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Formal *aza*-Michael additions to tropone: addition of diverse aryl- and alkylamines to tricarbonyl(tropone)iron and $[(C_7H_7O)Fe(CO)_3]BF_4$

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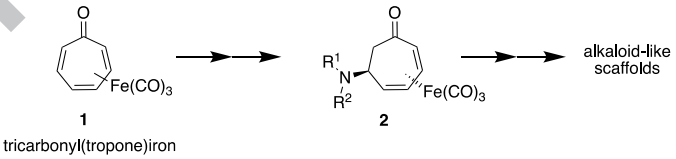
ABSTRACT: A formal *aza*-Michael addition to tropone by way of tricarbonyl(tropone)iron and/or the tetrafluoroborate salt formed *via* protonation of the complex is reported. Tricarbonyl(tropone)iron smoothly undergoes the direct *aza*-Michael reaction with unhindered aliphatic amines under solvent free conditions in good yields. Meanwhile, the known cationic complex $[(C_7H_7O)Fe(CO)_3]BF_4$ (whose reaction with a small number of nucleophiles was previously reported) undergoes addition with an even broader array of amine nucleophiles. Finally, it was discovered that protecting the *aza*-Michael adduct as a carbamate was necessary for oxidative demetallation of the complex.

Keywords: iron diene complexes, *aza*-Michael reaction, tropone, solvent free

Tropone and its η^4 complex with an iron tricarbonyl fragment (tricarbonyl(tropone)iron (**1**) – readily synthesized from tropone[1]) are versatile synthetic building blocks that can be elaborated to a variety of complex scaffolds containing seven-membered rings. Whereas tropone typically reacts with nucleophiles at the 2- and 7-positions[2,3] and also participates in cycloaddition reactions[4–6] at those positions, forming an η^4-diene complex with iron(0) fundamentally alters the reactivity of tropone. A notable illustration of the synthetic utility of **1** is Pearson and co-worker's stereocontrolled synthesis of heptitols[7] from **1**, which was adapted by Soulié and co-workers in the synthesis of a polyhydroxylated nortropane skeleton.[8,9] Furthermore, the uncomplexed double bond of **1** has been shown to act as an enone equivalent in reactions with, for example, dienes,[10,11] tetrazines,[12] nitrile oxides,[13] diazoalkanes,[14,15] and organozinc reagents.[16] A similar addition of amine nucleophiles would furnish adducts containing several functional handles for further synthetic elaboration, whether in the form of the η^4-complexed diene or the corresponding free conjugated diene (Scheme 1). Thus, a formal *aza*-Michael addition to tropone and/or **1** serves as a potential starting point for the synthesis of complex amines containing a seven-membered carbocyclic ring common to a number of biologically active alkaloids (including several monoterpenoid indole alkaloids[17] and some *Daphniphyllum* alkaloids[18]).



Scheme 1. *Aza*-Michael adducts of tricarbonyl(tropone)iron: potential precursors for complex amines

Eisenstadt reported that the cationic complex **3** (synthesized from **1** in two steps[19,20]) could react with aniline or *tert*-butylamine to give formal *aza*-Michael adducts of **1**.[21] However, no other amine nucleophiles were investigated and demetallation of the products was also not reported. In addition to further exploring this chemistry, we were interested in developing a novel, *direct aza*-Michael addition of **1** without the need for pre-forming the cationic complex **3**. Herein, we describe our thorough exploration of the scope and reactivity of **3** toward various amine nucleophiles. In addition, we report the first direct *aza*-Michael addition of unhindered aliphatic amines to **1** as well as conditions for demetallation to reveal the dienone functionality.

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