A detailed mechanistic investigation based on spectroscopic and crystallographic analysis revealed that a putative reductive elimination to forge C(sp^3)—OC(sp^3) using I_2 might not be operative. We isolated a paramagnetic bimetallic Ni^{III} intermediate featuring a unique Ni_2(OR)_2 (OR = alkoxide) diamond-like core complemented by a μ-iodo bridge between the two Ni centers, which remains stable at low temperatures, thus permitting its characterization by NMR, EPR, X-ray, and HRMS. At higher temperatures (>−10 °C), such bimetallic intermediate thermally decomposes to afford large amounts of elimination products together with iodoalkanols. Observation of the latter suggests that a C(sp^3)—I bond reductive elimination occurs preferentially to any other challenging C—O bond reductive elimination. Formation of cyclized THF rings is then believed to occur through cyclization of an alcohol/alkoxide to the recently forged C(sp^3)—I bond. The results of this article indicate that the use of F_2 oxidants permits the challenging C(sp^3)—O(C(sp^3)) bond formation at a high-valent nickel center to proceed in good yields while minimizing deleterious elimination reactions. Preliminary investigations suggest the involvement of a high-valent bimetallic Ni^{III} intermediate which rapidly extrudes the C—O bond product at remarkably low temperatures. The new set of conditions permitted the elusive synthesis of diethyl ether through reductive elimination, a remarkable feature currently beyond the scope of Ni.

**INTRODUCTION**

Dialkyl ethers constitute one of the most valuable functional groups, and their synthesis represents one of the oldest strategies to build chemical complexity. As a result, formation of C—O bonds through the union of two organic fragments has prevailed one of the most powerful technologies, finding application across the chemical sciences: from covalent linkages and solid supports to crucial motifs in biologically active compounds. From a synthetic point of view, formation of the C—O bond has largely relied on the venerable Williamson ether synthesis, which involves the union of an alcohol and an alkyl halide through a S_N2 reaction in the presence of a strong base (Scheme 1A). The high practicality and scalability of this transformation has placed it as a cornerstone reaction in both academic and industrial settings. Yet, the nucleophilic mechanism of the reaction is in turn its Achilles heel: the reaction efficiency is largely affected by the competitive alkoxide- or base-promoted E1 and E2 processes when secondary and tertiary alkyl halides are utilized. To circumvent these limitations, organic chemists have devoted their efforts in developing many strategies to produce highly coveted ethers—electrochemistry, organocatalysis, Lewis acid/base catalysis, among others. Nevertheless, one of the most promising alternatives in the literature to forge C—O bonds relies on the mediation of transition metals. Exploiting their redox properties, transition metal catalysis has been demonstrated to be one of the pillars in the construction of these linkages. For example, Chan-Lam or Ullmann couplings

**Scheme 1. (A) Williamson Ether Synthesis (Advantages and Pitfalls); (B) Existing Methods for C(sp^3)—O Bond Formation Using Ni Catalysts; (C) C(sp^3)—O—C(sp^3) Bond Formation from High-Valent Ni**

A. C(sp^3)—O(C(sp^3)) bond formation: Williamson synthesis

B. Reductive elimination of C—O bonds from nickel complexes: a mechanistic overview

C. This work: Mechanistic analysis leads to C(sp^3)—O(C(sp^3)) bond formation at a Ni center

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have experienced great success and found broad application for the synthesis of a myriad of highly relevant ethers. Despite the advantages associated with these methods, they have been largely dominated by linkages such as C(sp²)−O−C(sp³) and C(sp³)−O−C(sp³). In addition, Pd catalysis has also experienced tremendous development in this front, providing catalytic methods for C(sp³)−O bond formation. Yet, Pd complexes that permit construction of dialkyethers (C(sp³)−O−C(sp³)) through reductive elimination still present severe challenges. A remarkable example of the formation of cyclic ethers is the Co-catalyzed radical cyclization of alkenols from Mukaiyama, which has found ample success in various synthetic endeavors.

Other first-row transition metals (Cu, Fe, Ni) have also been demonstrated to excel as catalysts in various C−O coupling strategies. In particular, Ni-catalyzed transformations have gained tremendous momentum for their enormous capabilities in forging C−heteroatom bonds. A seminal work by Hartwig described the possibility to forge C(sp³)−O−C(sp³) bonds using Ni(COD), and dppf as the optimal catalytic system. Encompassing Hartwig’s precedent, Stradiotto described a general C(sp²)−O bond formation from L₃NiIII complexes capitalizing on a newly designed set of phosphine-based ligands (L = CyPAd-DalPhos). More recently, methods that replace the phosphine by light irradiation, which rapidly forge the C(sp²)−O bond. Mechanistic investigations on these latter approaches revealed that C(sp³)−O bond formation can proceed either via a NiIII intermediate or via an excited NiII complex after energy transfer. In 2020, Ackermann and co-workers developed a nickel-catalyzed electrochemical C(sp²)−Oalkoxylation, which proceeds through a NiIII intermediate.

Recently, Nocera reported a NiI-catalyzed etherification protocol that mimics the reactivity of photoredox-catalyzed couplings without the use of a light source or photocatalyst. Similarly to the metallaphotoredox protocols, it is believed that the high oxidation state of the NiIII intermediate provides the necessary driving force to undergo C(sp³)−O bond linkage upon reductive elimination. Whereas realization of C(sp³)−O−C(sp³) through reductive elimination at a Ni center is well preceded and studied, a fundamental mechanistic understanding of the analogous process to forge dialkyl ethers through C(sp³)−OC(sp³) reductive elimination still remains elusive with virtually no systematic studies on their feasibility.

In the 1990s, Hillhouse provided one of the first examples of C(sp³)−O−C(sp³) bond formation from well-defined oxanickelacycles (1a−e) bearing bipyridine ligands and using stoichiometric I₂ as oxidant. In these seminal reports, involvement of high-valent nickel species such as NiIII−I or NiIV−I complexes was suggested; yet, minimal evidence was provided, and such intermediates remained purely speculative. Interestingly, when I₂ was replaced by other oxidants such as O₂ or ferrocenium (Fc⁺) the C(sp³)−OC(sp³) bond formation was not observed. In addition, higher yields were obtained for those complexes where β-hydride elimination is hampered by the limited conformations of the oxanickelacycles. As a result, formation of the C(sp³)−OC(sp³) bond was limited to cyclic products, as exemplified by the incapacity of I₂ to deliver the corresponding acyclic dialkyl ether. On the basis of these early results, Love and co-workers capitalized on the I₂-promoted C−O bond formation and applied it to the oxanickelacyclobutane 1g bearing a 1,2-bis(di-tert-butylphosphino)ethane (dtbpe) as the ligand. The authors observed rapid and clean formation of the corresponding epoxide in good yield along with almost quantitative formation of the corresponding (dtbpe)Ni₃ (3). In this case, deleterious β-hydride elimination is not operative due to the presence of a ketone. To the best of our knowledge, these reports represent solitary examples present in the literature regarding formation of dialkyl ethers from well-defined organometallic species. Despite the powerful reactivity observed, no evidence of the intermediates involved has been reported. Yet, fundamental understanding of the key parameters that govern this particular transformation would provide tremendous insights for the design of future catalytic C(sp³)−O−C(sp³) ether syntheses. Herein, we report a comprehensive mechanistic study on the transformation originally described by Hillhouse: characterization of the reaction intermediates revealed formation of a robust and paramagnetic NiIII dimer, which thermally decomposes to afford primarily elimination products. Additional mechanistic data suggests that direct C(sp³)−OC(sp³) reductive elimination from such NiIII intermediate to forge simple THF rings is highly unlikely. On the contrary, experimental evidence supports an alternative mechanism based on a preferential C(sp³)−I reductive elimination followed by an intramolecular Sn2 reaction. Yet, all of these drawbacks were overridden by the replacement of I₂ by fluorine-containing oxidants which prevent not only competitive C−X reductive elimination but also deleterious elimination side reactions. In this manner, high yields of the cyclized tetrahydrofurans were obtained.

**RESULTS AND DISCUSSION**

Initially, we considered that oxanickelacycles 1a and 1b provided an excellent platform to investigate an oxidative C(sp³)−OC(sp³) bond formation (Scheme 3). Both complexes represent challenging substrates to undergo intramolecular C−O bond formation (Scheme 2A) due to the dynamic behavior of the alkoxide anion as a result of the fluxionality of the alkyl backbone. Subsequently, diverse
conformations of the CH and CH₂ groups can be adopted which could lead to unproductive β-hydride elimination or simple E2. With these potential drawbacks in mind, we set out to synthesize nickelacyclopetanes 4a and 4b as described in the literature.27-29 The corresponding 1,4-alkyldibromides (1.0 equiv) were reacted with an excess of Ni(COD)₂ (2.0 equiv) and bipyridine (bipy, 4.0 equiv) at −78 °C in THF. After warming up to 25 °C, the mixture is filtered and the dark-green complexes 4a and 4b are obtained in 69% and 50% yield, respectively (step 1, Scheme 3). Subsequently, 4a and 4b were subjected to O-atom insertion using N₂O following Hillhouse and co-workers.31

Other single-electron oxidants were tested, such as photocatalyst 4CzIPN (2,4,5,6-tetra(9H-carbazol-9-yl)-isophthalonitrile (5)).35 which would also lead to cationic NiIII intermediates. Yet, no desired THF ring 2b could be detected in the crude mixture. These results suggest that a C(sp³)–O bond formation in good yield. To gain further insight into the C–O bond-forming event, the reaction reported by Hillhouse and co-workers was repeated: complex 1b (1.0 equiv) was reacted with I₂ (1.1 equiv) in CD₄Cl₂ at 25 °C.36 To our surprise, upon addition of I₂ to a solution of 1b, the color of the reaction mixture quickly changed from deep purple to orange. After 20 min of stirring at 25 °C, brown solids precipitated from the solution. At this point, the solids were filtered off and the filtrate was analyzed by ¹H NMR and GC-MS. After solubilizing the solids, pent-4-en-2-ol (6b, 45%) were obtained, presumably through side-elimination reactions. More importantly, peaks relative to 5-iodopentan-2-ol (7b, 10%) were detected and successfully assigned. The presence of 7b was further confirmed by GC-MS. After solubilizing the solids, analysis by ¹H NMR revealed a set of broad paramagnetic peaks, suggesting the presence of ligated bipy–Ni species. HRMS analysis of the solid indicated that a possible structure could be (bipy)NiI₂, although dimeric compounds could not be ruled out. Slow crystallization in CD₄Cl₂ at −20 °C led to crystals suitable for X-ray analysis, which unequivocally
confirmed formation of a polymeric (bipy)NiI₂ (8) consisting of octahedral Ni complexes linked together by μ-iodo bridges (Scheme 5B).

Considering the redox potential of iodine (E_{1/2}(I₂/I⁻) = +0.21 V vs Fc/Fc), it is reasonable to assume formation of a high-valent nickel NiIII–I complex upon mixing 1a and 1b with I₂. However, similarly to the case of Fe³⁺, formation of Ni³⁺ is highly unlikely. To investigate whether NiIII intermediates are formed in the reaction system, we decided to monitor the reaction by ¹H NMR at low temperature. Upon adding a cold solution of I₂ (1.1 equiv) to a solution of 1a in a J-Young tube at -90 °C, a rapid color change was observed from deep purple to deep orange (Scheme 5C). Complete conversion of 1a to a new set of well-defined signals was observed. The ¹H NMR spectrum at -90 °C exhibits peaks ranging from -930 to +237 ppm, pointing to a paramagnetic complex (Scheme 5D). Upon storing a concentrated solution at -237 ppm, pointing to a paramagnetic complex (Scheme 5C). Complete conversion of 1a to a new set of well-defined signals was observed. The ¹H NMR spectrum at -90 °C exhibits peaks ranging from -930 to +237 ppm, pointing to a paramagnetic complex (Scheme 5D). Upon storing a concentrated solution at -90 °C, good-quality crystals formed. X-ray analysis unambiguously determined that the intermediate consisted of a symmetric cationic NiIII bimetallic complex (9a). This complex represents a unique and unprecedented structure of a dinuclear NiII with several structural and electronic interesting features (Figure 2). First, 9a contains two NiII atoms in an octahedral arrangement with a large Ni–Ni distance of 2.84 Å, thus suggesting no metal–metal interaction. In addition, 9a features a rather unique μ-iodo bridge unifying both Ni atoms with a highly strained NiI–NiI angle of 80.7°. As a result, the I is bridging both NiII centers through an elongated Ni–I bond (NiI–NiI = 2.92 Å). It is important to mention that NiIII dimers with one bridging halogen atom have been recently proposed as intermediates in C(sp²)–C(sp³) bond formation. However, the most striking feature of 9a is the diamond-like core formed by the Ni atoms and the alkoxide ligands. Two μ₂-bridging alkoxide anions join the two Ni centers in a highly symmetric environment (NiI–O1 = NiI–O2 = NiI–O1 = NiI–O2 = 2.00 Å) with angles of NiI–NiI–NiI = 92.7° and O1–NiI–O2 = 79.5°. The Ni–O distances for 9a are in the range of other bis(μ₂-oxide)-bridging NiIII complexes known in the literature. The complex is complemented by the bipyridine ligands with similar Ni–N distances for both N (NiI–N1, 1.99 Å; NiI–N2, 2.05 Å). Finally, the remaining position of the octahedron is occupied by the alkyl residue with Ni–C(sp³) distances resembling those reported for other NiIII–C(sp³) bonds (NiI–C1, 2.013 Å). A parallel behavior was observed when complex 1c was reacted with I₂. However, attempts to obtain crystals of the NiII intermediate were unsuccessful. Bimetallic complexes 9a and 9b were further characterized by HRMS both in ESI⁺ and in ESI⁻ modes. Finally, due to the paramagnetic nature of complexes 9a and 9b, further structural and electronic characterization was attempted by electron paramagnetic resonance (EPR).

The EPR spectra of complexes 9a and 9b were recorded at the X-band, 30 K, and are depicted in Figure 3. As expected, the EPR spectra of 9a and 9b are very similar but show subtle differences in line splitting and intensity ratio between the different spectral features. The multiple line splitting suggests an electron–electron spin–spin interaction between the two NiIII centers. This means that the dimer structure found in the
solid state (Figure 2) is retained in solution for both complexes. Making use of the symmetry properties of the dimer complex,40 we were able to simulate the EPR spectra as shown in Figure 3. The g-matrix principal values obtained for 9a (2.081, 2.155, 2.279) and 9b (2.084, 2.144, 2.287) are similar to what has been observed for a similar N,N-ligand-coordinated NiIII monomer complex (2.03, 2.14, 2.20).40 The magnetic interaction between the two NiIII centers is dominated by the dipolar contribution found to be (0.9, 1.1, −2)*517 MHz for 9a and (0.9, 1.1, −2)*517 MHz for 9b. The J coupling between the two NiIII centers is very small (50 MHz), and its effect on the EPR is only visible as a small splitting at the center of the spectrum. As confirmed by DFT analysis,31 the two NiIII centers effectively behave as isolated S = 1/2 systems. This is in agreement with NMR analysis, estimating the magnetic susceptibility of the dimer complex using the Evans method to be S = 1/2 for each NiIII center.31

Having identified and characterized 9, we set out to explore its reactivity. Upon slowly warming solutions of 9a and 9b in CD2Cl2 from −90 to 25 °C, several interesting observations were made. First, the chemical shifts of complexes 9a and 9b are highly dependent on the temperature, which further confirms the paramagnetic nature of 9.35 Moreover, 9a and 9b have a remarkable stability across a wide range of temperatures, from −90 to −10 °C. Beyond −10 °C, rapid evolution of 9a and 9b to terminal alkenes 6a and 6b and iodoalcohols 7a and 7b is observed. While traces of THF could be detected in the case of 9a, no detectable amount of the C(sp3)−OC(sp3) bond formation product 2b was observed for 9b.34 This last observation indicates that the C(sp3)−I reductive elimination is kinetically more favorable to any other C−O bond-forming event at Ni. Whereas such C(sp3)−I bond formation proceeds via a reductive elimination from NiIII−I or direct attack of the I counterion to the Ni−C(sp3) bond in a Sn2 fashion is currently unknown.42,45 However, a similar system was recently reported by Diao, suggesting that C(sp3)−I bond formation could proceed through monomeric square pyramid NiIII complexes.40 Hence, it is plausible to think that after dissociation of 9a and 9b, a similar process could be operative.

The absence of 2b upon warming 9b to 25 °C together with rapid consumption of oxanickelacycle 1b at −90 °C toward preferential formation of 6b and 7b led us to consider that the C(sp3)−OC(sp3) bond formation pathway accounting for the ca. 10−14% yield of 2b may arise from a slow intramolecular cyclization of the iodoalkoxide/iodoalcohol in a Sn2 fashion.46 Indeed, after 48 h of reaction time in the NMR tube without stirring, the iodoalcohol formed initially slowly evolves to form 2b (Scheme 6).31 It is well established that 5-iodoalkoxides can undergo intramolecular S-exo-tet cyclization to afford cyclic ethers.47 This experimental evidence supports the lack of reactivity when attempting formation of open-chain ethers such as Et2O (2f) due to the much slower rates for intermolecular Sn2 reactions.48

With these results in hand, we addressed such a defying and elusive reductive elimination. It was clear that other oxidants that enable access to high-valent Ni species should be scrutinized.49 When I2 was replaced by Umemoto’s reagent (S-((trifluoromethyl) dibenzothiophenium triflate, TDTT, 10a),33a a low yield of 2b was observed (10%). A reduced amount of side product 6b was obtained when CD3CN was used instead. During monitoring studies at variable temperatures, HCF3 (boiling point = −82.1 °C) was detected. Formation of fluoroform suggests the involvement of CF3−Ni−H intermediates and points to alkenol 6b being formed through β-hydride elimination pathways. In addition to alkenol 6b and HCF3, other byproducts containing C(sp3)−CF3 were also identified by 19F NMR, which was consistent with formation of high-valent Ni intermediates.50 Despite the low yields, to the best of our knowledge, this challenging C(sp3)−CF3 bond formation is unprecedented at a Ni center. At this point, it was quite evident that competitive C(sp3)−X reductive eliminations (X = I, CF3) should be suppressed if the challenging C(sp3)−O−C(sp3) is to be achieved. Hence, we speculated that the presence of F ligands in the coordination sphere of a high-valent Ni intermediate would dramatically reduce the observed side reactions due to the high kinetic barrier to forge C(sp3)−F bonds.52 When 1b was mixed with 1.05 equiv of XeF2 in CD2Cl2 or CD3CN, immediate reaction took place and the desired ether 2b was observed as the major product in 60% or 47% yield, respectively.10a,52,53 Interestingly, formation of 6b remained minor in CD3CN, and could be largely suppressed in CD3CN (8%). It is important to mention that products derived from a putative C(sp3)−F reductive elimination were only observed in trace amounts.31 In this line, when XeF2 was replaced by Selectfluor (10c) in CD3CN a similar outcome was obtained with a 45% yield of 2b along with a minimal amount of 6b (10%). We then investigated several commercially available substituted 1-fluoro-pyridinium salts (10d−f) as they have increased solubility in CH3CN.44 Using 10d, 45% 2b and <5% 6b were obtained. Gratifyingly, when using NFTPB (10e, N-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate) and NFTPT (10f, N-fluoro-2,4,6-trimethylpyridinium triflate) an
increase in the yield of 2b was observed (61% and 63%, respectively). Notice that when using BF₄⁻ as counterion, formation of 6b could be minimized to a residual 8%. As expected, 2a was also obtained in a satisfactory 56% and 63% yield when using 10e and 10f, respectively (Scheme 7B).

Scheme 7. (A) Screening of Oxidants for the Oxidatively Induced C(sp³)−OC(sp³) Bond Formation; a (B) Application to the Synthesis of THF

A. Screening of fluorinated oxidants in the reductive elimination

![Scheme 7A](image)

B. Application to the Synthesis of THF via reductive elimination

![Scheme 7B](image)

Having identified a set of conditions that enable formation of cyclic C(sp³)−OC(sp³) bonds at high-valent Ni centers, we speculated that a similar pathway should be valid for acyclic ethers. In order to study this possibility, an acyclic precursor was synthesized through a two-step sequence for 50 h at 25 °C. A similar result was obtained using 10e. Formation of 2f from 1f represents a unique example of C(sp³)−OC(sp³) bond formation and contrasts with the results obtained from Hillhouse, where C(sp³)−OC(sp³) bond formation from acyclic NiII complexes could not be achieved (see Scheme 2A). This unprecedented result for unbiased, acyclic substrates combined with the use of simple pyridinium salt 10e as a mild oxidant provides an interesting proof-of-concept for the development of new strategies based on Ni and may open the door to new avenues for catalytic dialkyl ether syntheses in the future.

Successful formation of C(sp³)−O−C(sp³) bonds using N-fluoropyridinium reagents posed the question of what is the exact nature of the high-valent Ni species involved in the process. On the basis of the CV results for 2b (Figure 1) together with the oxidation results using Fe⁺, O₂, and 4CzIPN photocatalyst (Scheme 4), it is evident that access to NiIII species is facile, yet, cationic NiIII are not capable of C−O bond formation due to fast elimination side reactions. It is important to point out that owing to the extremely fast reaction rates for C−O bond formation, mechanistic investigations on this particular system pose an experimental challenge. Indeed, 1a, 1b, 10e, and 10f react at ~90 °C in <1 min, and no Ni intermediates could be detected spectroscopically (1H and 31P NMR). Attempts to stabilize high-valent Ni species using tripodal ligands (tris(pyrazolyl)borate 56 or tris(pyridyl)methane) resulted in degradation or failed to incorporate O to the NiII−C(sp³) bond. To our delight however, a signal could be detected by EPR from reaction of 1b with 10f. Such species were very short lived, but a sufficient amount could be trapped after rapid (1 s) mixing at ~95 °C (melting point of PhMe) and subsequent freezing in liquid N₂ (Scheme 9A).

Scheme 8. (A) Synthesis of (bipy)NiEt₂ 11 and (bipy)Ni(Et)(OEt) 1f; a (B) Oxidatively Induced Synthesis of Diethyl Ether from Nickel Complex 1f

A. Synthesis of the allyl-alcohol NiII precursor

![Scheme 8A](image)

B. Unprecedented oxidatively-induced acyclic ether bond formation

![Scheme 8B](image)

"Reaction conditions: (step 1) Ni(acac)₂ (1 equiv), bipy (1 equiv) Et₄AlOEt (3 equiv) in Et₂O, from ~50 to 25 °C, 50 h, 11 87% isolated yield; (step 2) 11 (1 equiv), N₂O (1 atm) in THF at 25 °C, 1f 63% isolated yield. Reaction conditions: oxanickelacycle 1f (1 equiv), 10e and 10f (1.05 equiv) in CD₂CN at 25 °C, 1 min. Yields determined by ¹H NMR using mesitylene as internal standard.
Spectrometry Results and Postulated Mechanistic Pathways

**Scheme 9. (A) EPR of int-I at 20 K**

(A) EPR of the mixture of 1b + 10f in PhMe/CH2Cl2

(B) Mass Spectrometry Results and Postulated Mechanistic Pathways

**Experimental conditions:** Power = 2.0 mW, modulation (100 kHz) amplitude 7.5 G. Dotted red trace represents the Easyspin (es) simulation with parameters $g = (2.103, 2.200, 2.227)$. Dipolar interaction $D$(int-I) = 299 MHz. J coupling = 100 MHz.

A as a major contributor. Moreover, another possible pathway could involve direct reductive elimination from the dinuclear complex int-I (path b), which has been postulated for certain C–heteroatom and C–C bond-forming events. In an attempt to discern between mechanistic pathways, we carried out the oxidation of 1b with only 0.5 equiv of 10f. In this case, one-half of the yield of 2b observed in Scheme 7A was obtained (35–40%) without trace amounts of 6b. The absence of elimination byproducts suggests that cationic NiIII species might not be present and adds additional evidence about path a not being operative. However, the variety of pathways by which the C–O bond could be formed manifests the need for further mechanistic investigations to fully elucidate the nature of the intermediates involved.

**CONCLUSIONS**

In conclusion, we studied the seminal I2-promoted C–O bond formation reported by Hillhouse toward formation of cyclic ethers (2a and 2b). A detailed mechanistic investigation revealed formation of 9a and 9b, an unprecedented NiIII bimetallic structure as a cationic intermediate, which was fully characterized by NMR, EPR, HRMS, and X-ray in the case of 9a. These paramagnetic complexes feature a unique Ni2(OR)2 (OR = alkoxide) diamond-like core complemented by a μ-iodo bridge between the two Ni centers. The anionic counterion of the complexes consists of the linear I3−, which remains in the outer sphere of the robust bimetallic cation. Thermal decomposition of 9 beyond ~10 °C leads primarily to elimination products (6). In addition, substantial amounts of iodoalkanols (7) were detected through preferential C(sp3)–I reductive elimination. The low yields obtained for 2a and 2b are postulated to arise from an intramolecular S82 reaction from 7 over long periods of time. This manifests that the original mechanistic picture for direct C(sp3)–OC(sp3) bond formation through reductive elimination is extremely challenging for simple THF rings. Cyclic voltammetry studies as well as a survey of oxidants identified the use of fluoropyridinium reagents 10e and 10f as excellent candidates to afford good yields of 2 while minimizing formation of elimination byproducts (6). In addition, this new set of conditions was successfully applied in the elusive synthesis of acyclic diethyl ether (2f) from a well-defined NiII complex. Preliminary mechanistic studies revealed that upon oxidation of 1 with 10, a highly reactive intermediate could be detected in solution by EPR and HRMS, which is consistent with a NiIII dimeric structure (int-I). Efforts to fully characterize the high-valent species involved after oxidation and prior to reductive elimination are currently under investigation in our laboratory. We believe the findings reported here open the door to new avenues for Ni catalysis and could aid practitioners in the field to unravel novel metal-catalyzed ether synthesis.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c07381.

Experimental procedures and analytical data (1H, 19F, and 13C NMR, EPR, X-ray, HRMS, CV) (PDF)

CIF file for compound 8, also available free of charge from the www.ccdc.cam.ac.uk under CCDC number 2014828 (CIF)

CIF file for compound 9a, also available free of charge from the www.ccdc.cam.ac.uk under CCDC number 2014830 (CIF)

CIF file for compound S1, also available free of charge from the www.ccdc.cam.ac.uk under CCDC number 2014829 (CIF)

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