

Room-Temperature Aerobic C–CN Bond Activation in Nickel(II) Cyanomethyl Dicarboranyl Complex

Mohammad Jahirul Islam, Kyoung Chul Park, Olivia M. Manley, Mark D. Smith, Thomas M. Makris, and Dmitry V. Peryshkov*



Cite This: <https://doi.org/10.1021/acs.organomet.3c00216>



Read Online

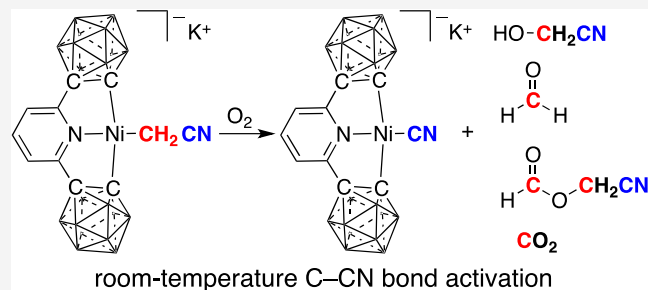
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: We report the synthesis and characterization of a nickel(II) complex of the dicarboranyl CNC dianionic pincer ligand, which activates acetonitrile by C–C bond cleavage. Deprotonation of the relatively acidic C–H bond of the coordinated acetonitrile with potassium *t*-butoxide led to the formation of the C-bound cyanomethylene ligand at the metal center. Unlike most previously characterized Ni(II) cyanoalkyls, the resulting complex exhibited quick transformation under aerobic conditions at room temperature to afford CNC-ligated nickel(II) cyanide, indicating facile cleavage of the C–CN bond. The cyanoalkyl and cyanide complexes were isolated in excellent yields and characterized by NMR spectroscopy and single-crystal X-ray



diffraction. Carbon-containing products of the aerobic C–CN bond activation are hydroxyacetonitrile, formaldehyde, cyanomethyl formate, and carbon dioxide.

INTRODUCTION

The activation of strong single C–C bonds in organic substrates is an area of intensive research motivated by its relevance to a wide range of transformations, such as hydrogenolysis, cross-coupling reactions, and group transfer.^{1–5} Cleavage of carbon–carbon bonds in organonitriles for decyanation,^{6,7} cross-coupling,^{8,9} and transfer cyanation^{10–12} is an attractive but challenging direction, in part due to the stability of nitriles associated with the increased bond strength (ca. 120 kcal/mol for the C–C bond in acetonitrile, which is larger than that in a typical unstrained alkane, ca. 90 kcal/mol) and largely weak interactions of the single carbon–carbon bonds with metal centers.^{13,14}

Low-valent transition metals, such as Co(I), Rh(I), Ni(0), and Pd(0), promote oxidative addition of the C–C bond of nitriles representing the major activation strategy reported in the literature.^{15–21} (Scheme 1). Nickel-containing systems are prominently featured in nitrile bond activation.^{19,20} In the majority of reported cases, this type of activation occurs *via* the formation of a η^2 -side-on-C \equiv N coordinated intermediate, the structure of which is supported by NMR spectroscopy data, crystallographic studies, and computational investigations.^{22–25} Mechanistic studies have demonstrated the reversibility of C–CN bond cleavage for aromatic nitriles. A number of nickel-promoted coupling and arylocyanation reactions that proceed with carbon–carbon bond activation in nitriles have been reported.^{26–29}

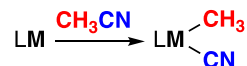
Besides the C–CN oxidative addition pathway, several examples of mechanistically different copper-promoted C–C

bond cleavage of acetonitrile have been reported. In 2001, Mascharak and co-workers discovered the cleavage of the C–C bond of acetonitrile by a copper(II) center supported by the pyridinedicarboxamidate NNN-pincer ligand.³⁰ However, the fate of the CH₃ fragment and the mechanism of this bond-breaking process were not established. A related pyridinedicarboxamidate-supported Cu(II) hydroxide complex in acetonitrile solution has been shown to convert to the corresponding copper(II) cyanide upon exposure to air in the presence of sodium hydroxide.³¹ Incidentally, an isostructural nickel hydroxide complex was also reported to convert to cyanide under similar conditions; however, the product identity was proposed only on the basis of FTIR data and elemental analysis.³¹ In 2004, Lu and co-workers explored the activation of the C–C bond of acetonitrile by a dinuclear Cu(II) cryptate complex to afford a cyanide-bridged dinuclear copper cryptate complex and methanol.³² However, Nelson and co-workers were unable to replicate the activation of acetonitrile under similar reaction conditions.³³ Recently, copper-mediated catalytic cyanation of aromatic C–H bonds with a wide substrate scope by utilizing acetonitrile as a cyanide source has been developed.¹² Notably, the majority of

Received: May 4, 2023

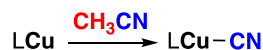
Scheme 1. Modes of Activation of H₃C–CN Bonds of Acetonitrile

oxidative addition to low-valent M:

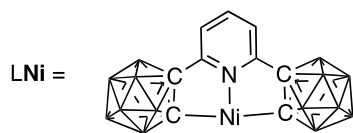
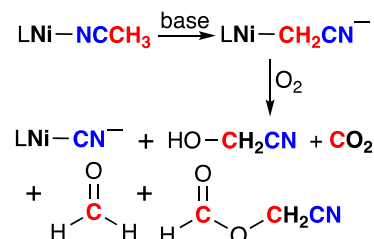


M = Ni(0), Pd(0), Co(I), Rh(I),...

Cu(II)-promoted oxidation:



this work:



these copper-promoted activation examples of the H₃C–CN bond have not closely tracked the transformation of the parent methyl group.

As mentioned above, nickel complexes play a significant role in the activation of nitriles through the oxidative addition to zero-valent nickel centers. Recently, we reported the synthesis of a pyridine-backbone bis-*ortho*-carboranyl CNC dianionic pincer ligand (C₅H₃N)(C₂B₁₀H₁₁)₂ (**1**, L-H), and its Ni(II) acetonitrile-ligated complex {(C₅H₃N)(C₂B₁₀H₁₀)₂}Ni(CH₃CN) (**2**, LNi-NCCH₃).³⁴ Polyhedral boranes and carboranes are three-dimensional structures that have been used in ligand design due to their unique electronic and steric properties.^{35–42} For example, the rigidity and extensive steric hindrance of boron clusters can be used to impose control of the coordination modes of a ligand around a metal center. Additionally, the electronic properties of boron clusters can be tailored to modulate the properties of their metal complexes.

Herein, we report the first example of facile acetonitrile C–C bond activation at room temperature by the nickel(II) center in **2** that proceeds through the initial formation of C-bound cyanoalkyl intermediate K[{(C₅H₃N)(C₂B₁₀H₁₀)₂}Ni(CH₂CN)] (**3**, K[LNi-CH₂CN]) in the presence of a base. Upon exposure to dioxygen, the C–C bond activation of the C-bound cyanomethylene group in complex **3** occurred rapidly at room temperature to afford cyanide complex K[{(C₅H₃N)(C₂B₁₀H₁₀)₂}Ni(CN)] (**4**, K[LNi-CN]). The identity of carbon-containing products ascending from the methyl group of acetonitrile was established with the use of ¹³C labeling and NMR spectroscopy. We found that the aerobic H₃C–CN bond cleavage results in the formation of hydroxyacetonitrile, formaldehyde, cyanomethyl formate, and carbon dioxide along with cyanide (Scheme 1).

RESULTS AND DISCUSSION

The pincer-type pro-ligand 2,6-dicarboranylpyridine (**1**) has been synthesized using the recently reported route that involves S_NAr aromatic nucleophilic substitution reaction of carbon–fluorine bonds of 2,6-difluoropyridine with the C-metalated carborane cluster.^{34,43} The pro-ligand **1** possesses two remaining C–H carboranyl bonds that are weakly acidic⁴⁴ and can be transformed into a dianionic pincer-type CNC ligand. The high degree of steric hindrance and the rigidity of this pincer ligand limit the range of suitable metal centers that can be accommodated in its pocket, and only its nickel(II) complexes have been reported to date. In addition, while this article was under review, a report on the phosphorus center supported by **1** has been disclosed in a preprint service.⁴⁵ We prepared acetonitrile-ligated Ni(II) complex **2** following our previously reported procedure.³⁴

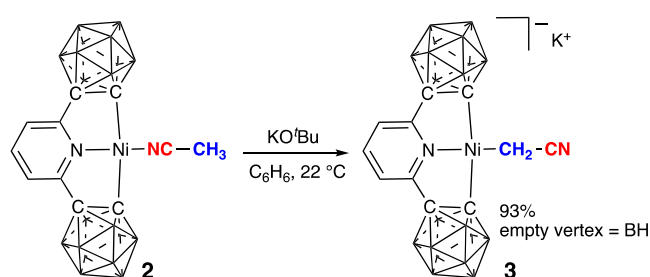
The redox behavior of the dicarboranyl pro-ligand **1** and its nickel complex **2** was studied. The cyclic voltammogram of **1** in 0.1 M TBAPF₆ in THF showed an irreversible reduction event at –1.19 V vs SCE, which is expected to occur on carborane clusters (see the Supporting Information for details). Icosahedral neutral C₂B₁₀H₁₂ carboranes possess an accessible LUMO energy level that renders them electron acceptors in electrochemical or chemical reduction. Upon reduction, *closo*-C₂B₁₀H₁₂ carboranes undergo a transformation to mono- or dianionic *nido*-C₂B₁₀H₁₂ cages that feature opening of the cluster.^{46–49} Significant structural rearrangements occur during cluster opening upon reduction, causing irreversible appearance of the cyclic voltammograms. At the same time, C₂B₁₀H₁₂ clusters are resistant to oxidation with voltammograms normally lacking oxidation events.

Compared to the free ligand **1**, the reduction of the carborane clusters in complex **2** in 0.1 M TBAPF₆ in THF exhibited a peak at a higher potential of –1.40 V vs SCE, presumably due to the stabilization of both of the carborane clusters upon coordination with the Ni(II) center *via* carbon vertices. A related oxidation event with a smaller current on a return wave was observed at –0.56 mV vs SCE (see the Supporting Information for details). No electrochemical oxidation events for the nickel complex **2** were observed, which is consistent with its stability and a relative difficulty of the formation of the Ni(III) center in the electron-withdrawing C-carboranyl coordination environment. Therefore, the potential promotion of the oxidative reactivity in this system is unlikely to involve direct metal–ligand redox cooperativity and, if any, would be metal-centered. The ligand **1** will likely influence a metal center *via* electron-withdrawing effects and its rigidity and steric hindrance.

The C-bound carboranyl groups are regarded as electron-withdrawing substituents in the organic chemistry of carboranes.⁵⁰ In complex **2**, coordination to C-carboranyles renders the nickel center relatively electron-deficient, which is manifested by a higher value of the ν(C≡N) of 2332 cm^{–1} of the coordinated acetonitrile ligand in the FTIR spectrum. The relatively electron-poor environment of the nickel center was also corroborated by the IR stretching frequency value for the putative carbonyl complex {(C₅H₃N)(C₂B₁₀H₁₀)₂}Ni(CO), ν(CO) = 2123 cm^{–1} that can be prepared in situ upon exposure of the solution of **2** in dichloromethane to 1 atm of CO. This carbonyl complex reverted to the starting complex **2** when the CO atmosphere was replaced with nitrogen. It has been reported that electron-deficient cationic nickel (II)

complexes with *N*-heterocyclic carbene ligands facilitate deprotonation of the α -CH bonds of nitriles.⁵¹ In this context, we hypothesized that the C–H bonds of the acetonitrile ligand in **2** are rendered acidic enough to be deprotonated by an appropriately strong base, such as KO^tBu. Indeed, the reaction of **2** and KO^tBu in benzene solution under nitrogen cleanly produced a new single product according to the ¹H NMR spectroscopy. Air-free workup afforded a yellow powder sample of a cyanomethyl nickel(II) complex K-[[{(C₅H₃N)(C₂B₁₀H₁₀)₂}Ni(CH₂CN)] (3) in 93% yield that was characterized by an array of NMR spectroscopy techniques, mass spectroscopy, and single-crystal X-ray crystallography (Scheme 2). Complex **3** can also be prepared in the reaction of **2** and LiHMDS in toluene.

Scheme 2. Deprotonation of Coordinated Acetonitrile Ligand in **2** and Its Conversion to Cyanoalkyl Group in **3**



In the ¹H NMR spectrum of **3** in CD₂Cl₂, a characteristic resonance for the C-bound cyanomethyl protons was observed at 0.63 ppm. The ¹³C NMR spectrum contained a resonance at –12.9 ppm, which corresponds to the methylene carbon atom of the cyanomethyl group. The ¹¹B and ¹¹B{¹H} NMR spectra revealed a set of partially overlapping signals in the range from –3.53 to –11.27 ppm. The FTIR spectrum of a solution of **3** in methylene chloride under nitrogen atmosphere exhibited characteristic absorption bands ν (B–H) at 2580 cm^{–1} as well as ν (C≡N) at 2188 cm^{–1}.

No exchange has been observed between **3** and CD₃CN at room temperature. At the same time, complete deuteration of the cyanoalkyl group has been observed upon heating **3** and excess CD₃CN in C₆D₆ solution at 100 °C for a week. The same complex containing Ni–CD₂CN group was also prepared starting from the deuterioacetonitrile-containing analogue of complex **2** in a reaction with KO^tBu.

Single crystals of 3·C₆D₆ were grown by slow evaporation of benzene from a solution inside a nitrogen-filled glovebox. The compound crystallizes in the space group C2/m. The anionic complex [[{(C₅H₃N)(C₂B₁₀H₁₀)₂}Ni(CH₂CN)][–] possesses crystallographically imposed mirror symmetry, in which the mirror plane passes through the C5, N1, Ni1, C6, C7, and N2 atoms (Figure 1). The potassium ion is coordinated to the N2 atom of the cyanomethyl group (K1–N2 distance is 2.744(2) Å) and additionally interacts with three B–H cluster bonds of two adjacent molecules of **3**.

The C-bound cyanomethyl CH₂CN group exhibits the Ni1–C6–C7 angle of 100.3(2)°. The bond distances within the group are C6–C7 = 1.432(5) Å, which corresponds to a single bond, and C7–N2 = 1.154(5) Å, which corresponds to a triple bond. The N1–Ni1–C6 bond angle of 174.7(2)° slightly deviates from linearity. The C1–Ni1–N1 and C1–Ni1–C1A bond angles are 86.8(1) and 173.5(2)°, respectively, resulting in the square-planar coordination geometry of the nickel

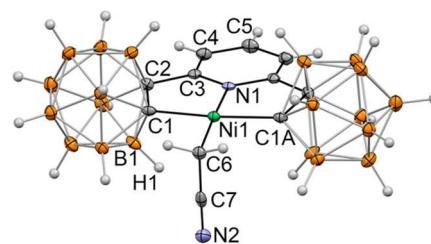


Figure 1. Displacement ellipsoid plot (50% probability level) of the anionic cyanoalkyl nickel complex [[{(C₅H₃N)(C₂B₁₀H₁₀)₂}Ni(CH₂CN)][–] in **3**. Potassium cations and benzene solvate molecules are not shown.

center. The τ_4 value for this structure is 0.08. The length of the nickel–cyanomethyl bond Ni1–C6 is 1.946(3) Å. The N1–Ni1 bond distance in the anionic complex **3** (1.917(3) Å) is elongated in comparison with that in the neutral parent complex **2** (1.882(2) Å), while C1–C2 (1.683(3) Å) and Ni1–C1 (1.930(2) Å) bond lengths are close in **2** and **3** (Figure 1).

Complex **3** is stable as a solid or in the solution under nitrogen atmosphere for weeks at room temperature. However, when the benzene solution of **3** was exposed to air, within minutes, a gradual decrease in intensity of its yellow color was observed, suggesting its instability. After evaporation of volatiles, the ¹H NMR spectrum of resulting light-yellow microcrystals was obtained in CD₂Cl₂, which revealed the complete disappearance of the methylene proton resonance at 0.63 ppm of the cyanomethyl group in **3**, and a significant downfield chemical shift of the ligand pyridine ring protons.

Intriguingly, the single-crystal X-ray diffraction studies revealed the formation of a cyanide nickel(II) complex K[[{(C₅H₃N)(C₂B₁₀H₁₀)₂}Ni(CN)] (4, Figure 2). The complex **4** crystallized from anhydrous deuterated benzene solution with the formation of a K₄X₄ cubane-type core, in which four [[{(C₅H₃N)(C₂B₁₀H₁₀)₂}Ni(CN)][–] anions are coordinated to four potassium ions forming a distorted K₄N₄ cube with the range of K–N distances from 2.781(3) to 2.955(3) Å. Three of the four potassium ions are also coordinated to either one or two C₆D₆ molecules, and the fourth cation is surrounded by B–H bonds of three neighboring carborane clusters. For the coordinated cyano group, the Ni1–C20 and C20≡N2 bond distances are 1.838(4) Å and 1.156(5) Å, respectively. Within the complex, the Ni1–N1 distance is 1.901(3) Å and the Ni1–C11 bond length is 1.918(4) Å. The carboranyl cluster C11–C12 bond length is 1.674(5) Å. The angles around the nickel center are N1–Ni1–C20 = 174.6(2)° and C19–Ni1–C11 = 173.7(2)°, corresponding to the square-planar geometry. The τ_4 value for this structure is 0.08. The cyanide ligand is linearly coordinated with a Ni1–C20–N2 angle of 175.6(3)°. Bond distances and angles involving the three other crystallographically independent potassium and nickel atoms of the cubane-type complex are similar.

A related cyanide-bridged complex K[[{(C₅H₃N)(C₂B₁₀H₁₀)₂}Ni(μ-CN)]{(C₅H₃N)(C₂B₁₀H₁₀)₂}Ni] (5, see the Supporting Information for crystallographic details) crystallized from a benzene solution containing water as a minor fraction with an apparent loss of a half of an equivalent of KCN from **4**. Two nickel centers in **5** are directly bridged by the cyanide ligand forming a dimer. The structural parameters of **5** show no significant deviation from those of **4**. Complex **5** is a minor product of the reaction, as evidenced by the absence

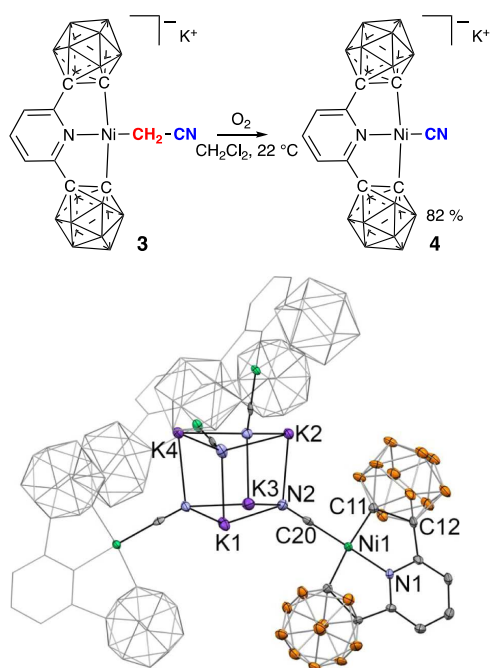


Figure 2. (Top) Synthesis of cyanide complex **4** upon exposure of the cyanomethylene complex **3** to oxygen. (Bottom) Displacement ellipsoid plot (50% probability level) of the anionic cyanide nickel complex $[\{(C_5H_3N)(C_2B_{10}H_{10})_2\}Ni(CN)]^-$ in the crystal structure of the solvate $4 \cdot C_6D_6$. The complex consists of tetrameric units with cyanide ligands bridged by potassium ions forming a pseudocubane K_4N_4 core. Solvent benzene molecules as well as all hydrogen atoms are omitted for clarity.

of its signals in the mass spectra of the reaction mixture where only **4** is detected.

The unexpected formation of the cyano $C \equiv N$ group from the cyanomethyl moiety indicated the activation of the $C-CN$ bond of acetonitrile, possibly assisted by moisture or oxygen in air. Notably, the previous reports on nickel(II) cyanoalkyl complexes have, in some cases, explicitly described their water and air stability, or reported handling of these compounds under inert atmosphere without mentioning decomposition pathways.^{52–55} At the same time, the reactivity studies of Pd(II) and Pt(II) alkyls with dioxygen leading to crystallographically characterized peroxo products have been reported.^{56–60}

No formation of methanol was detected either in the 1H NMR spectrum or in the GC–MS traces after the addition of water to a solution of **3** in CD_2Cl_2 in air. Furthermore, the addition of the degassed portion of D_2O to the solution of **3** under nitrogen did not lead to changes in the 1H NMR spectrum. In contrast, the addition of dry oxygen to a degassed solution of **3** in CD_2Cl_2 at room temperature in a J Young valve NMR tube led to rapid changes in its 1H NMR spectrum. Within 30 min after the addition, the 1H NMR spectrum exhibited a new resonance at 9.69 ppm, which corresponds to formaldehyde, along with the signals of the ligand **L** for the cyanide complex **4**. While its formation is facile at room temperature, we found that the synthesis of complex **4** on a preparative scale was best achieved upon addition of dioxygen to **3** and heating at 60 °C.

In several reported instances of H_3C-CN bond cleavage in acetonitrile promoted by copper complexes, the ultimate fate of the methyl fragment is unclear or has been disputed.^{30,32,33}

To follow the transformations of the methylene moiety of **3** during the $C-C$ bond cleavage, we synthesized an isotopomer complex $\{(C_5H_3N)(C_2B_{10}H_{10})_2\}Ni(^{13}CH_3CN)$ **2a** utilizing ^{13}C -enriched acetonitrile ($^{13}CH_3CN$, 99% ^{13}C) and converted it to $K[\{(C_5H_3N)(C_2B_{10}H_{10})_2\}Ni(^{13}CH_2CN)]$ **3a** (Figure 3).

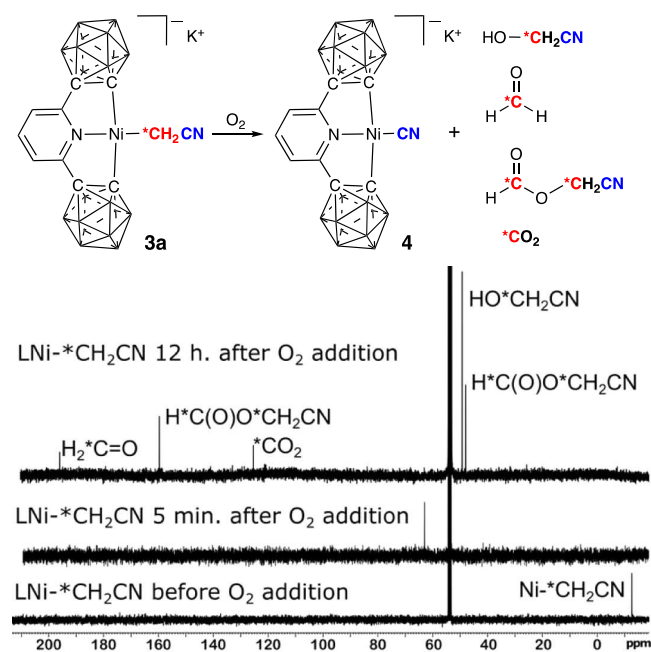


Figure 3. Tracking of carbon-containing products in the $C-C$ bond-breaking transformation during the conversion of ^{13}C -enriched $K[\{(C_5H_3N)(C_2B_{10}H_{10})_2\}Ni(^{13}CH_2CN)]$ **3a** to $K[\{(C_5H_3N)(C_2B_{10}H_{10})_2\}Ni(CN)]$ **4**. The ^{13}C NMR spectra of the reaction mixture demonstrate the reaction progression and identity of the ^{13}C -enriched products.

With the ^{13}C -enriched (ca. 52% $LNi-^{13}CH_2CN$ and 48% $LNi-^{12}CH_2CN$) complex in hands, we carried out a time-controlled experiment, where we observed the complete disappearance of the 1H and ^{13}C resonances of the methylene moiety in **3a** within 5 min of oxygen addition. Moreover, the 1H and ^{13}C NMR spectra exhibited new resonances at 4.50 ppm (doublet, $J_{CH} = 154$ Hz) and 62.9 ppm, respectively, which confirmed the rapid conversion of **3a** to a single intermediate that proved to be short-lived. Within the next 15 min, the intensity of the 1H resonance at 4.50 ppm drastically decreased, and several new signals appeared in the range from 4.19 to 5.01 ppm. The ^{13}C - 1H HSQC and HMBC NMR spectra in CD_2Cl_2 confirmed the formation of carbon dioxide $^{13}CO_2$ ($\delta = 125.2$ ppm),⁶¹ along with formaldehyde $H^{13}CHO$ ($\delta = 195.6$ ppm),⁶² hydroxyacetonitrile $HO^{13}CH_2CN$ ($\delta = 49.4$ ppm),^{63,64} and cyanomethyl formate $H^{13}C(O)-O^{13}CH_2CN$ ($\delta = 159.4$ and 48.1 ppm)^{65,66} as the eventual ^{13}C -enriched products (Figure 3 and Supporting Information). These results shed some light on the observed $C-C$ bond cleavage and the formation of the cyanide complex **4**. Apparently, the oxidation of the cyanoalkyl group in **2** leads to the formation of hydroxyacetonitrile, which is known to decompose into formaldehyde and hydrogen cyanide.⁶⁷ The 1H NMR spectrum of a recently structurally characterized cyanoalkoxide of germanium(II) contained the signal for the $Ge-OCH_2CN$ methylene protons at 4.16 ppm, which can be compared with the signal at 4.50 ppm for the short-lived

intermediate after **3a** oxygen exposure.⁶⁸ The sequence of steps for the subsequent formation of more oxygenated cyanomethyl formate and carbon dioxide is less clear at the moment. Notably, when a solution of **3a** was treated with approximately one equivalent of oxygen, the short-lived intermediate referenced above was stable at room temperature for several hours. After that time, only H¹³CHO was detected in the ¹³C NMR spectrum, suggesting that the formation of the other observed ¹³C-enriched products, for example, CO₂, occurs under excess dioxygen in this system.

Additionally, UV–visible spectroscopy was employed to follow the C–CN bond-breaking process. The spectrum of **3** in dichloromethane under nitrogen contained bands at 240, 386, and 412 nm (Figure 4a and green trace in Figure 4c). Upon addition of oxygen, a relatively short-lived intermediate state that exhibited bands at 260, 360, and 412 nm was generated immediately (dashed blue line in Figure 4c). Within 10 min, the spectrum changed to contain additional bands at 286, 332, and 483 nm (dashed red line in Figure 4c). Within 2 h, the spectrum of the mixture resembled that of the independently prepared cyanide complex **4** (compare the black line in Figure 4b,c). These spectral changes, while do not reveal the precise structure of the intermediates involved, are in agreement with the sequence and rates of the observed changes in ¹H and ¹³C NMR spectra discussed above.

To probe the unusual C–C bond activation of the cyanoalkyl group further, we carried out a quenching experiment. The elucidation of the reaction mechanism involving activation of dioxygen can be challenging since a variety of paths may be operative depending on the reaction conditions.^{69–72} As a representative of reactive oxygen species, the radical anion O₂^{•−} is considered as a potential green oxidant; however, in most cases, its detection and characterization are often elusive. The rapid reaction of **3a** with dioxygen may suggest a possible involvement of radical intermediates. Oxidation of triphenylphosphine to triphenylphosphine oxide is often indicative of the involvement of peroxide or superoxides under aerobic conditions.^{69,73,74} For example, recently, MacBeth, Berry, and co-workers demonstrated stoichiometric oxidation of PPh₃ by a monometallic superoxo cobalt complex.⁷⁵ In an attempt to probe the generation of active oxygen species, we added oxygen to a solution of **3** in CD₂Cl₂ that contained 1 equiv. of PPh₃. The ³¹P NMR spectrum exhibited a characteristic resonance at 29.3 ppm attributed to P(O)Ph₃ after 5 min of oxygen addition. The observed rapid oxidation of PPh₃ may indicate the involvement of nickel-bound superoxide intermediates generated upon oxygenation of **3a**.⁷⁴ In contrast, triphenylphosphine is stable in the presence of the parent acetonitrile complex **2** on air.

CONCLUSIONS

In summary, we report the reactivity of acetonitrile-ligated nickel(II) pyridyldicarbonyl with strong bases to selectively produce a methylenecyanide complex. The subsequent reaction with dioxygen at room temperature proceeds with the formation of cyanide ligand through the C–C bond activation of the cyanomethylene group. The use of ¹³C labeling of the starting acetonitrile allowed us to track transformations of the methylene group to confidently demonstrate for the first time that the predominant product of this aerobic oxidation is hydroxyacetonitrile and its corresponding alkoxide, which decompose into formaldehyde

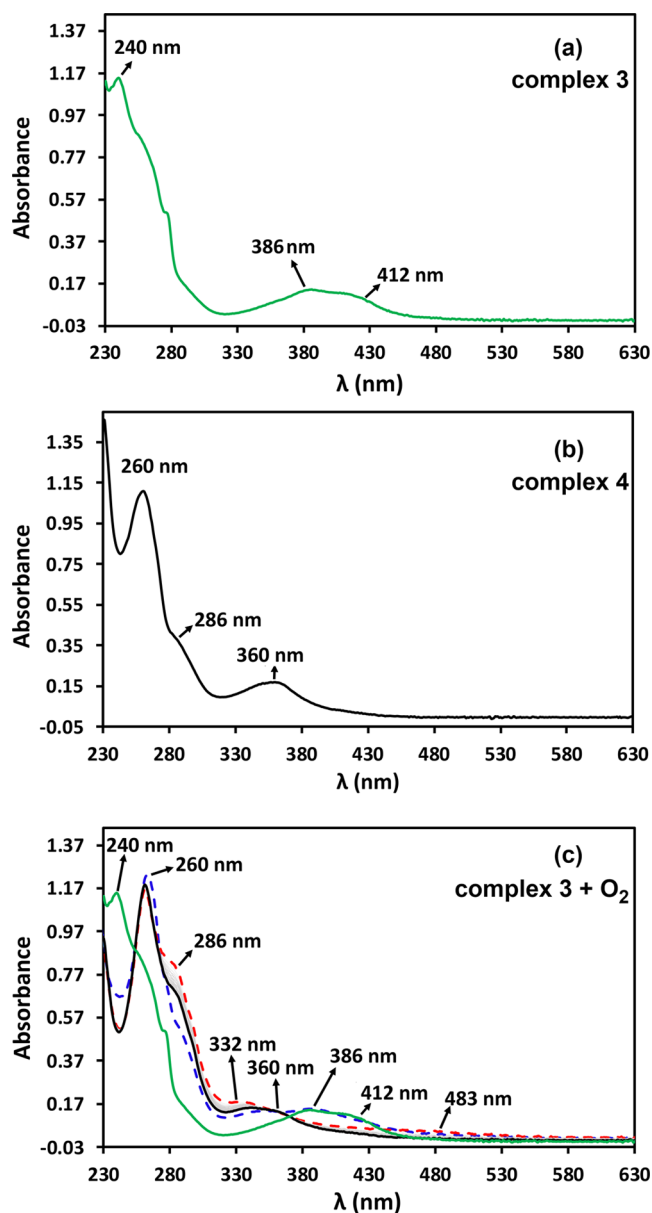


Figure 4. (a) UV–vis absorption spectrum of 0.05 mM **3** in dichloromethane. (b) UV–vis absorption spectrum of 0.05 mM **4** in dichloromethane. (c) UV–vis spectral changes after the addition of O₂ in a solution of 0.05 mM **3** in dichloromethane. Curves: green line, pure **3**; dashed blue line, **3** + O₂ after 5 min (first intermediate); dashed red line, **3** + O₂ after 10 min (second intermediate); black line, formation of **4** after 2 h.

and cyanide. The other observed products are cyanomethyl formate and carbon dioxide. The reported chemistry is a new mode of C–C bond activation of nitriles that does not utilize low-valent nickel species but instead involves apparent oxidation of the nickel–carbon bond.

MATERIALS AND METHODS

All synthetic manipulations, unless stated otherwise, were carried out either in a nitrogen-filled VAC dry box or on a dual manifold Schlenk-style vacuum line.⁷⁶ The solvents were sparged with nitrogen, passed through activated alumina, and stored over activated 4 Å Linde-type molecular sieves. Deuterated solvents C₆D₆ and CD₂Cl₂ were degassed and stored over activated 4 Å Linde-type molecular sieves. NMR spectra were recorded using Varian spectrometers at 400 (¹H),

100 (^{13}C), 128 (^{11}B) MHz, reported in δ (parts per million) and referenced to the residual $^1\text{H}/^{13}\text{C}$ signals of the deuterated solvent or an external $\text{BF}_3(\text{Et}_2\text{O})$ ($^{11}\text{B}(\delta)$: 0.0 ppm) standard.

The starting pro-ligand $(\text{C}_5\text{H}_3\text{N})(\text{C}_2\text{B}_{10}\text{H}_{11})_2$ (**1**) and its Ni(II) acetonitrile-ligated complex $\{(\text{C}_5\text{H}_3\text{N})(\text{C}_2\text{B}_{10}\text{H}_{10})_2\}\text{Ni}(\text{CH}_3\text{CN})$ (**2**) were prepared according to the previously reported procedure.³⁴ *ortho*-Carborane $\text{C}_2\text{B}_{10}\text{H}_{12}$ (Boron Specialties) and *n*-butyllithium solution (*n*-BuLi, 2.5 M solution in hexane), were used as received. Acetonitrile $^{13}\text{C}_3\text{H}_3\text{N}$ (99% ^{13}C -enriched at the methyl carbon, Cambridge Isotope Laboratories) was degassed and stored over molecular sieves in a glovebox.

Synthesis of $\text{K}\{[(\text{C}_5\text{H}_3\text{N})(\text{C}_2\text{B}_{10}\text{H}_{10})_2]\text{Ni}(\text{CH}_2\text{CN})\}$ (3**).** A portion of potassium *tert*-butoxide (26 mg, 0.23 mmol) was added to a solution of 2,6-bis(carboranyl)pyridine nickel(II)(acetonitrile) (**2**) (100 mg, 0.22 mmol) in benzene (5 mL) under nitrogen atmosphere. Dissolution of the complex was observed in 30 min, resulting in a light-yellow solution. The mixture was stirred at room temperature for 12 h, after which time volatiles were removed under vacuum. The resulting solid was washed with hexanes (3 mL \times 3 mL) and dried under vacuum (101 mg, 93% yield). Single crystals were grown from a benzene solution of **3** and contained benzene inclusion molecules.

^1H NMR (CD_2Cl_2): δ 7.71 (t, 1H, $\text{C}_5\text{H}_3\text{N}$), 7.21 (d, 2H, $\text{C}_5\text{H}_3\text{N}$), 3.10–1.30 (overlapping, 20H, B–H, $\text{C}_2\text{B}_{10}\text{H}_{10}$), 0.63 (s, 2H, CH_2CN). $^{11}\text{B}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ –3.85, –6.63, –10.86. ^{13}C NMR (CD_2Cl_2): δ 158.0 ($\text{C}_5\text{H}_3\text{N}$), 138.4 ($\text{C}_5\text{H}_3\text{N}$), 120.4 ($\text{C}_5\text{H}_3\text{N}$), 133.2 (CH_2CN), 82.9 ($\text{C}_2\text{H}_{10}\text{B}_{10}$), 81.42 ($\text{C}_2\text{H}_{10}\text{B}_{10}$), –12.89 (CH_2CN). Anal. Calcd. for $\text{C}_{11}\text{H}_{25}\text{B}_{20}\text{KN}_2\text{Ni}$: C, 26.46; H, 5.05; N, 5.61. Found: C, 27.27; H, 5.78; N, 5.33.

Synthesis of $\text{K}\{[(\text{C}_5\text{H}_3\text{N})(\text{C}_2\text{B}_{10}\text{H}_{10})_2]\text{Ni}(\text{CN})\}$ (4**).** Excess of dioxygen gas was added to a degassed solution of $\text{K}\{[(\text{C}_5\text{H}_3\text{N})(\text{C}_2\text{B}_{10}\text{H}_{10})_2]\text{Ni}(\text{CH}_2\text{CN})\}$ (50 mg, 0.20 mmol) in benzene (10 mL). The mixture was stirred at 60 °C for 24 h, after which time volatiles were removed under vacuum. The pale-yellow solid was washed with hexanes (3 mL \times 3 mL) and dried under vacuum (40 mg, 82% yield). Single crystals were grown from a benzene solution of **4** and contained benzene solvate and inclusion molecules.

^1H NMR (C_6D_6): δ 6.24 (d, 2H, $\text{C}_5\text{H}_3\text{N}$), 6.15 (t, 1H, $\text{C}_5\text{H}_3\text{N}$), 3.80–1.90 (overlapping, 20H, B–H, $\text{C}_2\text{B}_{10}\text{H}_{10}$). $^{11}\text{B}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ –3.14, –6.47, –9.82. ^{13}C NMR (CD_2Cl_2): δ 159.5 ($\text{C}_5\text{H}_3\text{N}$), 140.5 ($\text{C}_5\text{H}_3\text{N}$), 120.9 ($\text{C}_5\text{H}_3\text{N}$), 82.0 ($\text{C}_2\text{H}_{10}\text{B}_{10}$), 76.0 ($\text{C}_2\text{H}_{10}\text{B}_{10}$). Anal. Calcd. for benzene solvate $\text{C}_{34}\text{H}_{47}\text{B}_{20}\text{KN}_2\text{Ni}$: C, 51.19; H, 5.94; N, 3.51. Found: C, 50.26; H, 5.17; N, 3.86.

Synthesis of $\text{K}\{[(\text{C}_5\text{H}_3\text{N})(\text{C}_2\text{B}_{10}\text{H}_{10})_2]\text{Ni}(^{13}\text{CH}_3\text{CN})\}$ (2a**).** A portion of ^{13}C -labeled acetonitrile ($^{13}\text{CH}_3\text{CN}$, 2-13C 99%) (0.068 mL, 1.30 mmol) was added to a solution of 2,6-bis(carboranyl)pyridine nickel(II)(acetonitrile) (30 mg, 0.065 mmol) in methylene chloride (5 mL). The mixture was stirred at 65 °C for 6 h, after which time volatiles were removed under vacuum.

^1H NMR (CD_2Cl_2): δ 7.79 (t, 1H, $\text{C}_5\text{H}_3\text{N}$), 7.21 (d, 2H, $\text{C}_5\text{H}_3\text{N}$), 2.38 (t, 3H, CH_3CN). ^{13}C NMR (CD_2Cl_2): δ 3.99 (CH_3CN).

Synthesis of $\text{K}\{[(\text{C}_5\text{H}_3\text{N})(\text{C}_2\text{B}_{10}\text{H}_{10})_2]\text{Ni}(^{13}\text{CH}_2\text{CN})\}$ (3a**).** A portion of potassium *tert*-butoxide (2.6 mg, 0.023 mmol) was added to a solution of $\{[(\text{C}_5\text{H}_3\text{N})(\text{C}_2\text{B}_{10}\text{H}_{10})_2]\text{Ni}(^*\text{CH}_3\text{CN})\}$ (10 mg, 0.022 mmol) in benzene (5 mL) under nitrogen atmosphere. The mixture was stirred at room temperature for 12 h, after which time volatiles were removed under vacuum. The resulting solid was washed with hexanes (3 mL \times 3 mL) and dried under vacuum.

^1H NMR (CD_2Cl_2): δ 7.71 (t, 1H, $\text{C}_5\text{H}_3\text{N}$), 7.23 (d, 2H, $\text{C}_5\text{H}_3\text{N}$), 3.10–1.30 (overlapping, 20H, B–H, $\text{C}_2\text{B}_{10}\text{H}_{10}$), 0.62 (t, 2H, CH_2CN). ^{13}C NMR (CD_2Cl_2): δ –12.58 (CH_2CN).

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.3c00216>.

Characterization data (NMR spectra and crystallographic details) (PDF)

Accession Codes

CCDC 2258920–2258922 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

CCDC 2258920–2258922 contain the supplementary crystallographic data for this paper.

■ AUTHOR INFORMATION

Corresponding Author

Dmitry V. Peryshkov – Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, United States; orcid.org/0000-0002-5653-9502; Email: peryskhov@sc.edu

Authors

Mohammad Jahirul Islam – Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, United States

Kyoung Chul Park – Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, United States

Olivia M. Manley – Department of Molecular and Structural Biochemistry, North Carolina State University, Raleigh, North Carolina 27695, United States

Mark D. Smith – Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, United States

Thomas M. Makris – Department of Molecular and Structural Biochemistry, North Carolina State University, Raleigh, North Carolina 27695, United States; orcid.org/0000-0001-7927-620X

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.organomet.3c00216>

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This material is based in part upon work supported by the National Science Foundation under Awards CHE-1654301 and CHE-2154828.

■ REFERENCES

- (1) Chen, F.; Wang, T.; Jiao, N. Recent Advances in Transition-Metal-Catalyzed Functionalization of Unstrained Carbon–Carbon Bonds. *Chem. Rev.* **2014**, *114*, 8613–8661.
- (2) Murakami, M.; Ishida, N. Potential of Metal-Catalyzed C–C Single Bond Cleavage for Organic Synthesis. *J. Am. Chem. Soc.* **2016**, *138*, 13759–13769.
- (3) Fumagalli, G.; Stanton, S.; Bower, J. F. Recent Methodologies That Exploit C–C Single-Bond Cleavage of Strained Ring Systems by Transition Metal Complexes. *Chem. Rev.* **2017**, *117*, 9404–9432.
- (4) Lutz, M. D. R.; Morandi, B. Metal-Catalyzed Carbon–Carbon Bond Cleavage of Unstrained Alcohols. *Chem. Rev.* **2021**, *121*, 300–326.
- (5) Souillart, L.; Cramer, N. Catalytic C–C Bond Activations via Oxidative Addition to Transition Metals. *Chem. Rev.* **2015**, *115*, 9410–9464.
- (6) Patra, T.; Agasti, S.; Akanksha; Maiti, D. Nickel-Catalyzed Decyanation of Inert Carbon–Cyano Bonds. *Chem. Commun.* **2012**, 49, 69–71.

- (7) Patra, T.; Agasti, S.; Modak, A.; Maiti, D. Nickel-Catalyzed Hydrogenolysis of Unactivated Carbon–Cyano Bonds. *Chem. Commun.* **2013**, *49*, 8362–8364.
- (8) Zhang, J.-S.; Chen, T.; Yang, J.; Han, L.-B. Nickel-Catalyzed P–C Bond Formation via P–H/C–CN Cross Coupling Reactions. *Chem. Commun.* **2015**, *51*, 7540–7542.
- (9) Tobisu, M.; Kinuta, H.; Kita, Y.; Rémond, E.; Chatani, N. Rhodium(I)-Catalyzed Borylation of Nitriles through the Cleavage of Carbon–Cyano Bonds. *J. Am. Chem. Soc.* **2012**, *134*, 115–118.
- (10) Schmalz, H.-G. A Molecular Shuttle for Hydrogen Cyanide. *Science* **2016**, *351*, 817.
- (11) Fang, X.; Yu, P.; Morandi, B. Catalytic Reversible Alkene–Nitrile Interconversion through Controllable Transfer Hydrocyanation. *Science* **2016**, *351*, 832–836.
- (12) Kou, X.; Zhao, M.; Qiao, X.; Zhu, Y.; Tong, X.; Shen, Z. Copper-Catalyzed Aromatic C–H Bond Cyanation by C–CN Bond Cleavage of Inert Acetonitrile. *Chem. – Eur. J.* **2013**, *19*, 16880–16886.
- (13) Tobisu, M.; Chatani, N. Catalytic Reactions Involving the Cleavage of Carbon–Cyano and Carbon–Carbon Triple Bonds. *Chem. Soc. Rev.* **2008**, *37*, 300–307.
- (14) Nakao, Y. Metal-Mediated C–CN Bond Activation in Organic Synthesis. *Chem. Rev.* **2021**, *121*, 327–344.
- (15) Xu, H.; Williard, P. G.; Bernskoetter, W. H. C–CN Bond Activation of Acetonitrile Using Cobalt(I). *Organometallics* **2012**, *31*, 1588–1590.
- (16) Li, X.; Sun, H.; Yu, F.; Flörke, U.; Klein, H.-F. C–F Bond Cleavage and Unexpected C–CN Activation by Cobalt Compounds Supported with Phosphine Ligands. *Organometallics* **2006**, *25*, 4695–4697.
- (17) Evans, M. E.; Li, T.; Jones, W. D. C–H vs C–C Bond Activation of Acetonitrile and Benzonitrile via Oxidative Addition: Rhodium vs Nickel and Cp* vs Tp' (Tp' = Hydrotris(3,5-Dimethylpyrazol-1-Yl)Borate, Cp* = HS-Pentamethylcyclopentadienyl). *J. Am. Chem. Soc.* **2010**, *132*, 16278–16284.
- (18) Evans, M. E.; Jones, W. D. Controlling the Selectivity for C–H and C–CN Bond Activation at Rhodium: A DFT Examination of Ligand Effects. *Organometallics* **2011**, *30*, 3371–3377.
- (19) Ateşin, T. A.; Li, T.; Lachaize, S.; Brennessel, W. W.; García, J. J.; Jones, W. D. Experimental and Theoretical Examination of C–CN and C–H Bond Activations of Acetonitrile Using Zerovalent Nickel. *J. Am. Chem. Soc.* **2007**, *129*, 7562–7569.
- (20) García, J. J.; Arévalo, A.; Brunkan, N. M.; Jones, W. D. Cleavage of Carbon–Carbon Bonds in Alkyl Cyanides Using Nickel(0). *Organometallics* **2004**, *23*, 3997–4002.
- (21) Munjanja, L.; Torres-López, C.; Brennessel, W. W.; Jones, W. D. C–CN Bond Cleavage Using Palladium Supported by a Dippe Ligand. *Organometallics* **2016**, *35*, 2010–2013.
- (22) Churchill, D.; Shin, J. H.; Hascall, T.; Hahn, J. M.; Bridgewater, B. M.; Parkin, G. The Ansa Effect in Permethylmolybdenocene Chemistry: A [Me₂Si] Ansa Bridge Promotes Intermolecular C–H and C–C Bond Activation. *Organometallics* **1999**, *18*, 2403–2406.
- (23) Garcia, J. J.; Brunkan, N. M.; Jones, W. D. Cleavage of Carbon–Carbon Bonds in Aromatic Nitriles Using Nickel(0). *J. Am. Chem. Soc.* **2002**, *124*, 9547–9555.
- (24) Taw, F. L.; White, P. S.; Bergman, R. G.; Brookhart, M. Carbon–Carbon Bond Activation of R–CN (R = Me, Ar, ⁱPr, ^tBu) Using a Cationic Rh(III) Complex. *J. Am. Chem. Soc.* **2002**, *124*, 4192–4193.
- (25) Schaub, T.; Döring, C.; Radius, U. Efficient Nickel Mediated Carbon–Carbon Bond Cleavage of Organonitriles. *Dalton Trans.* **2007**, 1993–2002.
- (26) Miller, J. A.; Dankwardt, J. W.; Penney, J. M. Nickel Catalyzed Cross-Coupling and Amination Reactions of Aryl Nitriles. *Synthesis* **2003**, *2003*, 1643–1648.
- (27) Nakao, Y.; Oda, S.; Hiyama, T. Nickel-Catalyzed Arylcyanation of Alkynes. *J. Am. Chem. Soc.* **2004**, *126*, 13904–13905.
- (28) Reilly, S. W.; Lam, Y.; Ren, S.; Strotman, N. A. Late-Stage Carbon Isotope Exchange of Aryl Nitriles through Ni-Catalyzed C–CN Bond Activation. *J. Am. Chem. Soc.* **2021**, *143*, 4817–4823.
- (29) Delcaillau, T.; Boehm, P.; Morandi, B. Nickel-Catalyzed Reversible Functional Group Metathesis between Aryl Nitriles and Aryl Thioethers. *J. Am. Chem. Soc.* **2021**, *143*, 3723–3728.
- (30) Marlin, D. S.; Olmstead, M. M.; Mascharak, P. K. Heterolytic Cleavage of the C–C Bond of Acetonitrile with Simple Monomeric CuII Complexes: Melding Old Copper Chemistry with New Reactivity. *Angew. Chem., Int. Ed.* **2001**, *40*, 4752–4754.
- (31) Zhang, X.; Zhang, Z.; Xiang, S.; Zhu, Y.; Chen, C.; Huang, D. Base Induced C–CN Bond Cleavage at Room Temperature: A Convenient Method for the Activation of Acetonitrile. *Inorg. Chem. Front.* **2019**, *6*, 1135–1140.
- (32) Lu, T.; Zhuang, X.; Li, Y.; Chen, S. C–C Bond Cleavage of Acetonitrile by a Dinuclear Copper(II) Cryptate. *J. Am. Chem. Soc.* **2004**, *126*, 4760–4761.
- (33) Bond, A. D.; Derossi, S.; Jensen, F.; Larsen, F. B.; McKenzie, C. J.; Nelson, J. Squeezing the [Cu–OH··H₂O–Cu]³⁺ Bridge by Cryptate Encapsulation. *Inorg. Chem.* **2005**, *44*, 5987–5989.
- (34) Islam, M. J.; Smith, M. D.; Peryshkov, D. V. Sterically Encumbered Dianionic Dicarboranyl Pincer Ligand (C₂H₃N)-(C₂B₁₀H₁₁)₂ and Its CNC Nickel(II) Complex. *J. Organomet. Chem.* **2018**, *867*, 208–213.
- (35) Grimes, R. N. *Carboranes*, 3rd ed.; Academic Press: Amsterdam; Boston, 2016.
- (36) Hawthorne, M. F. *Boranes and Beyond: History and the Man Who Created Them*; Springer: New York, NY, 2023. DOI: 10.1007/978-1-0716-2908-6.
- (37) Grimes, R. N. Carboranes in the Chemist's Toolbox. *Dalton Trans.* **2015**, *44*, 5939–5956.
- (38) Stauber, J. M.; Qian, E. A.; Han, Y.; Rheingold, A. L.; Král, P.; Fujita, D.; Spokoyny, A. M. An Organometallic Strategy for Assembling Atomically Precise Hybrid Nanomaterials. *J. Am. Chem. Soc.* **2020**, *142*, 327–334.
- (39) Fisher, S. P.; Tomich, A. W.; Lovera, S. O.; Kleinsasser, J. F.; Guo, J.; Asay, M. J.; Nelson, H. M.; Lavallo, V. Nonclassical Applications of Closo -Carborane Anions: From Main Group Chemistry and Catalysis to Energy Storage. *Chem. Rev.* **2019**, *119*, 8262–8290.
- (40) Fisher, S. P.; Tomich, A. W.; Guo, J.; Lavallo, V. Teaching an Old Dog New Tricks: New Directions in Fundamental and Applied Closo-Carborane Anion Chemistry. *Chem. Commun.* **2019**, *55*, 1684–1701.
- (41) Axtell, J. C.; Saleh, L. M. A.; Qian, E. A.; Wixtrom, A. I.; Spokoyny, A. M. Synthesis and Applications of Perfunctionalized Boron Clusters. *Inorg. Chem.* **2018**, *57*, 2333–2350.
- (42) Eleazer, B. J.; Peryshkov, D. V. Coordination Chemistry of Carborane Clusters: Metal-Boron Bonds in Carborane, Carboranyl, and Carboryne Complexes. *Comments Inorg. Chem.* **2018**, *38*, 79–109.
- (43) Anderson, K. P.; Mills, H. A.; Mao, C.; Kirlikovali, K. O.; Axtell, J. C.; Rheingold, A. L.; Spokoyny, A. M. Improved Synthesis of Icosahedral Carboranes Containing Exopolyhedral BC and CC Bonds. *Tetrahedron* **2019**, *75*, 187–191.
- (44) Jayaweera, H. D. A. C.; Rahman, M. M.; Pellechia, P. J.; Smith, M. D.; Peryshkov, D. V. Free Three-Dimensional Carborane Carbanions. *Chem. Sci.* **2021**, *12*, 10441–10447.
- (45) Bawari, D.; Jaiswal, K.; Toami, D.; Dobrovetsky, R. Hydrogen Splitting at a Single PIII-Center and Its Use for Hydrogenation. *ChemRxiv*, June 6, 2023, DOI: 10.26434/chemrxiv-2023-jg5x7.
- (46) Miller, J. R.; Cook, A. R.; Šimková, L.; Pospíšil, L.; Ludvík, J.; Michl, J. The Impact of Huge Structural Changes on Electron Transfer and Measurement of Redox Potentials: Reduction of Ortho-12-Carborane. *J. Phys. Chem. B* **2019**, *123*, 9668–9676.
- (47) McKay, D.; Macgregor, S. A.; Welch, A. J. Isomerisation of Nido-[C₂B₁₀H₁₂]²⁻ Dianions: Unprecedented Rearrangements and New Structural Motifs in Carborane Cluster Chemistry. *Chem. Sci.* **2015**, *6*, 3117–3128.

- (48) Kahlert, J.; Böhlting, L.; Brockhinke, A.; Stammer, H.-G.; Neumann, B.; Rendina, L. M.; Low, P. J.; Weber, L.; Fox, M. A. Syntheses and Reductions of C-Dimesitylboryl-1,2-Dicarba-Closo-Dodecaboranes. *Dalton Trans.* **2015**, *44*, 9766–9781.
- (49) Gange, G. B.; Humphries, A. L.; Royzman, D. E.; Smith, M. D.; Peryshkov, D. V. Metal-Free Bond Activation by Carboranyl Diphosphines. *J. Am. Chem. Soc.* **2021**, *143*, 10842–10846.
- (50) Spokoiny, A. M.; Machan, C. W.; Clingerman, D. J.; Rosen, M. S.; Wiester, M. J.; Kennedy, R. D.; Stern, C. L.; Sarjeant, A. A.; Mirkin, C. A. A Coordination Chemistry Dichotomy for Icosahedral Carborane-Based Ligands. *Nat. Chem.* **2011**, *3*, 590–596.
- (51) Oertel, A. M.; Ritleng, V.; Chetcuti, M. J.; Veiros, L. F. C–H Activation of Acetonitrile at Nickel: Ligand Flip and Conversion of N-Bound Acetonitrile into a C-Bound Cyanomethyl Ligand. *J. Am. Chem. Soc.* **2010**, *132*, 13588–13589.
- (52) Chakraborty, S.; Patel, Y. J.; Krause, J. A.; Guan, H. A Robust Nickel Catalyst for Cyanomethylation of Aldehydes: Activation of Acetonitrile under Base-Free Conditions. *Angew. Chem., Int. Ed.* **2013**, *52*, 7523–7526.
- (53) Fan, L.; Ozerov, O. V. Efficient Nickel Catalyst for Coupling of Acetonitrile with Aldehydes. *Chem. Commun.* **2005**, *35*, 4450–4452.
- (54) Tehranchi, J.; Donoghue, P. J.; Cramer, C. J.; Tolman, W. B. Reactivity of (Dicarboxamide)MII–OH (M = Cu, Ni) Complexes – Reaction with Acetonitrile to Yield MII–Cyanomethides. *Eur. J. Inorg. Chem.* **2013**, *2013*, 4077–4084.
- (55) Hasche, P.; Spannenberg, A.; Beweries, T. Study of the Reactivity of the [(PEICE2P)Ni(II)] (E1, E2 = O, S) Pincer System with Acetonitrile and Base: Formation of Cyanomethyl and Amidocrotonitrile Complexes versus Ligand Decomposition by P–S Bond Activation. *Organometallics* **2019**, *38*, 4508–4515.
- (56) Scheuermann, M. L.; Goldberg, K. I. Reactions of Pd and Pt Complexes with Molecular Oxygen. *Chem. – Eur. J.* **2014**, *20*, 14556–14568.
- (57) Sberegaeva, A. V.; Zavalij, P. Y.; Vedernikov, A. N. Oxidation of a Monomethylpalladium(II) Complex with O₂ in Water: Tuning Reaction Selectivity to Form Ethane, Methanol, or Methylhydroperoxide. *J. Am. Chem. Soc.* **2016**, *138*, 1446–1455.
- (58) Smoll, K. A.; Kaminsky, W.; Goldberg, K. I. Photolysis of Pincer-Ligated PdII–Me Complexes in the Presence of Molecular Oxygen. *Organometallics* **2017**, *36*, 1213–1216.
- (59) Boisvert, L.; Denney, M. C.; Hanson, S. K.; Goldberg, K. I. Insertion of Molecular Oxygen into a Palladium(II) Methyl Bond: A Radical Chain Mechanism Involving Palladium(III) Intermediates. *J. Am. Chem. Soc.* **2009**, *131*, 15802–15814.
- (60) Ho, S. K. Y.; Lam, F. Y. T.; de Aguirre, A.; Maseras, F.; White, A. J. P.; Britovsek, G. J. P. Photolytic Activation of Late-Transition-Metal–Carbon Bonds and Their Reactivity toward Oxygen. *Organometallics* **2021**, *40*, 4077–4091.
- (61) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29*, 2176–2179.
- (62) Dahn, H.; Péchy, P. Concerning the Chemical Shift Data (¹⁷O, ¹³C, ¹H) of Formaldehyde. *Magn. Reson. Chem.* **1996**, *34*, 723–724.
- (63) Panova, A.; Mersinger, L. J.; Liu, Q.; Foo, T.; Roe, D. C.; Spillan, W. L.; Sigmund, A. E.; Ben-Bassat, A.; Wagner, L. W.; O’Keefe, D. P.; Wu, S.; Petrillo, K. L.; Payne, M. S.; Breske, S. T.; Gallagher, F. G.; DiCosimo, R. Chemoenzymatic Synthesis of Glycolic Acid. *Adv. Synth. Catal.* **2007**, *349*, 1462–1474.
- (64) Claes, L.; Matthesen, R.; Rombouts, I.; Stassen, I.; De Baerdemaeker, T.; Depla, D.; Delcour, J. A.; Lagrain, B.; De Vos, D. E. Bio-Based Nitriles from the Heterogeneously Catalyzed Oxidative Decarboxylation of Amino Acids. *ChemSusChem* **2015**, *8*, 345–352.
- (65) Deutsch, J.; Niclas, H.-J. A Convenient Procedure for the Formylation of Amines and Alcohols Using Cyanomethyl Formate. *Synth. Commun.* **1993**, *23*, 1561–1568.
- (66) Ducek, W.; Deutsch, J.; Vieth, S.; Niclas, H.-J. A Simple and Convenient Synthesis of N-Formyl Amino Acid Esters Under Mild Conditions. *Synthesis* **1996**, *1996*, 37–38.
- (67) Ahmed, T. J.; Fox, B. R.; Knapp, S. M. M.; Yelle, R. B.; Juliette, J. J.; Tyler, D. R. Investigation of the Reactivity of Pt Phosphinito and Molybdocene Nitrile Hydration Catalysts With Cyanohydrins. *Inorg. Chem.* **2009**, *48*, 7828–7837.
- (68) Siwath, R. K.; Nagendran, S. Germylene Cyanide Complex: A Reagent for the Activation of Aldehydes with Catalytic Significance. *Chem. – Eur. J.* **2014**, *20*, 13551–13556.
- (69) Bonesi, S. M.; Protti, S.; Albini, A. Reactive Oxygen Species (ROS)-vs Peroxyl-Mediated Photosensitized Oxidation of Triphenylphosphine: A Comparative Study. *J. Org. Chem.* **2016**, *81*, 11678–11685.
- (70) Hayyan, M.; Hashim, M. A.; AlNashef, I. M. Superoxide Ion: Generation and Chemical Implications. *Chem. Rev.* **2016**, *116*, 3029–3085.
- (71) Cho, J.; Kang, H. Y.; Liu, L. V.; Sarangi, R.; Solomon, E. I.; Nam, W. Mononuclear Nickel(II)-Superoxo and Nickel(III)-Peroxo Complexes Bearing a Common Macrocyclic TMC Ligand. *Chem. Sci.* **2013**, *4*, 1502–1508.
- (72) Hu, C.-H.; Kim, S.-T.; Baik, M.-H.; Mirica, L. M. Nickel–Carbon Bond Oxygenation with Green Oxidants via High-Valent Nickel Species. *J. Am. Chem. Soc.* **2023**, *145*, 11161–11172.
- (73) Zeitler, H. E.; Kaminsky, W. A.; Goldberg, K. I. Insertion of Molecular Oxygen into the Metal–Methyl Bonds of Platinum(II) and Palladium(II) 1,3-Bis(2-Pyridylimino)Isoindolate Complexes. *Organometallics* **2018**, *37*, 3644–3648.
- (74) McNeece, A. J.; Jesse, K. A.; Xie, J.; Filatov, A. S.; Anderson, J. S. Generation and Oxidative Reactivity of a Ni(II) Superoxo Complex via Ligand-Based Redox Non-Innocence. *J. Am. Chem. Soc.* **2020**, *142*, 10824–10832.
- (75) Corcos, A. R.; Villanueva, O.; Walroth, R. C.; Sharma, S. K.; Bacsá, J.; Lancaster, K. M.; MacBeth, C. E.; Berry, J. F. Oxygen Activation by Co(II) and a Redox Non-Innocent Ligand: Spectroscopic Characterization of a Radical–Co(II)–Superoxide Complex with Divergent Catalytic Reactivity. *J. Am. Chem. Soc.* **2016**, *138*, 1796–1799.
- (76) Shriver, D. F.; Drezdson, M. A. *The Manipulation of Air-Sensitive Compound*, 2nd ed.; Wiley-Interscience: New York, 1986.