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Ni(COD)(DQ): An Air-Stable 18-Electron Ni(0)–Olefin Precatalyst

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Abstract: We report that Ni(COD)(DQ) (COD = 1,5cyclooctadiene, DQ = duroquinone), an air-stable 18-electron complex originally described by Schrauzer in 1962, is a competent precatalyst for a variety of nickel-catalyzed synthetic methods from the literature. Due to its apparent stability, use of Ni(COD)(DQ) as a precatalyst allows reactions to be conveniently performed without use of an inert-atmosphere glovebox, as demonstrated across several case studies.

The last decade has witnessed a renaissance in research into homogeneous nickel catalysis.^[1] Interest into the use of nickel stems from its ability to serve as an inexpensive alternative to precious metals in many catalytic transformations, including palladium-catalyzed crosscouplings, along with its capacity for facilitating unique types of bond construction, ranging from C–H activation to alkene functionalization.

The development of new synthetic methods leveraging nickel as a catalytic species hinges on the development and application of appropriate precatalysts; ones which are stable to heat, air, and moisture, and can efficiently form the catalytically active species under the desired reaction conditions (Scheme 1A-D).^[2] Prominent within the nickel precatalyst toolkit are nickel(0)-olefin complexes, originally pioneered by Wilke (Scheme 1D), including Ni(cdt) (cdt = alltrans-1,5,9-cyclododecatriene) and Ni(COD)₂ (COD = 1,5cyclooctadiene).^[3,4] Ni(COD)₂ in particular has found extensive use as a precatalyst and offers several advantages in this context. These include its enhanced stability as compared to Ni(cdt) by virtue of being a coordinatively-saturated 18-electron complex, its ability to efficiently associate various ancillary ligands in situ with concomitant dissociation of a COD ligand, and its low-valent nature, allowing it to directly engage in catalysis without prerequisite reduction. Other attributes of Ni(COD)2, however, are less desirable. Most notably it is sensitive to air, which typically necessitates use of an inert atmosphere glovebox for storage and reaction setup.^[5] These limitations have spurred the development of other families of nickel precatalysts in recent years (Scheme 1B and C), which offer advantages depending on the transformation of interest.

As part of an effort to broaden the portfolio of nickel(0)– olefin precatalysts, herein we describe the catalytic reactivity of Ni(COD)(DQ) (DQ = duroquinone), a complex that was

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Supporting information for this article is given via a link at the end of the document.

first described by Schrauzer in 1962.^[6,7] The structural properties^[8] and fundamental organometallic reactivity^[9] of Ni(COD)(DQ) have been previously studied, but to our knowledge its ability to serve as a precatalyst in organic transformations has not been previously documented. Ni(COD)(DQ) is isostructural and isoelectronic to Ni(COD)₂, both of which are 18-electron Ni(0)-olefin complexes.^[10] However, unlike Ni(COD)₂, Ni(COD)(DQ) is unique in its high air and moisture stability, in both solid and solution states, along with high thermal stability (being stable to storage at room temperature).

Scheme 1. Overview of the growing nickel precatalyst toolkit.



These practical features of Ni(COD)(DQ) when viewed through the lens of the versatile reactivity described herein make it a valuable addition to the growing repertoire of nickel precatalysts. In parallel to this study, Cornella and colleagues described a 16-electron nickel(0)-olefin complex, Ni(^Fstb)₃ (^Fstb = *trans*-1,2-bis(4-(trifluoromethyl)phenyl)ethane) and documented its ability to serve as a precatalyst for several different types of reactions.^[11]

We initiated our study by first attempting to prepare a series of nickel(0)–olefin complexes and testing their stability in air. To this end, we treated Ni(COD)₂ with various electron-

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deficient alkenes and dienes. Consistent with a previous literature report,^[12] well-defined 16-electron Ni(cod)(olefin) complexes could be prepared in this manner, with olefins such as dimethyl fumarate and maleic anhydride proving capable of displacing a single COD ligand. However, in the solid state these complexes proved to be unstable to air, decomposing within 30 seconds of air exposure, as evidenced by a color change from red to black. Analogously, we found that using quinones as reaction partners, we could obtain 18-electron Ni(COD)(quinone) complexes. Of the quinones tested, duroquinone (DQ) was especially effective, giving 79% yield on >8 g scale, of a red-colored, free-flowing solid that exhibited remarkable stability in air in comparison to Ni(COD)₂ (Scheme 2). In an effort to develop a more user friendly synthesis starting from air-stable Ni(II) precursors, we found that Ni(COD)(DQ) can be generated from Ni(acac)₂ in 60% yield using DIBAL-H as reductant or alternatively from NiCl₂(pyridine)₄ in 28% yield using sodium as reductant. Analytical data (X-ray) for material prepared by these routes were identical to previously reported data for Ni(COD)(DQ) (see Supporting Information), which was originally synthesized from highly toxic Ni(CO)₄ in the aforementioned 1962 report by Schrauzer.^[7,13]

Scheme 2. Gram-Scale Synthesis of Ni(COD)(DQ).



[a] Ellipsoids represent 50% probability; one of two inequivalent halfmolecules in the unit cell; hydrogen atoms omitted for clarity.

The structure and bonding of Ni(COD)(DQ) were first elucidated in 1965 by X-ray crystallography.^[9] During the course of the present study, a new data set was collected on a modern instrument, and the structure was solved and

deposited in the CCDC (1972401). To briefly summarize the key structural features noted in the original report,^[9] Ni(COD)(DQ) is monomeric in the solid state, possessing two crystallographically inequivalent half-molecules with the nickel center sandwiched between a DQ and COD ligand. The COD ligand adopts the same boat-form as in Ni(COD)2. The two pairs of olefin moieties in DQ and COD are orthogonal to one another, with nickel in tetrahedral geometry (the angle between COD olefins is 94°, and the angle between DQ olefins is 72°). Complexation to nickel distorts DQ, with the carbonyl groups puckering away from the nickel center and the methyl groups puckering towards the nickel center. The dihedral angle between the plane of four central ring carbons and the carbonyl groups is 6°. Significant π-back bonding from the nickel to the DQ ligand is evident from the C=O stretching IR signal (1553 cm⁻¹ in the complex, versus 1687 cm⁻¹ for free DQ).^[6]

Surprisingly, we were unable to find any information in the literature regarding the catalytic activity of Ni(COD)(DQ). Nevertheless, its structural similarity to Ni(COD)₂ led us to believe that it too could be a competent precatalyst in various reactions with in situ ligation from a phosphine, Nheterocyclic carbene, or nitrogen-based ligand. To test this idea, we evaluated the catalytic activity of Ni(COD)(DQ) in reactions from the literature that have been reported to proceed with different nickel precatalysts, with the hope of establishing that Ni(COD)(DQ) could function in a myriad of settings. For our initial experiments, we examined nickelcatalyzed variants of two key transformations of direct relevance to the pharmaceutical industry, Suzuki-Miyaura coupling and Buchwald-Hartwig amination. All reactions were set up outside of the glovebox using standard Schlenk technique, following procedures using reaction conditions that were otherwise identical to literature protocols, without additional optimization or development.

Scheme 3. Evaluation of Ni(COD)(DQ) as precatalyst in Suzuki–Miyaura
cross-coupling of aryl and heteroaryl coupling partners.[a-c]



1g (A) Ni(COD)(DQ): >99% [(dppf)Ni(cinnamyl)Cl]: 94%



1i (A) Ni(COD)(DQ): 85% [(dppf)Ni(cinnamyl)Cl]: 92%

[a] Reactions performed on 0.4 mmol scale. [b] Percentages represent isolated yields. Yields with [(dppf)Ni(cinnamyl)CI] and Ni(^Fstb)₃ are taken from Refs. 2d and 11. [c] Method A: K₃PO₄ (1.5 equiv), dioxane (0.4 M), 80 °C, 8 h; Method B: K₂CO₃ (1.5 equiv), MeCN (0.4 M), 50 °C, 12 h; the method is specified in parentheses after the compound number.

Ni(^Fstb)₃: >99%

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First we examined a nickel-catalyzed Suzuki-Miyaura method from Ge and Hartwig, reported to proceed effectively with 0.5 mol% [(dppf)Ni(cinnamyl)Cl] as the precatalyst.^[2d] By combining Ni(COD)(DQ) and dppf in equimolar ratio under otherwise identical reaction conditions, we were able to obtain comparable yields across a representative sampling of examples including simple aryl cases as well as more challenging heteroaryl cases (Scheme 3). In a few cases (1b, 1d, 1e, 1f, and 1i), the yields with Ni(COD)(DQ) (while still in the synthetically useful range) were lower than those of the original method, with the remaining material balance accounted for by unreacted aryl halide starting material. The origin of attenuated reactivity in these cases is currently under investigation. In one case (1h), it was also possible to make a direct comparison to Ni(^Fstb)₃,^[11] and for this product Ni(COD)(DQ) offered similarly high yield. Again, noting that further optimization was not conducted, which may be necessary for different precatalyst complexes to optimize yield.

Next, we examined a nickel-catalyzed aryl chloride amination protocol originally reported by Wolfe and Buchwald that was developed with Ni(COD)₂ as precatalyst (Scheme 4).^[14a] In two representative examples from the original publication, Ni(COD)(DQ) offered similar yields to Ni(COD)₂ (2a and 2b). Ni(COD)(DQ) can also be used to synthesized 2c, an example not reported in Ref. 14a, under the same conditions in comparable yield to Ni(COD)2. With 4-chlorobenzotrifluoride, an electrophile not included in the original Buchwald paper, it has been reported that the use of SIPr delivers high yields with morpholine as coupling partner.^[11,14b] Indeed, with in situ ligation of SIPr, Ni(COD)₂ and Ni(COD)(DQ) both facilitated C-N coupling comparable yields (2d-f). Due to the sensitivity of reaction components other than Ni(COD)(DQ)-presumably the base, NaO'Bu-slightly higher yields could be obtained when reagents other than Ni(COD)(DQ) were handled in the glovebox

Scheme 4. Evaluation of Ni(COD)(DQ) as a precatalyst in the amination of aryl chlorides. $^{\rm [a-c]}$



[a] Reactions performed on 0.1 mmol scale. [b] Percentages represent isolated yields. For Ni(COD)(DQ) experiments, the values in parentheses represent trials where the catalyst was massed outside of the glovebox and brought into the glovebox for subsequent manipulations; the values in brackets represent trials performed completely outside of the glovebox using Schlenk technique. Yields with Ni(COD)₂ for **2a** and **2b** are taken from Ref. 14a; yields with Ni(COD)₂ for **2c-f** were obtained during the course of this study. [c] Method A: dppf (10 mol%), NaO'Bu (1.4 equiv), PhMe (0.25 M), 100 °C, 24 h; Method B: SIPr+HCI (10 mol%), NaO'Bu (1.5 equiv), CPME (0.3 M), 100 °C, 24 h; the method is specified in parentheses after the compound number.

We next tested Ni(COD)(DQ) in four emerging types of synthetic methodology with nickel: the borylation of aryl halides^[15,16], C-H activation^[1e,17], alkene hydroarylation^[18], and decarboxylative cycloaddition^[19] (Scheme 5). Indeed, when we evaluated Ni(COD)(DQ) as a replacement for NiCl₂(dppp) in the catalytic coupling of HBpin and an aryl chloride, we observed comparable yields to an original report by Murata.^[15] Analogously, Ni(COD)(DQ) performed similarly to both Ni(COD)₂ and Ni(^Fstb)₃ in a substrate-directed C(aryl)-H activation/alkyne annulation developed by Chatani and colleagues, in which PPh3 and the bidentate pyridyl amide directing group presumably serve as ligands around nickel.^[11,17, 20] To evaluate the performance of Ni(COD)(DQ) in alkene functionalization reactions, we implemented it in 8-aminoquinoline directed hydroarylation of the an unactivated alkene as reported originally by Zhao and coworkers and found the yield to be comparable to that reported using Ni(COD)₂ as catalyst.^[18] Lastly, we tested Ni(COD)(DQ) in the synthesis of quinazolinediones via a decarboxylative cycloaddition of isatoic anhydrides and isocyanates as reported by Bristol-Myers Squibb. Ni(COD)(DQ) as catalyst afforded the desired product in good yield, albeit lower than that of the originally reported Ni(COD)₂ catalyst.^[19]

Scheme 5. Evaluation of Ni(COD)(DQ) as a precatalyst in (A) the borylation of aryl halides^[a], (B) C–H activation/alkyne annulation^[a], (C) directed hydroarylation of unactivated alkenes^[b], and (D) decarboxylative cycloaddition to form quinazolinediones^{[c],[d]}



[a] Reactions performed on 0.5 mmol scale. Yield with NiCl₂(dppp) was taken from Ref. 15. Yields with Ni(COD)₂ and Ni(^Fstb)₃ are taken from Refs. 17 and 11, respectively. [b] Reactions performed on 0.2 mmol scale. Yield with Ni(COD)₂ was taken from Ref. 18. [c] Reaction performed on 0.85 mmol scale. Yield with Ni(COD)₂ taken from Ref. 19. [d] Yield obtained by ¹H NMR using CH₂Br₂ as internal standard. Percentages represent isolated yields unless otherwise indicated.

To evaluate the solution-state stability of Ni(COD)(DQ) upon long-term storage, we prepared a solution in nondegassed, non-anhydrous methanol- d_4 . Periodic monitoring of this solution over time revealed no detectable changes in the ¹H NMR spectrum after ~4 days. After longer times (1 week), we observed peak broadening, consistent with partial decomposition (see Supporting Information). As mentioned above, in the solid-state, Ni(COD)(DQ) is a red, free-flowing solid that is indefinitely air stable. No detectable decomposition (as observed by ¹H NMR) could be observed

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after storing this complex for 3 months in a capped vial under air at room temperature (see Supporting Information).

Lastly, we performed a series of "stress tests" on Ni(COD)(DQ), subjecting it to air, protic solvents, and heat for several hours to examine if there was any impact on catalytic activity (Table 1 and Supporting Information). In particular, we found that dissolving Ni(COD)(DQ) in MeOH, H₂O, or a mixture of MeOH/H₂O and allowing the solution to stand open to air for 5 h did not lead to any detectable changes in the ¹H NMR spectrum or attenuation of catalytic activity (as assayed by Suzuki-Miyaura cross-coupling to form 1a) (entries 1-4). Similarly, heating solid Ni(COD)(DQ) in the oven for 4 h did not have a measurable effect on its composition or ability to serve as a cross-coupling precatalyst (entry 5). Notably, heating solid Ni(COD)2 in the oven under the same conditions for 1.5 h lead to decomposition (See Supporting Information), highlighting the difference in thermal stability. Remarkably, we found Ni(COD)(DQ) to be stable to silica gel chromatography using MeOH/DCM as eluent, providing additional avenues for purification (entry 6).

Table 1. Evaluation of the catalytic activity of Ni(COD)(DQ) after different stress tests.



Table 2. Photographs of a representative stress test (Table 1, Entry 4)



In conclusion we have found that Ni(COD)(DQ) possesses a previously underappreciated capacity to serve as a precatalyst for a variety of mechanistically distinct catalytic processes from the literature. In these cases in situ ligation with a variety of ligands was possible to generate an active catalyst without any additional reoptimization of the published conditions. The profound stability of Ni(COD)(DQ) makes it a promising new addition to the portfolio of nickel precatalysts, particularly for handling situations where it is not possible to completely exclude air and moisture, such as in large-scale manufacturing. Our future research will seek to elucidate the mechanism of catalyst initiation with Ni(COD)(DQ) and cultivate an understanding of when to deploy different nickel sources from the growing arsenal of precatalysts.

Experimental Section

Synthesis of Ni(COD)(DQ): To a 350 mL bomb flask was added 2,3,5,6-tetramethylcyclohexa-2,5-diene-1,4-dione (duroquinone, DQ) (5.37 g, 32.7 mmol) and a stir bar. The flask and contents were pumped into the glovebox and Ni(cod)₂ (9.00 g, 32.7 mmol) was added. Next, degassed DCM (120 mL) was added, and the flask was capped, removed from the glove box, and allowed to stir at 45 $^\circ\text{C}$ in an oil bath for 17 h. All subsequent manipulations were performed under air. The reaction was cooled to room temperature, and the crude reaction mixture was filtered through Celite with DCM as eluent to give a deep red homogeneous mixture. This mixture was concentrated in vacuo to give a dark red solid with residual COD liquid. To the resulting crude mixture was added a small amount of DCM (5 mL) followed by a large amount of pentanes (150 mL) resulting in the formation of a red precipitate. The mother liquor was then removed by pipetting and the precipitate was washed with DCM/pentanes (1:50) twice. Drying overnight under reduced pressure yielded 8.52 g (79%) of Ni(COD)(DQ) as a dark red solid. Characterization data match those reported in the literature.[12]

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Keywords: nickel • homogeneous catalysis • crosscoupling • precatalysts

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 Although initiation mechanism and rates may differ per specific
- [20] Although initiation mechanism and rates may differ per specific reaction and substrate, evaluation of initial reaction rates of this reaction showed no significant difference in initiation rates using Ni(COD)(DQ) in comparison to Ni(COD)₂ as catalyst (see Supporting Information for details).

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Old complex, new tricks: Ni(COD)(DQ) (COD = 1,5-cyclooctadiene, DQ = duroquinone) is a remarkably stable Ni(0)–olefin complex first described in the 1960s. Herein, we demonstrate its ability to serve as a precatalyst for a variety of nickel-catalyzed reactions.

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