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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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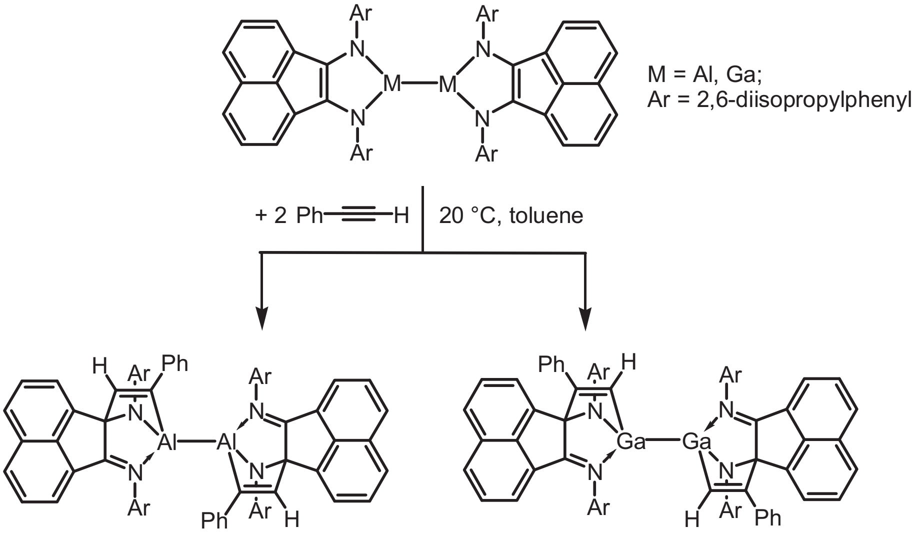


Scheme 1.

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

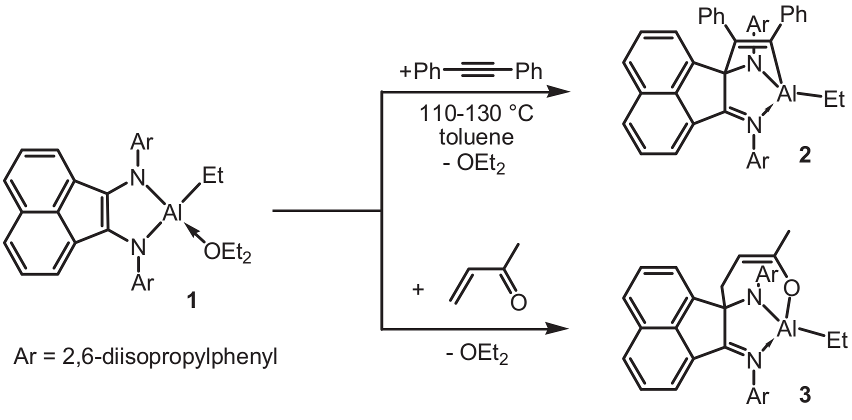
Here we report reactivity of ethyl-aluminum derivative (dpp-bian)AlEt(Et_2O) (**1**) toward diphenylacetylene and methylvinylketone. Reactivity of the mononuclear gallium including (dpp-bian)GaMe and (dpp-bian)$GaOCH_2CH_2NMe_2$ will be published elsewhere.

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.

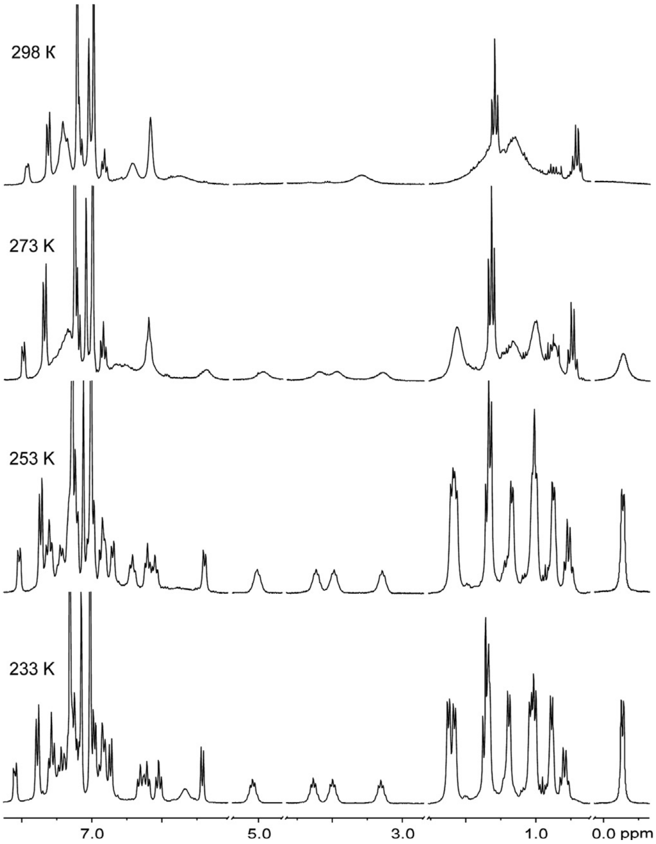


Fig. 1. Temperature dependence of ^{1}H NMR spectra of compound **2** (400 MHz, toluene-d$_8$).

spectroscopic data we may suggest that in solution at ambient temperature, a dynamic process was associated with the molecule of **2**. This process involved a migration of the alkyne moiety between two carbon atoms of the diimine fragment.

On the contrary, the ^{1}H NMR spectrum of complex **3** (Fig. 2) consists of a set of well resolved signals form all of the organic fragments. Again, the ^{1}H NMR data confirm unambiguously the amido-imino functionality of the chelating ligand. The isopropyl groups produced four septets (δ = 4.66, 3.81, 3.16 and 2.95 ppm) and eight doublets (δ = 1.59, 1.51, 1.43, 1.19, 1.17, 1.04, 0.45 and 0.25 ppm). The signals of the methylvinylketone moiety have been assigned on the basis of ^{1}H–^{1}H COSY NMR data. Diastereotopic protons in CH_2 group connected to a quaternary carbon atom of the diimine fragment generated two signals (δ = 3.24 and 1.97 ppm). Proton at the carbon–carbon double bond in the fragment [H(H)C(C)C(**H**)=C(CH_3)OAl] produced a signal at δ = 4.27 ppm, whereas a signal of CH_3 group in this fragment can be located at δ = 2.15 ppm. Due to the chirality of the aluminum atom in compound **3**, the CH_2 protons of the ethyl substituent at the metal are non-equivalent and gave raise to two quartets located at δ = 0.35 ppm.

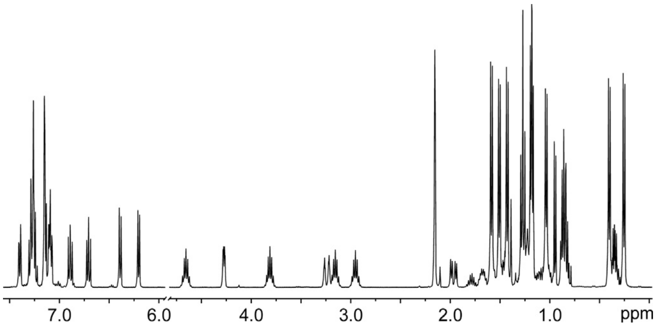


Fig. 2. ^{1}H NMR spectrum of compound **3** (400 MHz, benzene-d$_6$) at 298 K.

2.2. Molecular structures of complexes 2 and 3

Molecular structures of complexes **2** and **3** were determined by the X-ray crystallography and depicted in Figs. 3 and 4, respectively. Complexes **2** and **3** represent mononuclear four-coordinate aluminum species. The crystal structures of **2** and **3** prove that in each case the organic substrate is added across the Al–N–C fragment of metallacycle of starting complex **1**. Addition of diphenylacetylene is accomplished with the formation of new C–C and C–Al bonds. The reaction of complex **1** with methylvinylketone (1,3-π-conjugate) resulted in new C–C bond along with O–Al bond. Thus, the atoms C(1) and Al in molecules **2** and **3** become chiral after cycloaddition. In both cases the unit cells consist in pairs of *R* and *S* enantiomers.

A marked difference in the Al–N bond lengths in compounds **2** and **3** reflects amido-imino character of the N-chelating fragment. The valent Al–N(1) bonds (**2**, 1.8459(12) Å; **3**, 1.8240(12) Å) are remarkably shorter than coordinative Al–N(2) bonds (**2**, 2.0309(13) Å; **3**, 2.0005(13) Å). The C(1)–N(1) bonds (**2**, 1.4791(18) Å; **3**, 1.4734(19) Å) correspond well to a single carbon–nitrogen bond (1.472(5) Å) [9], while the bonds C(2)–N(2) (**2**, 1.2897(17) Å; **3**, 1.2934(18) Å) are close to double C=N bonds in dpp-bian (1.282(4) Å) [8]. An almost ideal trigonal planar environments of the atoms C(39) and C(40) in complex **2** are indicative of their sp^2 nature. The C(39)–C(40) bond length (1.3493(19) Å) is only slightly longer than a typical C–C double bond. The Al–C(40) bond (2.0115(15) Å) in compound **2** falls into the range of corresponding aluminum–carbon bonds in the products formed during addition of acetylene, phenylacetylene and methylphenylacetylene to diallane (dpp-bian)Al–Al(dpp-bian) (1.997(1)–2.023(5) Å) [4c]. Further, the Al–C(40) bond is well compared with Al–C(vinyl) bond

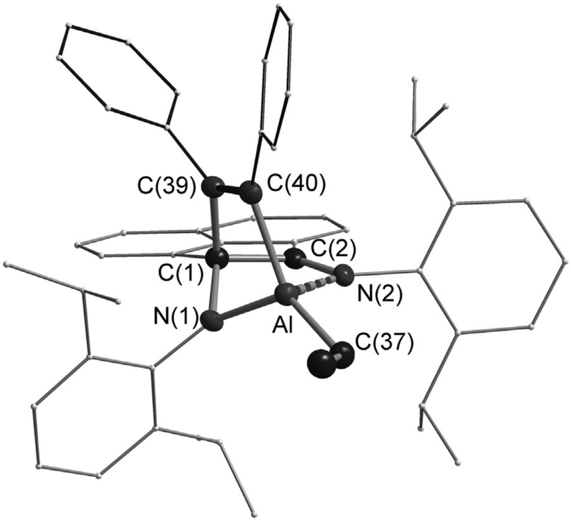


Fig. 3. Molecular structure of compound **2**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (°): Al–N(1) 1.8459(12), Al–N(2) 2.0309(13), Al–C(40) 2.0115(15), N(1)–C(1) 1.4791(18), N(2)–C(2) 1.2897(17), C(1)–C(2) 1.5439(19), C(1)–C(39) 1.6019(19), C(39)–C(40) 1.3493(19), Al–C(37) 1.9527(15), N(1)–C(1)–C(2) 105.80(10), N(2)–C(2)–C(1) 115.79(12), N(1)–C(1)–C(39) 108.29(11), C(2)–C(1)–C(39) 103.95(11), C(1)–C(39)–C(40) 112.87(12), C(1)–N(1)–Al 95.69(8), C(2)–N(2)–Al 102.63(9), N(1)–Al–N(2) 86.91(5).

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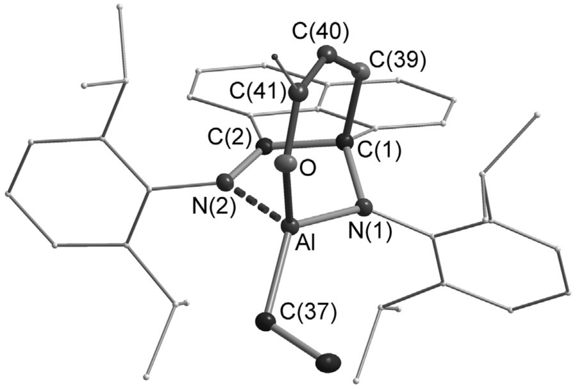
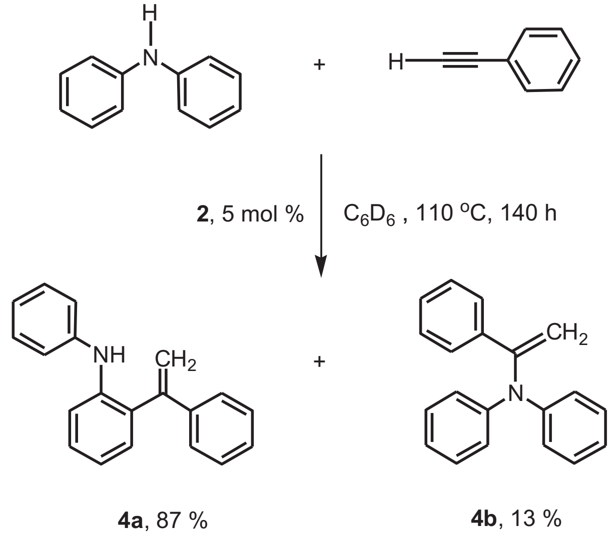


Fig. 4. Molecular structure of compound **3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (°): Al–N(1) 1.8240(12), Al–N(2) 2.0005(13), Al–O 1.7436(10), N(1)–C(1) 1.4734(19), N(2)–C(2) 1.2934(18), C(1)–C(2) 1.5357(19), C(1)–C(39) 1.5679(18), C(39)–C(40) 1.5109(18), C(40)–C(41) 1.342(2), C(41)–O 1.3552(18), Al–C(37) 1.9541(16), N(1)–C(1)–C(2) 106.93(11), N(2)–C(2)–C(1) 117.80(12), N(1)–C(1)–C(39) 114.16(11), C(2)–C(1)–C(39) 109.42(11), C(1)–C(39)–C(40) 122.86(12), C(39)–C(40)–C(41) 135.60(14), C(1)–N(1)–Al 106.54(8), C(2)–N(2)–Al 106.86(9), N(1)–Al–N(2) 87.87(5).



Scheme 3.

in $\{HC[(CMe)(NC_6H_3\text{-}2,6\text{-}i\text{-}Pr)]_2\}Al[NC(Ph)C_2(SiMe_3)_2]$ (1.99(2) Å) [10]. The bond C(1)–C(39) (1.6019(19) Å) in complex **2** is about 0.03 Å longer than corresponding distances in above mentioned addition products between alkynes and (dpp-bian)Al–Al(dpp-bian) [4c]. An elongation of C(1)–C(39) bond in **2** may be indicative of a weak interaction between atoms C(1) and C(39) and as a consequence there has been a cleavage of this bond in solution at ambient temperature (*vide supra*).

In compound **3**, a newly formed carbon–carbon bond (C(1)–C(39), 1.5679(18) Å) is close to the related bonds in the products of addition of acetylene, phenylacetylene and methylphenylacetylene to diallane (dpp-bian)Al–Al(dpp-bian) (1.564(5) Å, 1.557(3) Å and 1.585(7) Å, correspondingly). The bond distance of C(40)–C(41) (1.342(2) Å) corresponds well to a carbon–carbon double bond in alkenes.

2.3. *Test of complex **2** as catalyst for the reactions of alkynes with amines*

Catalytic activity of complex **2** was tested in reactions of alkynes with amines. 1-Aminonaphthalene has been chosen as one of the substrates because its reaction with phenylacetylene in the presence of 2 mol% of (dpp-bian)Ga–Ga(dpp-bian) proceeds with 100% conversion within 12 h resulting hydroamination (48%) and hydroarylation (52%) products [4b]. We have found that complex **2** (5 mol%) does not catalyze reaction of 1-aminonaphthalene with such alkynes as PhC≡CPh, PhC≡CMe and $HC{\equiv}CCH_2CH_2CH_2CH_3$ in C_6D_6 at 110 °C. In the presence of complex **2** (5 mol%), 1-aminonaphthalene reacts with phenylacetylene (C_6D_6, 110 °C) at a much slower rate than in the presence of (dpp-bian)Ga–Ga(dpp-bian); even after 160 h conversion of the reagents reached only 80%. However, a ratio of the products formed in the latter case is different as the hydroarylation product is dominating compared to the hydroamination one (77 and 23%, respectively). Since PhC≡CH is more reactive in cycloaddition reactions compared to PhC≡CPh one may suggest that the treatment of complex **2** with an excess of PhC≡CH in the course of catalytic test results in replacement of the internal alkyne with terminal one.

It is anticipated that a lower catalytic activity of complex **2** in the reactions of phenylacetylene with 1-aminonaphthalene, compared to (dpp-bian)Ga–Ga(dpp-bian), is caused by the formation of inactive Lewis base/acid adducts in the course of interaction of complex **2** with 1-aminonaphthalene. To avoid a complex formation between **2** and amine, a more sterically demanding diphenylamine was chosen. In the presence of 5 mol% of complex **2** at 110 °C in C_6D_6 a complete conversion of PhC≡CH and Ph_2NH to the products was achieved in 140 h. According to the ^1H–^1H and ^1H–^{13}C COSY NMR data, the mixture formed consists of hydroarylation product **4a** (87%) and Markovnikov's hydroamination product **4b** (13%) (Scheme 3).

The N–H proton of diphenylamine and ≡C–H proton of phenylacetylene show singlet signals at δ 5.14 and 2.77 ppm, respectively. After completion of the reaction, the ^1H NMR spectrum of the mixture exhibits a singlet at δ 5.53 ppm, which corresponds to the proton of amino group of the product **4a**. The signals of geminal protons in compound **4a** appear at 5.61 and 5.25 ppm, in compound **4b** – at δ 5.16 and 4.92 ppm (Fig. 5).

In order to compare a catalytic activity of compound **2** with other group 13 metal compounds, we have studied the reaction between diphenylamine and phenylacetylene in the presence of aluminum chloride as well as digallane (dpp-bian)Ga–Ga(dpp-bian). We have found that heating an equimolar mixture of PhC≡CH and Ph_2NH in the presence of 10 mol% of $AlCl_3$ at 110 °C resulted product **4b** in 78% yield within 20 h, whereas compound **4a** was not formed at all. Moreover, compound (dpp-bian)Ga–Ga(dpp-bian) in the similar conditions failed to catalyze the interaction between PhC≡CH and Ph_2NH.

3. Summary and conclusions

In conclusion, we have shown that alkylaluminum species consisting of dianionic dpp-bian ligand are more reactive toward alkynes compared to coordinatively unsaturated compound (dpp-bian)Al–Al(dpp-bian). Thus, the latter did not interact with PhC≡CPh [4c] even in refluxing toluene, while complex (dpp-bian) $AlEt(Et_2O)$ (**1**) reacted with this alkyne to give thermodynamically stable cycloadduct [dpp-bian(PhC=CPh)]AlEt (**2**). It is also worth mentioning that redox-active ligand in complex **1** deactivated aluminum–alkyl bond since no carbometallation in the reaction of **2** with PhC≡CPh occurred. Recently, we have found that even phenol did not protonate the Al–Et bond in **1**. On the other hand, protonation of one of the nitrogen atom took place to yield dpp-bian(H)–aluminum–phenolate derivative. Further, complex [dpp-

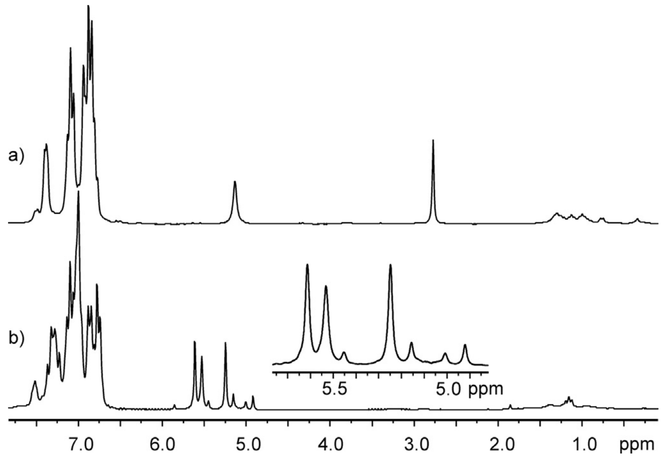


Fig. 5. ^1H NMR spectra (200 MHz, C_6D_6) of a mixture of $PhC{\equiv}CH$ and Ph_2NH (1–1) with 5 mol% of complex **2** present before (*a*) and after (*b*) heating at 110 °C within 140 h.

bian($CH_2{-}CH{=}C(Me){-}O$)]AlEt (**3**) is the first example of cycloaddition of the conjugated enone to the metal complex involving both the ligand and the metal. Finally, we have demonstrated that the aluminum complexes of the functionally labile ligands may catalyze reactions between alkynes and amines.

4. Experimental section

4.1. General data

All manipulations were carried out under vacuum using Schlenk technique. Solvents were condensed into reaction flasks from sodium/benzophenone prior to use. Phenylacetylene was purchased from Aldrich, degassed and stored over sodium metal. Compound **1** was prepared according to the literature procedure [11] and isolated by crystallization from toluene/hexane mixture (1:2). The deuterated solvents benzene-d_6 and toluene-d_6 (Aldrich) were dried at ambient temperature over sodium/benzophenone and, just prior to use, condensed under vacuum into NMR tubes containing the compound, for which the spectrum must be recorded. The NMR spectra were obtained on Bruker Avance III instruments; IR spectra were obtained on FSM 1201 instrument in Nujol.

4.1.1. Synthesis of [dpp-bian(PhC=CPh)]AlEt, 2

A mixture of 0.60 g (0.95 mmol) of complex **1** and of 0.36 g (2.02 mmol) of diphenylacetylene was heated at 110–130 °C in a closed evacuated ampoule. A color change of the melted mixture from deep blue to dark red was observed. While it is being heated, the flask was evacuated three times for 1–2 s to remove free diethyl ether formed within the reaction. Then the mixture was cooled to the ambient temperature, dissolved in hexane and filtered off. Crystallization from hexane at –30 °C afforded 0.53 g (76%) of compound **2** as red crystals. Mp: 169 °C. ^1H NMR (toluene-d_8, 400 MHz, 233 K, *J*/Hz): 7.57–7.52 (m, 1H, CH arom), 7.39 (d, 2H, CH arom, *J* = 7.5), 7.33–6.83 (m, 15H, CH arom), 6.65 (t, 1H, CH arom, *J* = 7.8), 6.61 (t, 1H, CH arom, *J* = 7.4), 6.52 (t, 1H, CH arom, *J* = 7.7), 6.21 (d, 1H, CH arom, *J* = 7.0), 5.04 (sept, 1H, $\mathrm{C\mathit{H}(CH_3)_2}$, *J* = 6.6), 3.64 (sept, 1H, $\mathrm{C\mathit{H}(CH_3)_2}$, *J* = 6.5), 3.50 (sept, 1H, $\mathrm{C\mathit{H}(CH_3)_2}$, *J* = 6.5), 3.15 (sept, 1H, $\mathrm{C\mathit{H}(CH_3)_2}$, *J* = 6.5), 1.62 (d, 3H, $\mathrm{CH(C\mathit{H}_3)_2}$, *J* = 6.5), 1.58 (d, 3H, $\mathrm{CH(C\mathit{H}_3)_2}$, *J* = 6.5), 1.36 (t, 3H, $\mathrm{AlCH_2C\mathit{H}_3}$, *J* = 8.0), 1.34 (d, 3H, $\mathrm{CH(C\mathit{H}_3)_2}$, *J* = 6.3), 1.19 (d, 3H, $\mathrm{CH(C\mathit{H}_3)_2}$, *J* = 6.5), 1.04 (d, 3H, $\mathrm{CH(C\mathit{H}_3)_2}$, *J* = 6.3), 1.01 (d, 3H, $\mathrm{CH(C\mathit{H}_3)_2}$, *J* = 6.5), 0.89 (d, 3H, $\mathrm{CH(C\mathit{H}_3)_2}$, *J* = 6.5), 0.80 (q, 2H, $\mathrm{AlC\mathit{H}_2CH_3}$, *J* = 8.0), –0.13 (d, 3H, $\mathrm{CH(C\mathit{H}_3)_2}$, *J* = 6.5). IR ($cm^{-1}$, Nujol): 1628 s, 1588 m, 1542 w, 1488 w, 1440 m, 1416 w, 1364 m, 1339 w, 1323 m, 1313 m, 1264 m, 1254 w, 1234 w, 1212 w, 1186 w, 1178 w, 1152 w, 1114 w, 1099 w, 1076 w, 1057 w, 1041 m, 1030 m, 1001 m, 973 m, 959 w, 932 m, 908 w, 884 w, 869 m, 832 m, 821 w, 800 m, 777 s, 760 s, 752 s, 713 m, 696 s, 679 w, 666 w, 636 w, 611 w, 603 m, 588 m, 557 w, 546 w, 500 w, 471 w. Anal. Calcd for $C_{52}H_{55}AlN_2$ (734.96): C, 84.90; H 7.48. Found: C, 83.86; H, 7.62%.

4.1.2. Synthesis of [dpp-bian($CH_2{-}CH{=}C(Me){-}O$)]AlEt, 3

To a solution of 0.36 g (0.57 mmol) of complex **1** in toluene (25 mL), 0.42 g (0.60 mmol) of 3-betene-2-on was added. The reaction mixture changed its color instantly from deep blue to brown. Toluene was removed under vacuum and the residue was dissolved in hexane. The resulting solution was cooled with liquid nitrogen for 1 min and stored at room temperature. After 16 h complex **3** was isolated as orange crystals (0.35 g, 86%). Mp: 111–113 °C (dec.). ^1H NMR (C_6D_6, 400 MHz, 298 K, *J*/Hz): 7.40 (dd, 1H, CH arom, *J* = 7.8, 1.76), 7.31–7.21 (m, 4H, CH arom), 7.14 (d, 1H, CH arom, *J* = 6.5), 7.12–7.06 (m, 2H, CH arom), 6.89 (dd, 1H, CH arom, *J* = 8.3, 7.3), 6.71 (dd, 1H, CH arom, *J* = 8.0, 7.5), 6.39 (d, 1H, CH arom, *J* = 7.3), 6.20 (d, 1H, CH arom, *J* = 7.0), 4.66 (sept, 1H, $\mathrm{CH(CH_3)_2}$, *J* = 6.8), 4.27 (dd, 1H, $\mathrm{HC(H)C(\mathit{H}){=}C(CH_3)OAl}$, *J* = 6.3, 2.3), 3.81 (sept, 1H, $\mathrm{C\mathit{H}(CH_3)_2}$, *J* = 6.8), 3.24 (dq, 1H, $\mathrm{\mathit{H}C(H)C(H){=}C(CH_3)OAl}$, *J* = 17.8, 2.3), 3.16 (sept, 1H, $\mathrm{C\mathit{H}(CH_3)_2}$, *J* = 6.8), 2.95 (sept, 1H, $\mathrm{C\mathit{H}(CH_3)_2}$, *J* = 6.8), 2.15 (s, 3H, $\mathrm{HC(H)C(H){=}C(C\mathit{H}_3)OAl}$), 1.97 (dd, 1H, $\mathrm{HC(\mathit{H})C(H){=}C(CH_3)OAl}$, *J* = 17.8, 6.3), 1.59 (d, 3H, $\mathrm{CH(C\mathit{H}_3)_2}$, *J* = 6.8), 1.51 (d, 3H, $\mathrm{CH(C\mathit{H}_3)_2}$, *J* = 6.8), 1.43 (d, 3H, $\mathrm{CH(C\mathit{H}_3)_2}$, *J* = 6.8), 1.27 (t, 3H, $\mathrm{AlCH_2C\mathit{H}_3}$, *J* = 8.2), 1.19 (d, 3H, $\mathrm{CH(C\mathit{H}_3)_2}$, *J* = 6.8), 1.17 (d, 3H, $\mathrm{CH(C\mathit{H}_3)_2}$, *J* = 6.8), 1.04 (d, 3H, $\mathrm{CH(C\mathit{H}_3)_2}$, *J* = 6.8), 0.40 (d, 3H, $\mathrm{CH(C\mathit{H}_3)_2}$, *J* = 6.8), 0.35 (dq, 2H, $\mathrm{AlC\mathit{H}_2CH_3}$, *J* = 8.2, 5.3), 0.25 (d, 3H, $\mathrm{CH(C\mathit{H}_3)_2}$, *J* = 6.8). IR ($cm^{-1}$, Nujol): 1721 w, 1653 s, 1622 s, 1596 m, 1588 m, 1488 w, 1436 s, 1420 m, 1359 s, 1329 w, 1319 s, 1259 s, 1234 w, 1221 w, 1188 s, 1157 w, 1137 w, 1100 m, 1086 s, 1059 s, 1040 m, 1007 m, 987 s, 979 w, 965 w, 951 w,

Table 1
Crystal data and structure refinement for **2** and **3**.

	2	**3**
Formula	$C_{52}H_{55}AlN_2$	$C_{42}H_{51}AlN_2O \times C_6H_{14}$
Temperature (K)	100(2)	100(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\overline{1}$ (no. 2)	$P2_1/c$ (no. 14)
a (pm)	993.96(9)	1066.56(5)
b (pm)	1054.16(10)	2683.65(13)
c (pm)	2104.97(19)	1551.66(8)
α (°)	100.543(2)	90
β (°)	102.718(2)	109.258(1)
γ (°)	98.046(2)	90
V (10^{-30} m^3)	2077.4(3)	4192.8(4)
Z	2	4
D_{calcd} (g cm^{-3})	1.175	1.130
μ (mm^{-1})	0.087	0.085
Crystal size (mm)	0.41 × 0.15 × 0.06	0.40 × 0.30 × 0.20
Theta range (°)	$2.03 \le \theta \le 27.00$	$2.02 \le \theta \le 26.00$
Index ranges	$-12 \le h \le 12$ $-13 \le k \le 13$ $-26 \le l \le 26$	$-13 \le h \le 13$ $-20 \le k \le 33$ $-19 \le l \le 18$
Independent Reflections	9005 [$R_{int} = 0.0362$]	8126 [$R_{int} = 0.0351$]
Reflections observed	19,379	24,812
Parameters	505	533
$R = \Sigma\|\|F_0\|-\|F_c\|\|/\Sigma\|F_0\|$ [$I > 2\sigma(I)$]	0.0517	0.0663
$wR_2 = \{\Sigma w(\|F_0\|^2-\|F_c\|^2)^2/\Sigma\|F_0\|^2\}^{1/2}$ [$I > 2\sigma(I)$]	0.1148	0.1862
$R = \Sigma\|\|F_0\|-\|F_c\|\|/\Sigma\|F_0\|$ (all data)	0.0887	0.0888
$wR_2 = \{\Sigma w(\|F_0\|^2-\|F_c\|^2)^2/\Sigma\|F_0\|^2\}^{1/2}$ (all data)	0.1256	0.2034
Max./min. residual (10^{30} e m^{-3})	0.356/–0.293	0.971/–0.839

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931 m, 920 m, 885 w, 874 w, 851 m, 838 s, 823 w, 802 s, 789 s, 769 s, 759 s, 698 s, 675 s, 657 s, 611 s, 579 w, 566 w, 544 m, 530 w, 520 w, 498 w, 478 m, 463 w. Anal. Calcd for $C_{42}H_{51}AlN_2O \times C_6H_{14}$ (713.0): C, 80.79; H, 9.12. Found: C, 80.16; H, 9.64%.

*4.1.3. Reaction between PhC≡CH and Ph_2NH in the presence of **2** in an NMR tube*

Phenylacetylene (0.102 g, 1.0 mmol), diphenylamine (0.169 g, 1.0 mmol) and compound **2** (0.037 g, 0.05 mmol) were placed in an NMR tube. Benzene-d_6 (0.6 mL) was added into this tube by condensation under vacuum, and then the tube was sealed off. The reaction mixture was heated in an oil bath at 110 °C during 140 h. The reaction was monitored by the ^{1}H NMR. Conversion of the reagents and amount of the products formed was determined from their integral intensities.

4.1.4. Crystallographic analyses

The data for **2** and **3** (Table 1) were collected on a Bruker SMART APEX diffractometer, using graphite monochromated MoKα radiation (ω-scan technique, $\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS-97 [12] and were refined on F^2 using SHELXL-97 [13]. SADABS [14] was used to perform area-detector scaling and absorption corrections. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter $U_{iso}(H) = 1.5U_{eq}(C)$ in CH_3-groups and $U_{iso}(H) = 1.2U_{eq}(C)$ in other fragments. Crystal of **3** contains a disordered solvate molecule of hexane in common position.

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