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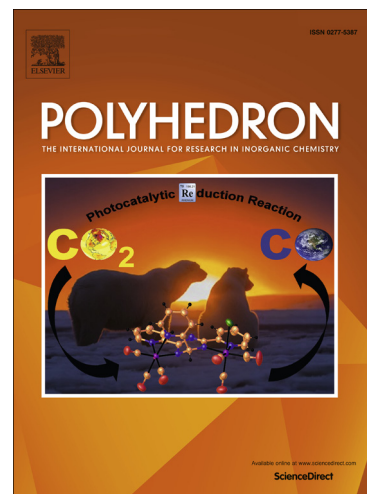
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## Stoichiometric carbon-carbon bond formation mediated by well defined Nb(III) complexes

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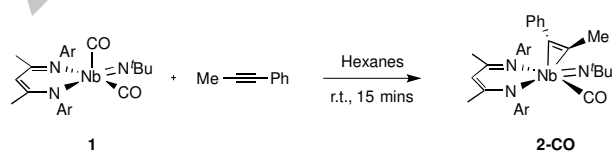
**Abstract.** The discovery of a Nb-mediated double coupling of terminal alkynes and carbon monoxide is reported. The Nb(III) complex (BDI)Nb(N<sup>t</sup>Bu)(CO)<sub>2</sub> reacts with two equivalents of *t*-butylacetylene to form a metal-bound yne-one-ene moiety resulting from coupling of CO to two equivalents of the terminal alkyne. Additionally, Z-alkene and  $\alpha,\beta$ -unsaturated imine formation from hydrogenolysis of an internal alkyne bound complex in the presence of an isocyanide ligand is described. <sup>1</sup>H NMR spectroscopy, and synthesis of a bromide analog support the involvement of an alkenyl iminyl ligand intermediate.

## 1. Introduction

The use of  $d^2$  early-transition metal complexes as reducing agents is a powerful tool in synthetic organic chemistry.<sup>1</sup> The ability to form C–C bonds *via* the reductive coupling of unsaturated organic molecules (alkenes, alkynes, ketones and ketimines) provides alternative routes to dienes, amino alcohols, diols, and bicyclic products. However, the small number of coordinatively unsaturated  $d^2$  complexes has limited the development of new coupling chemistry and these transformations are mainly observed with  $d^2$  metallocenes of group IV.<sup>2</sup> The most common reaction reported is the coupling of two alkynes, via the formation of a metallacyclopentadiene, to form a diene moiety that is released via acidic work-up.<sup>3</sup> Hydroformylation and hydroiminylation of alkenes and alkynes involving coupling with carbon monoxide or isocyanide to form an enone or enamine products is also known.<sup>4</sup> However, the coupling of a carbon monoxide and two alkynes,<sup>5</sup> as well as the formation of an  $\alpha,\beta$ -unsaturated imine from a metal-mediated reaction of alkyne and isocyanide,<sup>6</sup> remains rare.

In our effort to develop new group 5 catalysts,<sup>7</sup> we recently discovered the selective semi-hydrogenation of alkynes under H<sub>2</sub>:CO atmosphere, catalyzed by a complex **1**: a dicarbonyl niobium(III) imido supported by a BDI ligand (BDI = N,N-diisopropylphenyl- $\beta$ -diketiminate, Scheme 1).<sup>8</sup> Our mechanistic investigations revealed the involvement of an  $\eta^2$ -alkyne bound monocarbonyl intermediate, **2-CO**, which is rapidly formed via displacement of one equivalent of carbon monoxide. This species, which was isolated and characterized, then interacts with a molecule of H<sub>2</sub> to release the *cis*-alkene organic product and reform the dicarbonyl niobium catalyst.<sup>6</sup>

## SCHEME 1



Here we report the reaction between the dicarbonyl complex **1** and a terminal alkyne leading to an unusual coupling product, as well as hydrogenolysis of the NC<sup>t</sup>Bu bound analog of **2-CO**, resulting in both *Z*-alkene and  $\alpha,\beta$ -unsaturated imine formation.

## 2. Experimental

## 2.1 General methods

Unless otherwise noted, all reactions were performed using standard Schlenk line techniques or in an MBraun inert atmosphere box under an atmosphere of purified nitrogen (<1 ppm O<sub>2</sub>/H<sub>2</sub>O). Glassware, cannulae, and Celite were stored in an oven at *ca.* 160 °C. *n*-Pentane, *n*-hexane, Et<sub>2</sub>O and toluene, were purified by passage through a column of activated alumina, stored over 3 or 4 Å molecular sieves, and degassed prior to use.<sup>9</sup> Deuterated solvents (C<sub>6</sub>D<sub>6</sub>, C<sub>7</sub>D<sub>8</sub>) were dried over sodium/benzophenone, vacuum transferred to a storage flask containing activated molecular sieves, and degassed by three freeze-pump-thaw cycles before being stored in the dry box. PhC≡CMe and <sup>t</sup>BuC≡CH were stored over 4 Å activated molecular sieves and degassed by three freeze-pump-thaw cycles. 1,3,5-trimethoxybenzene was sublimed under static vacuum. (BDI)(CO)<sub>2</sub>Nb(N<sup>t</sup>Bu),<sup>10a</sup> (BDI)(Cl)<sub>2</sub>PyNb(N<sup>t</sup>Bu),<sup>10b</sup> (BDI)Nb(N<sup>t</sup>Bu)(PhC≡CMe)(L) with (L = CO and CN<sup>t</sup>Bu),<sup>8</sup> and Ph(MgBr)C=C(H)Me<sup>11</sup> were prepared using literature procedures. All other reagents were acquired from commercial sources and used as received. NMR spectra were recorded on Bruker AV-300, AVQ-400, AVB-400, DRX-500, AV-500, and AV-600 spectrometers. Chemical shifts were measured relative to residual solvent peaks, which were assigned relative to an external TMS standard set at 0.00 ppm. <sup>1</sup>H and <sup>13</sup>C NMR assignments were routinely confirmed by <sup>1</sup>H-<sup>1</sup>H (COSY, NOESY) or <sup>1</sup>H-<sup>13</sup>C (HSQC and HMBC) experiments. The uncorrected melting points were determined on an Optmelt SRS using sealed capillaries prepared under nitrogen. Elemental analyses were determined at the College of Chemistry, University of California, Berkeley. The X-ray structural determinations were performed at CHEXRAY, University of California, Berkeley on Bruker SMART 1000 or SMART APEX diffractometers. GC/MS analyses were performed using a Agilent 6890 N Network GC system coupled to a 5973 Network mass selective detector.

## 2.2 Synthesis and characterization

2.2.1 (BDI)(<sup>t</sup>BuCCC(O)(C(H)=C(H)<sup>t</sup>Bu)Nb(N<sup>t</sup>Bu), **3**

<sup>t</sup>BuC≡CH (48  $\mu$ L, 3.90 mmol, 5 equiv.) was added to a solution of **1** (0.51 g, 0.78 mmol, 1 equiv.) in hexane at

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