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Addition of diphenylacetylene and methylvinylketone to aluminum complex of redox-active diimine ligand

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ABSTRACT

Diphenylacetylene reacts with aluminum complex (dpp-bian)AlEt(Et_2O) (**1**) (dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) in the absence of any solvent at 110–130 °C under vacuum to give compound [dpp-bian(PhC═CPh)]AlEt (**2**). The reaction of methylvinylketone with complex **1** easily proceeds at ambient temperature in Et_2O and results in the formation of compound [dpp-bian(CH_2–CH═C(Me)–O)]AlEt (**3**). Both reactions proceed *via* addition of unsaturated organic substrate across Al–N–C bond sequence in complex **1**. Complexes **2** and **3** have been characterized by IR and ^1H NMR spectroscopy. Molecular structures of **2** and **3** have been determined by single-crystal X-ray analysis. Complex **2** was found to be catalyst for the reaction between phenylacetylene and diphenylamine. A full conversion of the reagents was achieved with 5 mol% of complex **2** in benzene in 140 h at 110 °C resulting *N*-phenyl-2-(1-phenylvinyl)aniline (**4a**) as the major product (87%).

1. Introduction

Since 2003, we have exploited redox-active 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian) as a ligand in the main group and the rare earth metal chemistry [1]. We have demonstrated that this particular ligand serves perfectly in the preparation of the metal–metal bonded species [2] as well as in the design of molecules possessing reversible metal-to-ligand electron transfer, so-called redox-isomerism phenomenon [1c,e]. The highlight of our research involves employment of the redox-active dpp-bian complexes of redox-inactive metals in organic synthesis and catalysis. Recently, the concept of using ligands that can store and release electrons during catalytic processes has been exploited in transition metal chemistry [3]. In our case, we have demonstrated that three-coordinate group 13 metal complexes, (dpp-bian)Ga–Ga(dpp-bian) and (dpp-bian)Al–Al(dpp-bian), may bind terminal and internal alkynes [4], thus emulating an ability of the *transition metal* ions to coordinate with organic π molecules. Alkynes add to aluminum and gallium dpp-bian complexes across M–N–C (M = Al, Ga) fragments resulting new C–C and C–M bonds (Scheme 1).

Most unusual feature of the cycloadducts shown in Scheme 1 is that they may eliminate alkyne under elevated temperatures. It is also worth mentioning that as the reactivity of transition metal complexes can be finely "tuned" by spectator ligands, a variation of the metal at dpp-bian may alter the course of its reactivity. Thus, on moving from Al to Ga the regioselectivity of the 2 + 3 cycloaddition is changing (Scheme 1). Definitely, the metal plays a specific role in this type of reactions. Another illustration of that is the fact that complex (dpp-bian)Ga–Ga(dpp-bian) is unreactive toward internal alkynes except very active alkyl-2-butynoates [5], while compound (dpp-bian)Al–Al(dpp-bian) reacts with PhC≡CMe. Recently, Yang and co-workers have shown that the reaction of compound [L^{2-}(THF)Al–Al(THF)L^{2-}] (L = [(2,6-*i*-$Pr_2C_6H_3$)NC(Me)]$_2$) with PhC≡CPh affords a product of insertion of the alkyne into Al–Al bond, while with phenylacetylene the cycloaddition product has been obtained [6].

An ability of complex (dpp-bian)Ga–Ga(dpp-bian) to coordinate phenylacetylene allows catalytic functionalization of this alkyne including its hydroamination and hydroarylation with anilines [4b]. It is worth mentioning that catalytic activity of the digallane in hydroamination of phenylacetylene with aromatic amines is comparable to the activity of transition metal-based systems [7]. Assuming that the alteration of the coordination sphere of the group 13 metal in dpp-bian complexes may influence the reactivity of the complex as a whole significantly, we investigated the

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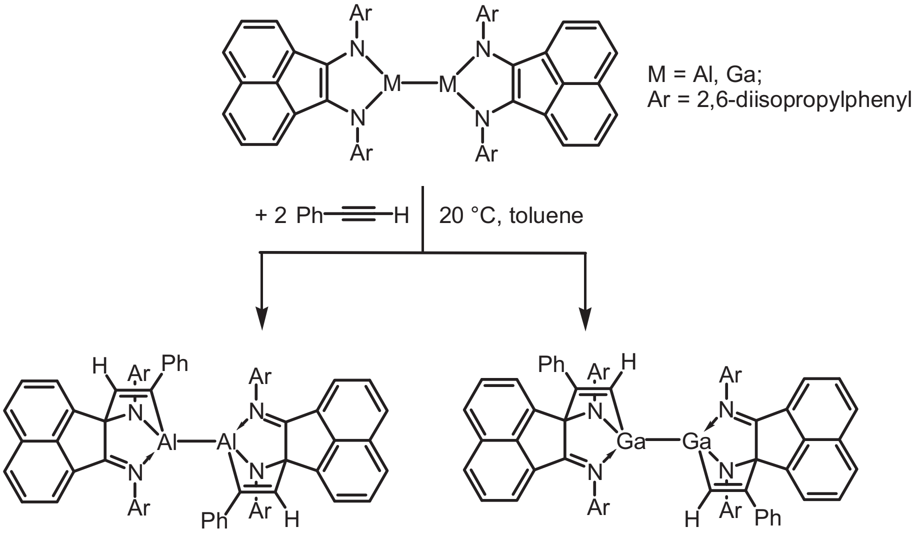


Scheme 1.

reactivity of the mononuclear four-coordinate aluminum and gallium species toward alkynes and other unsaturated organic molecules.

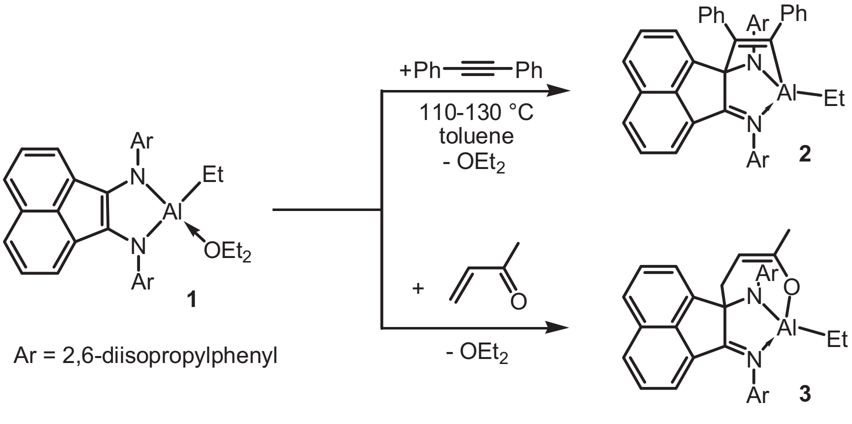
Here we report reactivity of ethyl-aluminum derivative (dpp-bian)AlEt(Et_2O) (**1**) toward diphenylacetylene and methylvinylketone. Reactivity of the mononuclear gallium including (dpp-bian)GaMe and (dpp-bian)$GaOCH_2CH_2NMe_2$ will be published elsewhere.

2. Results and discussion

*2.1. Synthesis and characterization of compounds [dpp-bian(PhC=CPh)]AlEt (**2**) and [dpp-bian(CH₂–CH=C(Me)–O)]AlEt (**3**)*

Reactions of complex (dpp-bian)AlEt(Et_2O) (**1**) with diphenylacetylene and methylvinylketone afford in good yields cycloaddition products [dpp-bian(PhC=CPh)]AlEt (**2**) and [dpp-bian(CH_2–CH=C(Me)–O)]AlEt (**3**) (Scheme 2). While with the methylvinylketone complex **1** readily reacts in toluene at ambient temperature, the reaction of **1** with PhC≡CPh does not proceed in solution even at elevated temperatures, for example, in toluene at reflux. However, adding complex **1** in melted diphenylacetylene (110–130 °C) allows elimination of the coordinated diethylether molecules and formation of cycloadduct **2**.

Compound **2** readily reacts with phenylacetylene but the attempts to isolate the product in individual state were failed. Compounds **2** and **3** were isolated as red and orange crystals by crystallization from hexane, respectively. Both the compounds were characterized by IR and NMR spectroscopy and their molecular structures were determined by single crystal X-ray diffraction. IR spectra of complexes **2** and **3** consist of C=N stretching vibration bands at 1628 and 1622 cm^{-1}. In the free dpp-bian the ν(C=N) vibrations are observed in the range 1642–1670 cm^{-1} [8]. Bands of medium intensity at 1588 cm^{-1} in the IR spectra of **2** and **3** correspond to the stretching vibrations of the carbon–carbon double bonds. It is expected that addition of unsaturated substrates to complex **1** should result in unsymmetrical amido-imino structure that, in turn, should become apparent in a number of unique resonances in the ^1H NMR spectrum. In contrast to our expectation, the ^1H NMR spectrum of complex **2**, recorded in toluene-d_8 at 298 K (Fig. 1), consists of broadened signals in an aliphatic range that could not be well assigned. However, lowering the temperature to 233 K effected the spectrum, which consists of expected signal set (Fig. 1), including four septets (δ = 5.04, 3.64, 3.50 and 3.15 ppm) and eight doublets (δ = 1.62, 1.58, 1.34, 1.19, 1.04, 1.01, 0.89 and −0.13 ppm) of four non-equivalent isopropyl groups. The ethyl group attached to aluminum atom produced a triplet (δ = 1.36 ppm) and a quartet (δ = 0.80 ppm). Based on the NMR



Scheme 2.