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Modification of aminoallenylidene complexes of chromium via exchange of the C3-bound amino group

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Dedicated to Professor F. Gordon A. Stone

Abstract

The aminoallenylidene(pentacarbonyl)chromium complexes $[(CO)_5Cr{=}C{=}C{=}C(NR^1R^2)Ph]$ (**1a**–**c**) react with dimethylamine by addition of the amine to the C1=C2 bond of the allenylidene ligand to give alkenyl(amino)carbene complexes $[(CO)_5Cr{=}C(NMe_2)CH{=}C(NR^1R^2)Ph]$ (**2a**–**c**) (R^1 = Me: R^2 = Me (**a**), Ph (**b**); R^1 = Et: R^2 = Ph (**c**)). In contrast, addition of a large excess (usually 20 equivalents) of ammonia or primary amines, H_2NR, to solutions of $[(CO)_5Cr{=}C{=}C{=}C(NMe_2)Ph]$ (**1a**) affords the aminoallenylidene complexes $[(CO)_5Cr{=}C{=}C{=}C(NHR)Ph]$ (**1d**–**w**) in which the dimethylamino group is replaced by NH_2 or NHR, respectively. In addition to simple amines such as methylamine, butylamine, and aniline, amines carrying a functional group (allylamine, propargylamine) and amino acid esters as well as amino terpenes and amino sugars can be used to displace the NMe_2 substituent. Usually the *Z* isomer (with respect to the partial C3–N double bond) is formed exclusively. Products derived from addition of H_2NR to the C1=C2 bond of **1a** are not observed. The amino group in **1d**–**w** is rapidly deprotonated by excess of amine to form iminium alkynyl chromates $[\mathbf{1d}\text{–}\mathbf{w}]^-$, thus protecting **1d**–**w** from addition of free amine to either C3 or across the C1=C2 bond. The iminium alkynyl chromates are readily reprotonated by acids or by chromatography on wet SiO_2 to reform **1d**–**w**.

Keywords: Allenylidene complexes; Chromium; Carbene complexes; Addition; Substitution

1. Introduction

The allenylidene ligand in allenylidene complexes, $[L_nM{=}C{=}C{=}C(R^1)R^2]$, is characterized by a succession of electrophilic and nucleophilic sites [1]. The atoms C1 and C3 exhibit electrophilic reactivity, the C2 atom is a nucleophilic center. From such a bonding situation, a diverse reactivity is to be expected. In recent years allenylidene complexes have evolved into valuable building blocks for C–C and C–X bond formation. For instance, heterocyclic organic skeletons like naphtho-furanyl [2], pyrazolo-pyrazolyl [3], azetidine [4], hexahydroquinoline [4], pyrido-pyrazolyl [5] or thiazinyl [5] ligands can be synthesized in a simple fashion. Additionally, optically pure alkynes with novel functionalities have been prepared by using ruthenium allenylidene complexes as starting compounds [6]. Some ruthenium allenylidene complexes have been shown to be excellent catalyst precursors for olefin metathesis [7,8].

Until now, mostly bis(aryl)-, aryl(alkyl)-, and bis(alkyl)-substituted allenylidene complexes were synthesized and used for further transformations. These complexes are easily prepared from 1,1-disubstituted propargylic alcohols by following Selegue's protocol [9]. Therefore, the majority of reactivity studies apply to complexes of this type. However, the bonding within the allenylidene chain and consequently the reactivity of allenylidene complexes should be influenced by the

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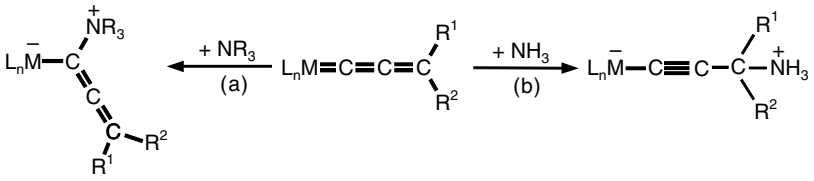


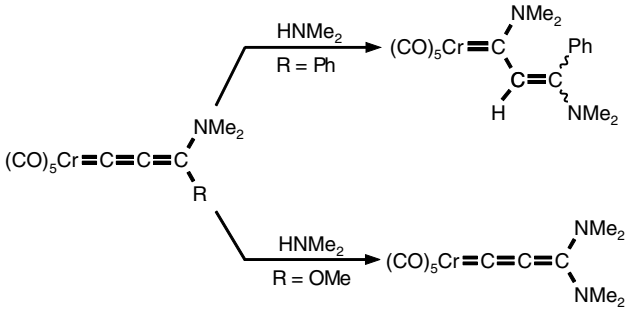
Scheme 1.

metal–ligand fragment on the one hand and the substitution pattern of the terminal carbon atom on the other hand.

Due to the electrophilicity of the metal-bound C1 and the terminal C3 atom of the allenylidene chain [10], nucleophiles will add either to the C1 or the C3. DFT calculations show that the relative orbital contributions of C1 and C3 to the LUMO are dependent on the substituents at C3. These substituents therefore play an important role in determining the regioselectivity of a nucleophilic attack [11]. All studies up to date revealed a strong preference for addition of an amine to the C1 atom (Scheme 1: path (a)) [12,13]. To the best of our knowledge, there is only one report on the addition of an amine to C3, that of NH_3 to the cationic $[(MeC\{CH_2PPh_2\}_3)(CO)_2Re{=}C{=}C{=}CPh_2]^+$ ion at 0 °C (Scheme 1: path (b)) [14]. The resulting ammonioalkynyl complex as the kinetic product slowly transforms within a few hours into the thermodynamically more stable C1 NH_3-adduct [14].

Recently, we developed a simple and efficient one-pot route to a variety of π-donor (amino) substituted allenylidene complexes [13]. The reactivity of these π-donor substituted complexes deviates from that of non-donor substituted allenylidene complexes. Our initial studies indicated that in such aminoallenylidene complexes, the "second" substituent at the C3 atom (the amino group being the "first" one) likewise considerably influences the reaction behavior towards Lewis bases. For instance, dimethylamino(*phenyl*) allenylidene complexes add dimethylamine across the C1=C2 bond to form, α,β-unsaturated aminocarbene complexes. In contrast, dimethylamine does not add to the C1=C2 bond of the corresponding dimethylamino(*methoxy*) allenylidene complexes but rather replaces the methoxy substituent to produce bis(dimethylamino)allenylidene complexes (Scheme 2) [13].

We now report that, surprisingly, the dimethylamino group in dimethylamino(phenyl)allenylidene complexes can likewise be displaced by other (even weaker basic) amines by applying suitable reaction conditions.



Scheme 2.

2. Experimental

2.1. General

All operations were performed under inert gas atmosphere using standard Schlenk techniques. Solvents were dried by distillation from CaH_2 (CH_2Cl_2), $LiAlH_4$ (pentane, Et_2O) and sodium benzophenone ketyl (THF). The silica gel used for chromatography (Baker, silica gel for flash chromatography) was argon saturated. The yields refer to analytically pure compounds and are not optimized. Instrumentation: ^1H NMR and ^{13}C NMR spectra were recorded with a Jeol JNX 400 spectrometer. Chemical shifts are reported relative to the residual solvent peaks. IR: Biorad FTS 60. MS: Finnigan MAT 312. Elemental analyses: Heraeus CHN-O-Rapid. The starting allenylidene complexes **1a** [15–17], **1b** [17], and **1c** [17], and the carbene complex **2a** [13] were prepared according to the literature procedures. The various amines were commercial products and used as supplied.

2.2. General procedure for the addition of dimethylamine to the C1=C2 bond of amino(aryl)-allenylidene complexes

A slight excess of dimethylamine was added at ambient temperature to a solution of 1 mmol of the allenylidene complexes **1** in 30 ml of Et_2O. The solution was stirred until TLC control of the reaction progress indicated complete conversion of **1**. The solvent was removed in vacuo and the residue chromatographed on silica at −20 °C using mixtures of pentane/CH_2Cl_2 as the eluant. The complexes **2** were obtained as yellow solids.