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Reductive C−C Coupling from α,β-Unsaturated Nitriles by Intercepting Keteniminates

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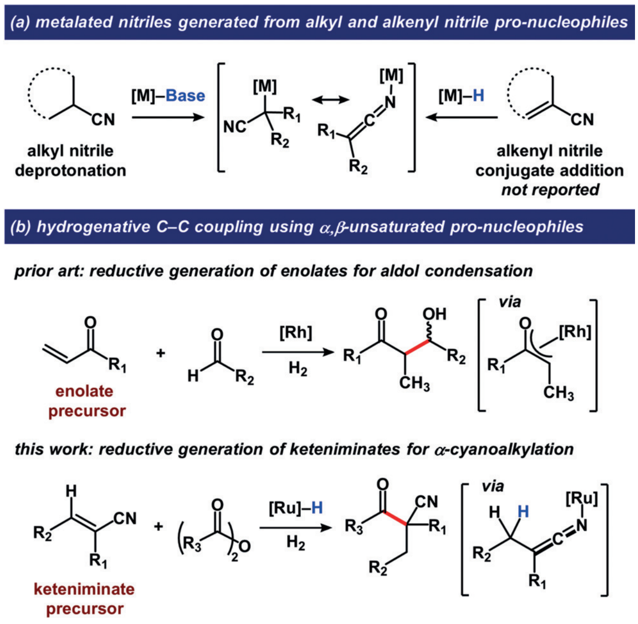
Abstract: *We present an atom-economic strategy to catalytically generate and intercept nitrile anion equivalents using hydrogen transfer catalysis. Addition of α,β-unsaturated nitriles to a pincer-based Ru−H complex affords structurally characterized κ-N-coordinated keteniminates by selective 1,4-hydride transfer. When generated in situ under catalytic hydrogenation conditions, electrophilic addition to the keteniminate was achieved using anhydrides to provide α-cyanoacetates in high yields. This work represents a new application of hydrogen transfer catalysis using α,β-unsaturated nitriles for reductive C−C coupling reactions.*

Nitrile anions are a diverse class of synthetic intermediates that provide access to highly functionalized products through nucleophilic addition and substitution reactions.[1] Analogous to enolates, nitrile anions are ambident nucleophiles that can react either as carbanions to provide α-functionalized cyano products,[1b–d] or as keteniminates to provide neutral ketenimines.[1d,2] Each product class has further synthetic utility as building blocks for natural products and pharmaceuticals; while α-cyano groups are easily derivatized, ketenimines further undergo nucleophilic, electrophilic, and/or cyclization reactions. To access the diverse chemical space of these nitrogen-containing compounds, new methods to generate and control the reactivity of nitrile anions are highly desirable.

The synthetic utility of nitrile anions is hindered by a lack of catalytic strategies available to generate them in situ from simple pro-nucleophiles. Alkyl nitriles are currently the major precursors to C- or N-metalated nitriles used in catalytic transformations (Scheme 1 a, left).[1b,c,3] Base-assisted deprotonation of alkyl nitriles with transition-metal catalysts has been successfully applied in a number of α-functionalization reactions; however, significant challenges remain. Methods that deliver products with all-carbon quaternary centers and/or provide high stereoselectivities are rare.[1b,c,4] These challenges may be addressed by designing new catalytic methods using pro-nucleophiles with distinct modes of activation. α,β-Unsaturated nitriles can generate nitrile anions through conjugate addition (Scheme 1 a, right), and are easily accessed from the corresponding ketone, aldehyde, or alkene in a single step.[5] Despite the potential for rapid multi-functionalization of α,β-unsaturated nitriles through conjugate addition, this mode of activation is virtually unexplored for catalytic applications.



Scheme 1. a) Formation of nitrile anions with alkyl nitrile or alkenyl nitrile pro-nucleophiles. b) Hydrogen-mediated reductive coupling using π-unsaturated substrates.

To contextualize the significance of expanding the pool of available pro-nucleophiles, it is useful to compare with well-established enolate chemistry; identifying new catalytic routes to form enolates or silyl enol ethers in situ has led to significant advances in selective reduction[6] and reductive C−C bond-forming reactions.[7] In particular, Krische and coworkers have developed reductive C−C coupling reactions using hydrogen transfer catalysts and π-unsaturated substrates.[7c,e] They reported that under catalytic hydrogenation conditions, α,β-unsaturated ketones generate enolates capable of participating in aldol condensations (Scheme 1 b).[7b] Our current work parallels these discoveries based on α,β-unsaturated ketones and is the first example of using alkenyl nitriles as pro-nucleophiles for hydrogenative C−C bond-forming reactions.

Although nitriles may undergo insertion into metal hydrides to afford imine-type products,[8] a second site of unsaturation may promote isomerization to form the resonance-stabilized nitrile anion/keteniminate. We previously reported that $HRu(bMepi)(PPh_3)_2$ (**1**; bMepi = 1,3-bis(6′-methyl-2′-pyridylimino)isoindoline)) is an excellent catalyst

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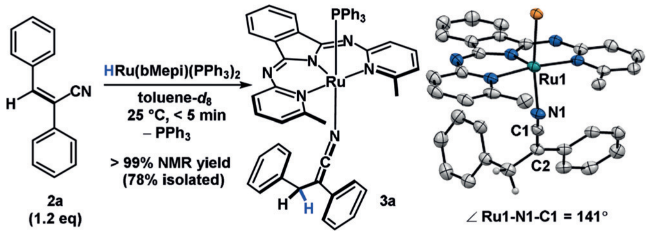
for reversible hydrogen transfer reactions of alcohols and amines.[9] For nitrile substrates, hydride insertion readily occurs to form imine-coordinated species, and the catalytically active Ru−H species can be directly (re)generated from H_2. Complex **1** exhibits unique reactivity with amines and nitriles, and has a high binding affinity for the intermediate imine.[9d,10] We hypothesized that this insertion reactivity would provide an entry point for evaluating hydrogenative C−C couplings with α,β-unsaturated nitriles.

We evaluated the insertion chemistry of α,β-unsaturated nitriles to Ru−H through stoichiometric addition of α-phenylcinnamonitrile (**2a**) to **1** (Scheme 2). When **2a**



Scheme 2. Formation of ruthenium–keteniminate complex **3a** by selective 1,4-hydride transfer. The solid-state structure is displayed with 50% probability ellipsoids.[27] The PPh_3 phenyl groups and hydrogen atoms, except for the -CH_2 group, are omitted for clarity.

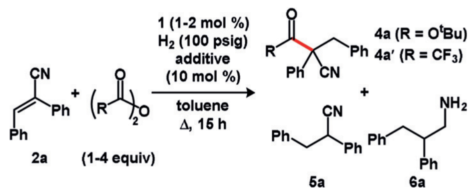
(1.2 equiv) was added to a toluene-d_8 solution of **1** at room temperature, quantitative conversion into a new species occurred within 5 min. ^{31}P NMR spectroscopy confirmed the disappearance of **1** ($\delta = 51$ ppm), concomitant with the appearance of free PPh_3 and a new resonance at $\delta = 39$ ppm. Complex **1** was also absent in the ^{1}H NMR spectrum, with no detectable H_2 or hydride-containing byproducts, consistent with a hydride insertion reaction. A phase-sensitive ^{1}H–^{13}C correlation experiment (HSQC) revealed the presence of a -CH_2 group ($\delta(^1\text{H}) = 3.21$ ppm; $\delta(^{13}\text{C}) = 34.5$ ppm), consistent with hydride addition to the least substituted carbon center of α-phenylcinnamonitrile (see the Supporting Information, Figure S5).

X-ray diffraction of single crystals unambiguously confirmed the insertion product as the ruthenium–keteniminate complex **3a**. The N-coordinated keteniminate has an elongated C1−N1 bond of 1.190(7) Å and a shortened C1−C2 bond of 1.369(7) Å. Analysis by IR spectroscopy revealed a bathochromic shift in the C−N stretching frequency between **2a** ($\nu_{CN} = 2218\ \text{cm}^{-1}$) and **3a** ($\nu_{CN} = 2210\ \text{cm}^{-1}$), consistent with C−N bond elongation upon formation of the C2=C1=N1 unit. These bond lengths and IR frequencies are consistent with those of known metal–keteniminate complexes and reflect the electronic delocalization from the partially negative C2 atom into the adjacent C1−N1 group.[11–13] A distinct feature of **3a** is the bent Ru-N1-C1 angle (141°), which is highly unusual for metalated keteniminates—only four structurally characterized keteniminate complexes exhibit M-N-C1 angles < 145°.[14–15] Moreover, all reported κ-N-Ru–keteniminate complexes exhibit nearly linear coordination (Ru-N1-C1 avg. 173°).[16] In addition to establishing a base-free route to form a keteniminate, the unique binding mode to Ru offers a new framework to develop subsequent reactivity.[17]

The linear geometry of substituted keteniminates allows for facile electrophilic additions to the C2 site, resulting in products with new all-carbon quaternary centers. Highly substituted carbon centers are desirable motifs for drug design and multistep syntheses.[18] When the electrophile is a carbonyl or acetate group, the resulting α-cyano compounds can be modified at either functional group to provide pharmaceutically relevant structural cores.[19] The most common entry point into α-cyano carbonyl products is through lithiated alkyl nitriles; however, in most cases, stoichiometric addition of lithium diisopropylamide (LDA) or ^{n}BuLi is required to unmask the nucleophilic carbon center.[4a,20] Silyl ketenimines are precursors to quaternary α-cyano carbonyl groups; however, stoichiometric base is also required.[2f] Interception of Ru keteniminates with a carbonyl electrophile under hydrogenative reductive coupling conditions could provide α-functionalized cyano compounds while avoiding stoichiometric waste (Table 1).

The addition of carbonyl electrophiles to α,β-unsaturated nitriles in the presence of H_2 presents a key challenge: Both the C=C and C≡N groups are susceptible to hydrogenation using **1**. Prior to evaluating reductive coupling with **2a**, we interrogated the hydrogenation reactivity using H_2 (100 psig) and **1** (1 mol%; Table 1, entry 1). Complete hydrogenation of

Table 1: Hydrogenative acylation of **2a** with **1**.



Entry	T [°C]	Additive (10 mol%)	Anhydride	Conv. [%]	4/5+6
1[a]	80	–	–	>99	0:99
2[b]	80	–	Boc_2O	>99	29:71
3[b]	80	LiO^{t}Bu	Boc_2O	>99	53:47
4[c]	100	LiO^{t}Bu	Boc_2O	>99	70:30
5[c]	100	–	$(CF_3CO)_2O$	>99	93:7
6[c]	100	DBU	Boc_2O	>99	95:5
7	100	DBU	Ac_2O	>99	89:11
8	100	DBU	$(C_6H_5CO)_2O$	>99	92:8

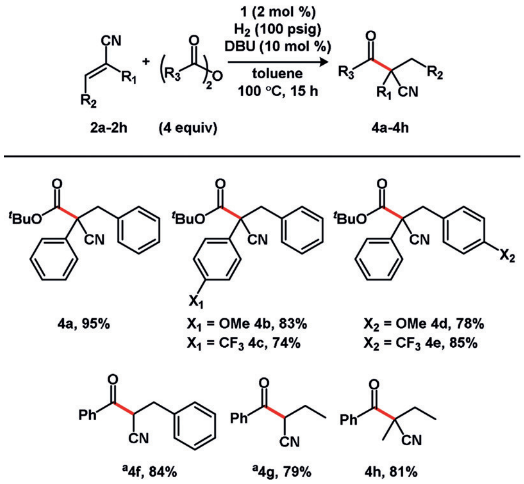
The conversions and product ratios were determined by NMR analysis with $PhSi(CH_3)_3$ as an internal standard. [a] **1** (1 mol%). [b] **1** (2 mol%), Boc_2O (2 equiv). [c] **1** (2 mol%), Boc_2O or $(CF_3CO)_2O$ (4 equiv).

2a (0.25 mmol) to amine **6a** occurred at 80 °C.[21] Reductive C−C coupling was evaluated using anhydrides based on the precedent for their electrophilic addition to α-cyano carbanions.[2f,22] When di-*tert*-butyl dicarbonate (Boc_2O, 1 equiv) was added to the hydrogenation reaction above under analogous conditions (80 °C), acylation of **2a** occurred to provide **4a** in 29% yield, and the remaining mixture (71%) was composed of hydrogenation products **5a** and **6a** (entry 2). Hydrogenative acylation was promoted with the addition of base, where 10 mol% of LiO^{t}Bu at 80 °C increased the selectivity for **4a** over hydrogenation products (53:47;

entry 3). Further optimization revealed that a higher temperature (100 °C), catalyst loading (2 mol % **1**), and concentration of Boc_2O (4 equiv) improved acylation selectivity, affording **4a** in 70 % chemical yield (entry 4).

The improved selectivity towards acylation with the addition of LiO^tBu may be due to 1) base-assisted H_2 heterolysis or 2) electrophilic activation of Boc_2O by Li^+. To determine whether a more activated electrophile further improves the reaction selectivity, we evaluated trifluoroacetic anhydride, $(CF_3CO)_2O$, in place of Boc_2O. Under base-free conditions, $(CF_3CO)_2O$ provided excellent selectivity for the acylated product **4a′** (93:7, entry 5). Anhydride reagents with decreased reactivity (such as Boc_2O) may be further activated with an appropriate nucleophile to promote hydrogenative acylation. We previously identified 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) as a compatible base under hydrogenation conditions with **1**.[23] When DBU was used in place of LiO^tBu to activate Boc_2O, the selectivity for **4a** dramatically improved (95:5, entry 6). These data indicate that the electrophilicity of the acylating agent influences reaction selectivity. Finally, the reductive acylation reaction is general to several representative anhydride reagents, and in addition to Boc_2O and $(CF_3CO)_2O$, we observed high yields using both acetic anhydride (89 %, entry 7) and benzoic anhydride (92 %, entry 8).[24]

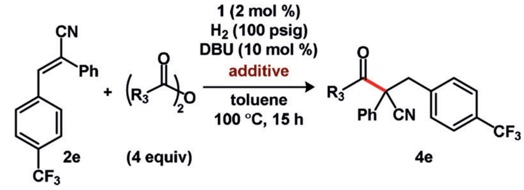
To assess the reaction scope and functional group compatibility, we examined α,β-unsaturated nitriles **2b**–**2h** with varying aryl and alkyl substitution (Scheme 3). Under the optimized reaction conditions with DBU and Boc_2O, diaryl α-cyanoacetates **4a**–**4e** were isolated in high yields ranging from 74–95 %. Alkyl substitution was also tolerated, although higher temperatures (150 °C) were required to obtain **4f** (84 %) and **4g** (79 %) from monoalkyl-substituted alkenyl nitriles **2f** ($R_1 = H$, $R_2 = C_6H_6$) and **2g** ($R_1 = H$, $R_2 = CH_3$) using DBU and $(C_6H_5CO)_2O$. In contrast, disubstituted 2,3-dimethylacrylonitrile (**2h**, $R_1 = R_2 = CH_3$) was reactive towards acylation with $(C_6H_5CO)_2O$ at 100 °C to provide **4h** (81 %).



Scheme 3. Synthesis of α-cyanoacetates **4a**–**4h** with Boc_2O or $(C_6H_5CO)_2O$, DBU, and **1**. Yields of isolated products after chromatography are reported. [a] Reaction performed at 150 °C in mesitylene.

Finally, we examined the functional group compatibility of the hydrogenative acylation reaction using **1** in the presence of several common functional groups (Table 2).[25]

Table 2: Hydrogenative acylation of **2e** in the presence of additives containing common functional groups.

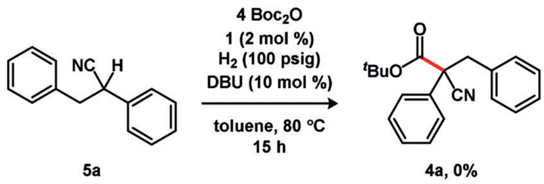


Entry	Additive (1 equiv)	Conv. [%]	Yield [%]
1	–	>99	86
2	*N*-benzylpyrrole	>99	88
3	2,4,6-collidine	>99	88
4	methyl benzoate	>99	86
5	*N*-methyl-*N*-phenylacetamide	>99	87
6	chlorobenzene	>99	86
7	2-vinylnapthalene	57	0

$R_3 = O^tBu$. Yields were determined by NMR spectroscopy using $PhSi(CH_3)_3$ as an internal standard.

Using **2e** and Boc_2O, the NMR yield of **4e** was assessed under standard conditions in the presence of potentially reactive additives. Notably, most additives tested did not decrease the yield of **4e** (entries 2–6). One limitation, however, was the incompatibility with hydrogen acceptors such as 2-vinylnaphthalene (entry 7), consistent with competitive hydrogenation by **1**.

As saturated nitriles are products under hydrogenation conditions with **1** and α,β-unsaturated nitriles, a feasible pathway to α-cyanoacetate products may first involve C=C hydrogenation followed by deprotonation of the acidic α-C–H bond (by base or **1**) prior to acylation. To evaluate this possibility, we subjected saturated nitrile **5a** to our reaction conditions (Scheme 4). No **4a** was formed as assessed by NMR spectroscopy (see Figures S54–S56). This suggests that **5a** does not undergo a base-assisted acylation. We attribute this result to competitive activation of the Boc_2O by DBU compared to deprotonation.[26] We also found that stoichiometric reactions between **3a** and Boc_2O quantitatively afforded **4a**, and that **3a** is a competent pre-catalyst. Under analogous conditions, **3a** provided identical yields of **4a** compared to reactions employing **1**, which is consistent with the intermediacy of **3a** during catalysis. Collectively, these results suggest that **1** provides a unique entry point to



Scheme 4. Acylation of **5a** does not proceed under reductive C–C coupling conditions with **1** and DBU.

nitrile anions for catalysis, which is distinct from the previously reported deprotonation pathways of alkyl nitriles. Selective 1,4-hydride addition to α,β-unsaturated nitriles is a key step for generating catalytically competent keteniminate intermediates for hydrogenative C–C coupling reactions.

In conclusion, we have introduced a new strategy to use catalytic hydrogen-mediated reductive coupling to generate and intercept nitrile nucleophiles. Hydride transfer to α,β-unsaturated nitriles from **1** affords ruthenium keteniminates that can be converted into α-cyanoacetate products under an H_2 atmosphere using catalytic DBU and **1**. Hydrogenative acylation enables the use of α,β-unsaturated nitriles as a new substrate class to access products containing all-carbon quaternary centers. Mechanistically distinct modes of nitrile activation are needed to discover new reactivity that parallels that of their oxygen-containing counterparts. We predict that the diverse reactivity available to keteniminates and nitrile carbanions may be accessible following H^- insertion by **1** to α,β-unsaturated nitriles. Current work is focused on exploring the scope in substrate and electrophile, as well as enantioselective acylation protocols.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: hydrogenative acylation · keteniminates · reductive C–C coupling · ruthenium · α,β-unsaturated nitriles

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[27] CCDC 1875848 (**3a**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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