrez, N. Rosas, *Organometallics* **1995**, *14*, 5438–5441. f) N. Satyanarayana, H. Alper, I. Amer, *Organometallics* **1990**, *9*, 284–286. g) H. Alper, I. Amer, G. Vasapollo, *Tetrahedron Lett.* **1989**, *30*, 2615–2616. h) H. Alper, G. Vasapollo, *Tetrahedron Lett.* **1989**, *30*, 2617–2618. i) J. Tjutrins, J. L. Shao, V. Yempally, A. A. Bengali, B. A. Arndtsen, *Organometallics* **2015**, *34*, 1802–1805.

[6] For the use of DMF as CO source in Ni-catalyzed carbonylation for the synthesis of symmetrical biaryl ketones, see: a) Y. Li, D.-H. Tu, B. Wang, J-Y. Lu, Y.-Y. Wang, Z.-T. Liu, Z.-W. Liu, J. Lu, *Org. Chem. Front.* **2017**, *4*, 569–572. For the synthesis of phthalimides, see: X. Wu, Y. Zhao, H. Ge, *J. Am. Chem. Soc.* **2015**, *137*, 4924–4927.

[7] a) Y. Hoshimoto, T. Ohata, Y. Sasaoka, M. Ohashi, S. Ogoshi, *J. Am. Chem. Soc.* **2014**, *136*, 15877–15880. b) Y. Hoshimoto, K. Ashida, Y. Sasaoka, R. Kumar, K. Kamikawa, X. Verdaguer, A. Riera, M. Ohashi, S. Ogoshi, *Angew. Chem. Int. Edit.* **2017**, *56*, 8206–8210.

[8] a) A. C. Wotal, R. D. Ribson, D. J. Weix, *Organometallics* **2014**, *33*, 5874–5881. b) M. Oçafrain, M. Devaud, M. Troupel, J. Perichon, *J. Chem. Soc. Chem. Comm.* **1995**, 2331–2332. c) E. Dolhem, M. Oçafrain, J. Y. Nédélec, J. M. Troupel, *Tetrahedron* **1997**, *53*, 17089–17096.

[9] S. D. Friis, A. T. Lindhardt, T. Skrydstrup, *Acc. Chem. Res.* **2016**, *49*, 594–605.

[10] The use of primary alkyl iodides as electrophiles in Pd-catalyzed carbonylation reactions has been studied by the Ryu group through the concept of light mediated Atom Transfer Carbonylation (ATC) as a way to surpress β-hydride elimination upon oxidative addition. For a review see: S. Sumino, A. Fusano, T. Fukuyama, I. Ryu, *Acc. Chem. Res.* **2014**, *47*, 1563–1574. Furthermore, Sargant and Alexanian have recently reported a Pd-catalyzed alkoxycarbonylation, of secondary alkyl bromides. B. T. Sargant, E. J. Alexanian, *J. Am. Chem. Soc.* **2016**, *138*, 7520–7523.

[11] The use of alkyl derived organometallic reagents in Pd-catalyzed carbonylative cross-coupling is limited, for examples, see; a) R. F. W. Jackson, D. Turner, M. H. Block, *J. Chem. Soc., Perkin Trans 1,* **1997**, 865–870. b) P. H. Lee, S. W. Lee, K. Lee, *Org. Lett.* **2003**, *5*, 1103–1106. c) N. A. Bumagin, P. G. More, I. P. Beletskaya, *J. Organomet. Chem.* **1989**, *365*, 379–387. d) Y. Wakita, T. Yasunaga, M. Kojima, *J. Organomet. Chem.* **1985**, *288*, 261–268. e) T. Ishiyama, M. Murata, A. Suzuki, N. Miyaura, *J. Chem. Soc. Chem. Comm.* **1995**, 295–296.

[12] O. Vechorkin, Z. Csok, R. Scopelliti, X. L. Hu, *Chem. Eur. J.* **2009**, *15*, 3889–3899.

[13] a) N. Grüger, H. Wadepohl, L. H. Gade, *Dalton Trans.* **2012**, *41*, 14028–14030. b) S. Kumar, G. Mani, S. Mondal, P. K. Chattaraj, *Inorg. Chem.* **2012**, *51*, 12527–12539. c) G. T. Venkanna, S. Tammineni, H. D. Arman, Z. J. Tonzetic, *Organometallics* **2013**, *32*, 4656–4663.

[14] V. Soni, R. A. Jagtap, R. G. Gonnade, B. Punji, *ACS Catal.* **2016**, *6*, 5666–5672.

[15] Inspiration to **NiL3** comes from Chatani and coworkers' extensive studies on Ni-catalyzed C–H activation applying a *N*,*N'*-bidentate directing group. For a recent and comprehensive overview on this work, see: N. Chatani, *Top. Organomet. Chem.* **2016**, *56*, 19–46.

[16] Products of the type **2d** are formed in a non-catalyzed reaction between benzyl bromides and the product ketone in the presence of *n*Pr-ZnBr.

[17] When subjecting **NiL3** (0.1 mmol) to cyclohexylzinc bromide (1 equiv.) at room temperature in THF-d_8 under argon, the solution turned black within minutes. Analysis by ^{1}H NMR after 1 and 16 h revealed a complex reaction mixture, with only minimal transmetallation product.

[18] a) J. Breitenfeld, J. Ruiz, M. D. Wodrich, X. L. Hu, *J. Am. Chem. Soc.* **2013**, *135*, 12004–12012. b) J. Breitenfeld, M. D. Wodrich, X. L. Hu, *Organometallics* **2014**, *33*, 5708–5715.

[19] a) K. C. MacLeod, J. L. Conway, L. M. Tang, J. J. Smith, L. D. Corcoran, K. H. D. Ballem, B. O. Patrick, K. M. Smith, *Organometallics* **2009**, *28*, 6798–6806. b) D. Zhu, P. H. M. Budzelaar, *Organometallics* **2010**, *29*, 5759–5761.

[20] A mechanistic manifold cannot be excluded, which involves a nickel(IV) species. The ligand rather than the metal center may be oxidized in a Ni(IV) pathway, as previously proposed in ref. 18a.

[21] TEMPO was found to be an unsuitable radical trap, as this species reacts with the nickel(II) alkyl complex **B**, leading to *O*-alkylation of TEMPO. A similar observation has previously been made: See ref. 18a.

[22] K. E. Poremba, N. T. Kadunce, N. Suzuki, A. H. Cherney, S. E. Reisman, *J. Am. Chem. Soc.* **2017**, *139*, 5684–5687.

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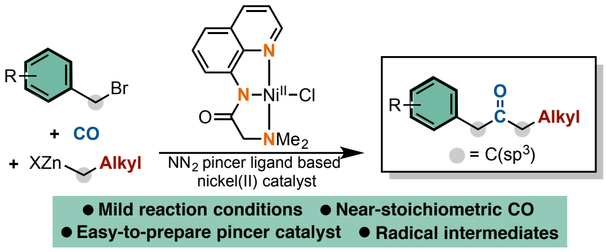

Hold tight: NN$_2$ type pincer ligand nickel(II) complexes are employed as catalysts in the carbonylative coupling of benzyl bromides and alkyl zinc reagents. The method relies on the controlled release of CO gas from a solid precursor, and thus circumvents the commonly encountered issue of Ni-catalyst deactivation upon CO-saturation. With this approach, the first examples of Ni-catalyzed carbonylative couplings of two sp^3-hybridized carbon centers are reported.

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