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Heterobimetallic Reductive Cross-Coupling of Benzonitrile with Carbon Dioxide, Pyridine, and Benzophenone

Arjun Mendiratta and Christopher C. Cummins*

Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue,
Room 2-227, Cambridge, Massachusetts 02139

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Described herein are heterobimetallic radical cross-coupling reactions between the benzonitrile adduct of the molybdenum(III) complex Mo(N[*t*-Bu]Ar)$_3$ (Ar = 3,5-$C_6H_3Me_2$) and titanium(III) complexes with carbon dioxide, pyridine, and benzophenone. The titanium(III) system employed was either Ti(N[*t*-Bu]Ar)$_3$ (Ar = 3,5-$C_6H_3Me_2$) or Ti(N[*t*-Bu]Ph)$_3$. Crystal structure studies are described for the Mo/PhCN/CO_2/Ti coupled system and for an analogue of the Mo/PhCN/Ph_2CO/Ti coupled system in which PhCN is replaced with 2,6-$Me_2C_6H_3CN$. In the case of the couplings involving pyridine and benzophenone, C–C bond formation takes place with dearomatization, with the new C–C bond being formed between the nitrile carbon of PhCN and the para carbon of pyridine or one of the benzophenone phenyl groups. Of the radical metal complex/substrate adducts invoked in this work, that between titanium(III) and CO_2 is the only one not directly observable. In all cases, the selective cross-coupling reactions are interpreted as arising by heterodimerization of titanium(III) substrate complexes (substrate = CO_2, py, or Ph_2CO) with the persistent molybdenum–PhCN radical adduct. All of the heterobimetallic coupling products are diamagnetic, and the metal ions Ti and Mo in them both are assigned to the formal 4+ oxidation state.

Electropositive metals can effect the reductive coupling of carbonyl compounds to form metal diolates as in the pinacol coupling.[1] This reaction was expanded in scope to include nitrile homocoupling through the use of niobium or tantalum halides as reductants,[2] and a variety of low-valent early-metal systems are active for the pinacol-type reductive coupling of organic nitriles.[1,3−7] The trivalent three-coordinate complexes M(N[*t*-Bu]Ar)$_3$ (M = Ti, Ar = 3,5-$Me_2C_6H_3$, **1a**; M = Ti, Ar = Ph, **1b**; M = Mo, Ar = 3,5-$Me_2C_6H_3$, **2**) are no exception because they mediate a variety of reductive couplings,[8,9] wherein frequently long-lived radical intermediates can be observed spectroscopically and/or intercepted by added traps. For example, ketyl radical **1**−$OCPh_2$ (in equilibrium with its dimer) accepts [H$^\bullet$] from *n*-Bu_3SnH to form diphenylmethoxide complex **1**−$OCHPh_2$.[9,10] Similarly, while **2** reacts with PhCN to form the expected product of reductive dimerization,[8] the long-lived intermediate **2**−NCPh is readily intercepted with 0.5 equiv of PhSSPh to furnish (Ar[*t*-Bu]N)$_3$Mo−N=C(Ph)SPh.[11] Now we report that the combination of **1** and **2** is uniquely capable of carrying out pinacol-type cross-couplings of benzonitrile with CO_2, benzophenone, and pyridine. The successful use of CO_2 as a substrate is noteworthy as an example of its *bimetallic* reductive coupling to give a product other than oxalate.[12] The remarkable CO_2 incorporation reaction highlighted herein is evocative of (though likely mechanistically distinct from) reverse radical decarboxylation[13,14] because it is a radical CO_2 uptake process transpiring with C−C bond formation.

Treatment of a purple, ethereal solution of **2**−NCPh at −100 °C with emerald green **1a** (1.0 equiv), followed rapidly by CO_2 (1.1 equiv, introduced via syringe), was found to elicit a color change to cherry red upon mixing. After workup, the new diamagnetic compound (Ar[*t*-Bu]N)$_3$Mo−N=C(Ph)C(O)O−Ti(N[*t*-Bu]Ar)$_3$ (**3a**) was isolated as dark red crystals in 60% yield (see Scheme 1).[15] We note that

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* To whom correspondence should be addressed. E-mail: ccummins@mit.edu. Tel: (617) 253-5332. Fax: (617) 258-5700.

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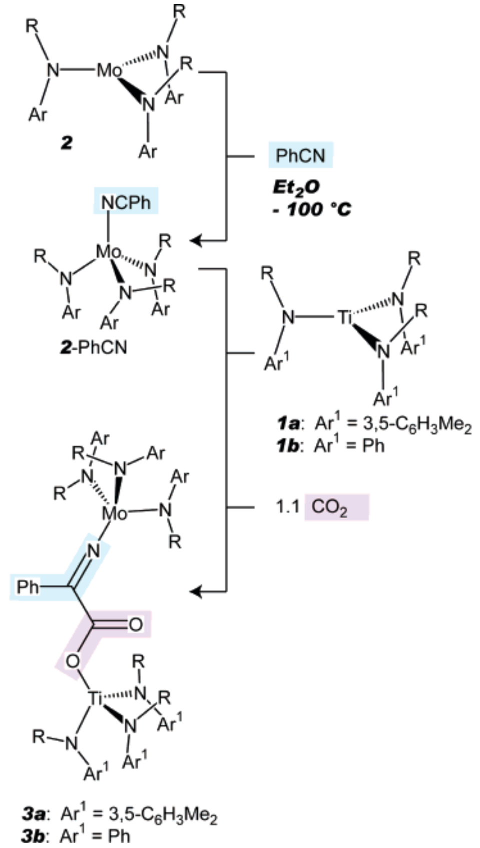
Scheme 1. Synthesis of **3a** and **3b** (R = *t*-Bu)



the ^{13}C-labeled variant, **3a**-^{13}C, is conveniently prepared from $^{13}CO_2$ and exhibits a signature ^{13}C NMR signal at 170.7 ppm for the labeled carbon. Also, a weak absorption in the IR at 1635 cm^{-1} (found at 1564 cm^{-1} for **3a**-^{13}C) is assigned to ν_{CO}. While an X-ray diffraction study of **3a** confirmed the proposed connectivity, end-over-end disorder prevented the determination of reliable metrical parameters. Fortunately, substitution of Ti(N[*t*-Bu]Ph)$_3$ (**1b**) for **1a** permitted the synthesis of (Ar[*t*-Bu]N)$_3$Mo−N=C(Ph)C(O)O−Ti(N[*t*-Bu]Ph)$_3$ (**3b**), for which a single-crystal X-ray diffraction study was accomplished without difficulty.

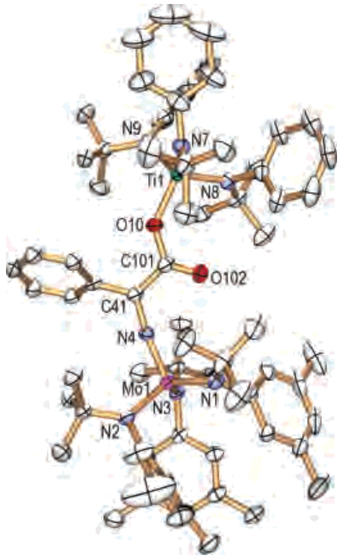
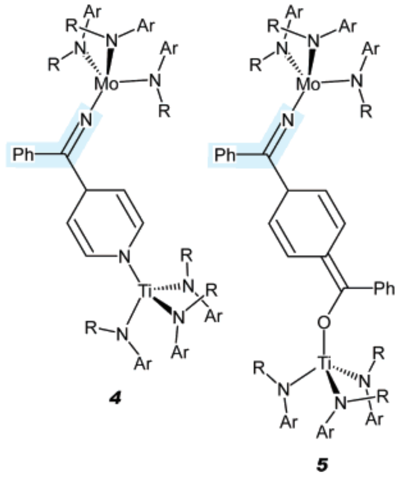


Figure 1. Solid-state structure of **3b** with ellipsoids drawn at 50% probability. Selected interatomic distances (Å) and angles (deg): average Mo1−N$_{amide}$, 1.962(3); Mo1−N4, 1.759(3); N4−C41, 1.350(5); C41−C101, 1.438(6); C101−O102, 1.220(5); O10−Ti1, 1.855(3); average Ti1−N$_{amide}$, 1.938(3); Mo1−N4−C41, 169.3(3); Ti1−O10−C101, 136.8(3).

The molecular structure of **3b**, shown in Figure 1, clearly features the freshly created, CO$_2$-derived, carboxyiminato unit that spans the Mo/Ti centers. The carboxyiminato moiety is both essentially planar and orthogonal to the plane of its phenyl substituent. The newly formed C41−C101 bond distance is 1.487(5) Å, while the N4−C41 distance is 1.350(5) Å. Both the latter value and the short Mo1−N4 distance of 1.759(3) Å are similar to corresponding parameters observed previously for molybdenum(IV) ketiminato complexes.[11,16] Multiple Mo1−N4 bonding is consonant with the nearly linear (169.9(3)°) Mo1−N4−C41 linkage. The Ti1−O10 distance (1.855(3) Å) is quite similar to the corresponding parameter reported for titanium trisanilide enolate **1a**−OC(=CH$_2$)NPhMe (1.847(3) Å),[9] and while the carboxylate residue interacts with Ti in a monodentate fashion, still the Ti1−O10−C101 angle is an acute 136.8(3)°. The Ti and Mo centers both experience a pseudotetrahedral coordination environment.

Chart 1



We have obtained two other structures related to that of **3** by using **2**−NCPh as a radical trap. Dark green **4** (Chart 1) is the product of radical heterocombination between the reversibly formed pyridine adduct **1a**−py[17] and **2**−NCPh, while green **5** stems from coupling of **2**−NCPh with one of the para carbons of titanium benzophenone ketyl radical **1**−OCPh$_2$.[18] As was the case for **3a**,[15] both **4** and **5** are formed in essentially quantitative yield, with the lower isolated yields being due to inefficiency in the crystallization of these lipophilic substances. Dearomatization similar to that

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(15) The yield of **3a** was essentially quantitative as assessed from proton NMR spectra of crude reaction mixtures. The isolated yield of only 60% is due to losses incurred in the purification by crystallization of this lipophilic substance.

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(17) Figure S1 in the Supporting Information is the electronic absorption spectrum of **1a** in the presence of varying amounts of pyridine.

(18) Compound **5′**, with 2,6-Me$_2$C$_6$H$_3$CN in place of PhCN, has also been synthesized and structurally characterized. See the Supporting Information.

observed in the structure of Gomberg's dimer[19] is a feature of interest in the reactions leading to **4** and **5**, reactions distinct from the CO_2/PhCN coupling in that the **1a**−$OCPh_2$[9] and **1a**−py[17] adducts are spectroscopically observable. Proposed intermediate **1a**−CO_2 (implied in Scheme 1) has so far eluded direct detection despite substantial effort expended in this regard; the interception in solution of putative **1a**−CO_2 by traps other than **2**−NCPh has also been investigated (see the Supporting Information).

The reductive cross-couplings described herein proceed with both Ti and Mo being converted from the 3+ to the 4+ oxidation state and are attractively interpreted in terms of trapping of radical titanium(III) substrate complexes by the persistent **2**−NCPh radical. While **2**−NCPh is not an aggressive radical[20] and quite likely thermodynamically incapable of directly attacking stable systems such as the CO_2 molecule, its persistence in high concentration in solution makes it an ideal radical trap. The three examples of selective radical cross-coupling presented herein illustrate the principle termed "the persistent radical effect".[21] Remarkable is the fact that products **3**−**5** incorporate four different reactant molecules added to solution in sequence with zero byproducts.

The fixation of carbon dioxide by metal-mediated coupling with unsaturated organic molecules has focused on alkene and alkyne substrates,[22,23] dating to seminal work by Hoberg on such nickel(0)-induced C−C couplings.[24−26] Mindful of carbon management as an important societal concern,[27] we might now consider pursuit of *radical carboxylation* as a potential alternative reaction pathway for fixation of the key atmospheric CO_2 molecule.

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Supporting Information Available: Complete synthetic procedures and characterization data for all new compounds, details of the attempted observation and trapping of **1a**−CO_2, and tables of crystallographic data in CIF format for **3b** and **5′**. This material is available free of charge via the Internet at http://pubs.acs.org.

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