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Hydroarylation of Alkynes with Phenols in the Presence of Gallium Complexes of a Labile N-Ligand: Synthesis of Chromenes

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Dedicated to Professor Nikolay S. Zefirov on occasion of his 80th anniversary

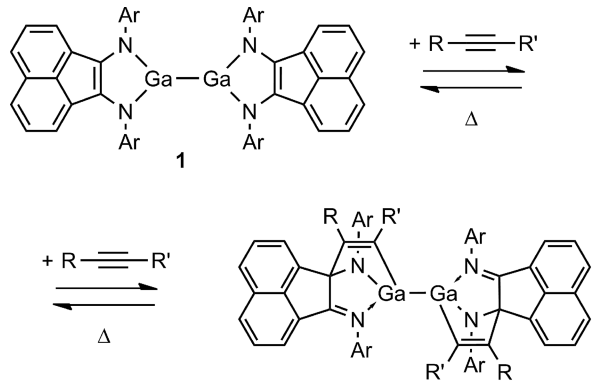
Keywords: Alkynes / N ligands / Ligand effects / Gallium / Hydroarylation / Oxygen heterocycles

In the presence of (dpp-bian)Ga–Ga(dpp-bian) (**1**) and [dpp-bian(Ph)C=C(H)]Ga–Ga[(H)C=C(Ph)dpp-bian] (**2**) {dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene}, phenylacetylene reacts with 1-naphthol to give 2-(1-phenylvinyl)-naphthalen-1-ol (**3**). In solution in the presence of complexes **1** or **2**, compound **3** undergoes further dimerization to give 2-[4-methyl-2,4-diphenyl-3,4-dihydro-2*H*-benzo[*h*]chromen-2-yl]naphthalen-1-ol ($C_{36}H_{28}O_2$), whose diastereomers **4** and **5** were isolated in crystalline form. Diastereomer **4** is the kinetically favored product, which, however, undergoes conversion into diastereomer **5** in solution at elevated temperature. The structures of **4** and **5** were determined by single-crystal X-ray analysis. The catalytic activity of complexes **1** and **2** in the hydroarylation reactions of phenylacetylene and some other alkynes with different arenes has been investigated. By the reaction of phenylacetylene with 3,5-di-*tert*-butylphenol, 5,7-di-*tert*-butyl-4-methyl-2,4-diphenyl-4*H*-chromene (**7**) has been prepared for the first time.

Introduction

In the beginning of the 1990s, Elsevier and van Asselt reported the first metal complexes of 1,2-bis(arylimino)acenaphthenes (bians).[1] Subsequent studies led to the preparation of robust late-transition-metal catalysts based on bians for olefin polymerization.[2] With few exceptions, in the transition-metal complexes reported to date, the bians act as neutral chelating ligands. One of the most popular ligands of this family is 1,2-bis[(2,6-diisopropylphenyl)-imino]acenaphthene (dpp-bian). In the beginning of the 2000s, we reported a stepwise reduction of dpp-bian with sodium metal to give the dpp-bian tetraanion.[3] Since the reduction process is completely reversible, the dpp-bian can be assigned to a group of redox-active ligands (e.g., *ortho*-benzoquinones).

A major research interest of our group is the application of redox-active complexes of "redox-inactive" metal ions (e.g., Mg^{2+}, Ca^{2+}, Ga^{3+}, Al^{3+}, etc.) for organic synthesis. We have shown that main-group metal complexes of the dpp-bian dianion (bis-amido metal species) show reactivities that can be compared with those of complexes of redox-active transition metals. Main-group metal complexes of the noninnocent dpp-bian ligand show two types of ligand-centered reactivity. The first one involves single-electron transfer from the dpp-bian dianion to the substrate to give either complexes with a dpp-bian radical anion,[4] or complexes with a C(imine)-substituted[4d,5] amido-imino ligand. The second one involves a HOMO–LUMO interaction between the metal complex and the substrate. This latter mode of reactivity also gives complexes with C(imine)-substituted amido-imino ligands. An illustrative example of this could be the addition of alkynes to group 13 metal complexes,[6] as for instance, to digallane (dpp-bian)Ga–Ga(dpp-bian) (**1**) (Scheme 1).[6a,6c]



Scheme 1. Addition of alkynes to complex (dpp-bian)Ga–Ga(dpp-bian) (**1**).

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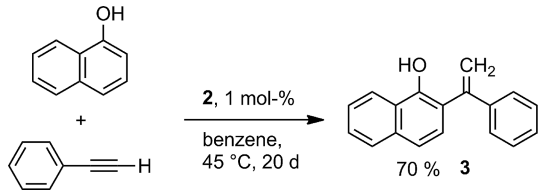
In 2012, we demonstrated that compound **1** has a high catalytic activity in the hydroamination of alkynes with primary aromatic amines.[6c] The corresponding imines were obtained with yields up to 99%. The reaction between 1-aminonaphthalene and phenylacetylene in the presence of compound **1** (2 mol-%) gives two products, i.e., *N*-naphthyl-1-phenylethan-1-imine and 2-(1-phenylvinyl)naphthalen-1-amine (1:1 molar ratio), as a result of hydroamination and hydroarylation processes. With 1-aminoanthracene, phenylacetylene reacts in the presence of digallane **1** to give exclusively 2-(1-phenylvinyl)anthracen-1-amine as the product of hydroarylation of phenylacetylene. To determine whether complexes **1** and **2** are able to catalyze the addition of other aromatic substrates to alkynes, we have studied the reactions of phenylacetylene with naphthols. The results obtained, together with data on some other tests of the catalytic activity of **1** and **2**, are described in this paper.

Results and Discussion

The hydroarylation of alkynes with arenes in the presence of transition-metal catalysts has been well reviewed.[7] We have found that compound **2** serves as a catalyst for the reaction between 1-naphthol and phenylacetylene: at 45 °C within 20 d hydroarylation product **3** was obtained in 70% yield (Scheme 2). At 90 °C, the reaction proceeds much more quickly, and gives product **3** in a good yield already within a few hours. However, at elevated temperatures product **3** undergoes further transformation (vide infra).



Scheme 2. Arylation of phenylacetylene with 1-naphthol in the presence of compound **2**.

To follow the progress of the formation of compound **3**, we monitored the reaction by NMR spectroscopy in C_6D_6 at 90 °C. The ^{1}H NMR spectra of the starting mixture (phenylacetylene + 1-naphthol) as well as compound **3** are shown in Figure 1.

The single resonances at δ = 5.00 and 2.77 ppm arise from the OH and HC≡C groups, respectively. After a reaction time of 1 h, a new set of signals started to grow. The new signals at δ = 5.51 and 5.70 ppm correspond to the diastereotopic protons on the carbon–carbon double bond, and the signal at δ = 6.00 ppm arises from the OH group of product **3**. After a reaction time of 1 h, the conversions of the starting materials were 3 and 30% in the presence of complexes **1** and **2**, respectively. We believe that the differ-

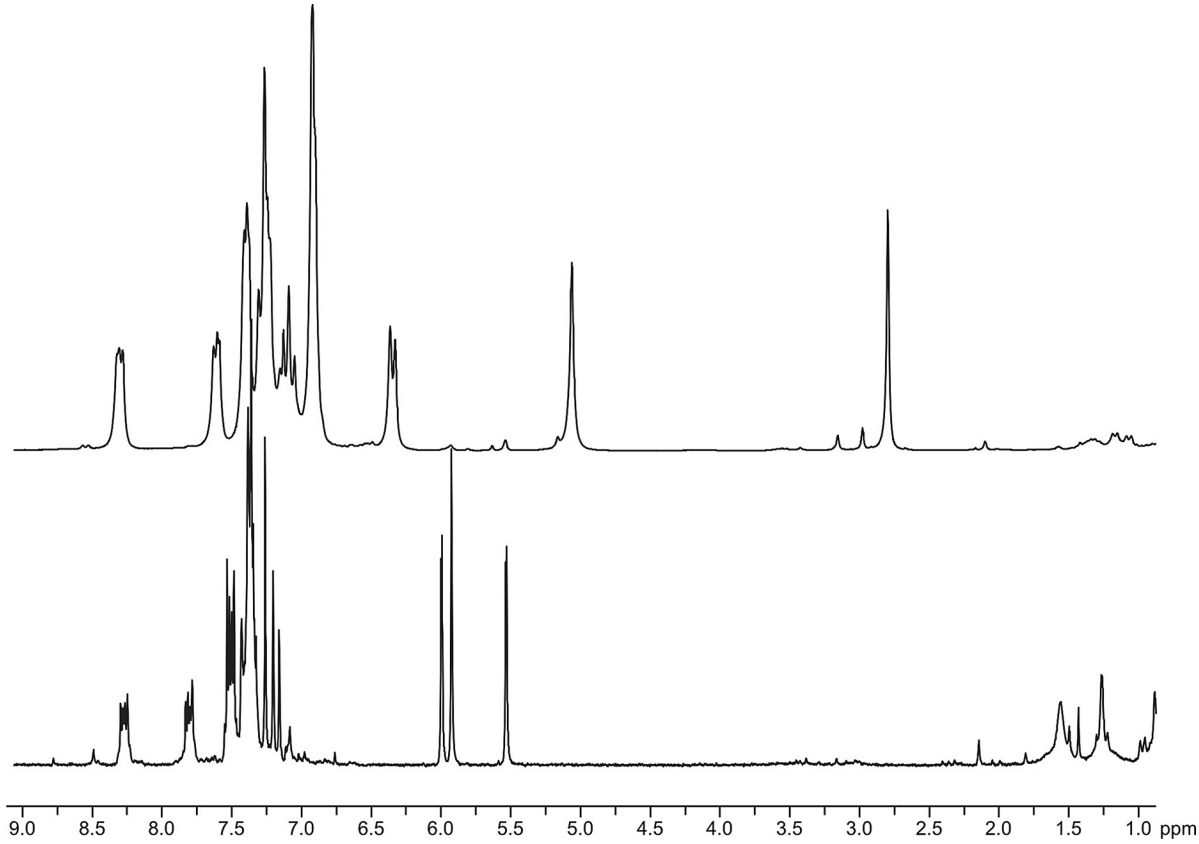
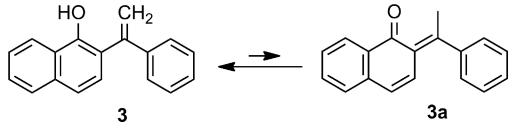


Figure 1. ^{1}H NMR spectra (293 K, 200 MHz, C_6D_6) of a mixture of phenylacetylene + 1-naphthol (top), and product **3** (bottom) isolated from hexane. The resonances at δ = 1.75–0.50 ppm correspond to light petroleum in the sample.

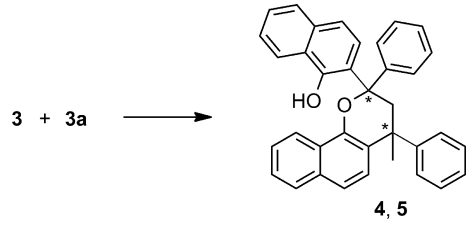
ence in the reaction rates can be explained by a partial decomposition of complex **1** during the course of the reaction with 1-naphthol, before the interaction of complex **1** with phenylacetylene took place. The best yield of the product **3** (70%) was observed after 2.5 h. Only three examples of the formation of compound **3** in the presence of a catalyst have been reported. Thus, with heterogeneous catalyst FeAl-KIT-5,[8] compound **3** was obtained in 73% yield after 6 h at 80 °C. The formation of compound **3** in 70% yield has also been achieved in the presence of $GaCl_3$ (10 mol-%, 110 °C).[9] Furthermore, compounds **1** and **2** are more active than the gallium dithiocarbamate complex (dppbian)Ga(S_2CNMe_2); in the presence of 2 mol-% of the latter compound at 85 °C, product **3** was obtained in 40% yield after 7 h.[6e] The application of organogallium complexes in molecular catalysis has recently been reviewed.[10]

NMR monitoring of the progress of the formation of product **3** in the presence of **2** as catalyst revealed that after 70% conversion of a mixture 1-naphthol + phenylacetylene into product **3**, a subsequent reaction began to take place. After a further 24 h, the signals of compound **3** had almost completely disappeared, and a new spectrum had appeared. Among other signals, this spectrum had singlet signals at δ = 1.43, 1.62, 8.98, and 9.15 ppm. Analysis of the spectrum allowed us to conclude that compound **3** exists as two tautomers (Scheme 3) that can react with each other.



Scheme 3. Tautomerization of compound **3**.

After the full conversion of compound **3**, diastereomeric compounds **4** and **5** were isolated from the reaction mixture and were separated from each other by column chromatography. Crystallization from light petroleum/benzene (4:1) gave crystalline **4** and **5** in 16 and 8% yields, respectively. Compounds **4** and **5** are the result of [4+2] cycloaddition reactions between **3** and **3a** (Scheme 4).



Scheme 4. Formation of compounds **4** and **5**.

In the X-ray crystal structures (vide infra) of compounds **4** and **5**, both enantiomers are present in the unit cell in each case. These are shown in Figure 2.

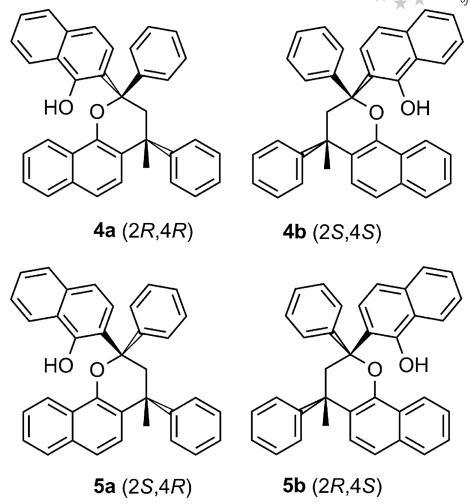


Figure 2. Enantiomeric pairs of compounds **4** and **5** present in the unit cells.

Diastereomers **4** and **5** were characterized by ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectra of compounds **4** and **5** are shown in Figure 3. The methyl groups at C-4 in **4** and **5** (see Figures 4 and 5) give rise to signals at δ = 1.51 and 1.82 ppm, respectively. Due to the chiral atoms C-2 and C-4, the protons at C-3 become diastereotopic and produce doublets (**4**: δ = 3.43 and 3.14 ppm; **5**: δ = 3.46 and 3.25 ppm). The coupling constants for the protons at C-3 in **4** and **5** are 0.58 and 0.44 Hz, respectively. The aromatic protons in **4** and **5** lie in the range δ = 8.65–7.00 and 9.85–6.75 ppm, respectively.

The molecular structures of **4** (Figure 4) and **5** (Figure 5) were determined by single-crystal X-ray analysis. The crystal data and structure refinement details for **4** and **5** are presented in Table 1. Both compounds crystallized in the centrosymmetric space group $P2_1/c$: their unit cells consist in each case of two enantiomeric pairs. As expected, the heterocycles in **4** and **5** are not flat. Atoms O-1, C-4, C-5, and C-6 are almost perfectly positioned in one plane, whereas atoms C-2 and C-3 deviate from this plane in opposite directions. For instance, in compound **5**, atoms C-2 and C-3 deviate from the plane O-1–C-4–C-5–C-6 by 0.28 and 0.44 Å, respectively.

In compound **5**, the planes of the phenyl rings are almost parallel; the distance between their *ipso*-carbon atoms is 3.13 Å. This value is significantly shorter than the interplane distance in graphite (3.35 Å). All the cycles (except the heterocycles) in **4** and **5** are flat, thus indicating their aromaticity. The hydrogen bonds O-2–H···O-1 in compounds **4** and **5** are 1.90(1) and 1.76(2) Å, respectively.

We also investigated whether the formation of products **4** and **5** from compound **3** could occur without a catalyst (such as complexes **1** and **2**). We found that in benzene, compound **3** remained unchanged at ambient temperature, as well as after heating (90 °C) for several hours. In contrast, in the presence of complexes **1** and **2** at 90 °C, compound **3** was converted into products **4** and **5**. For instance,

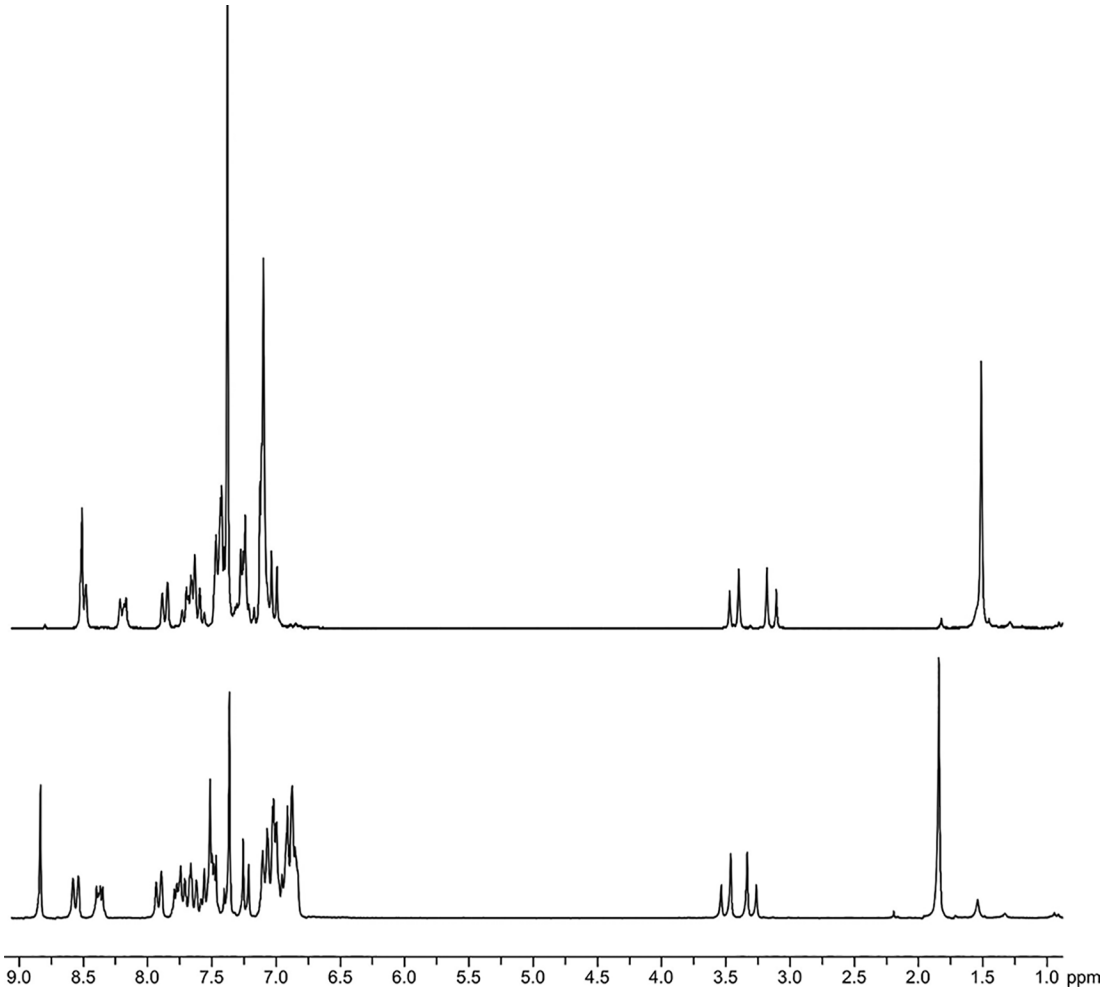


Figure 3. ^{1}H NMR spectra (293 K, 400 MHz, $CDCl_3$) of diastereomeric **4** (top) and **5** (bottom).

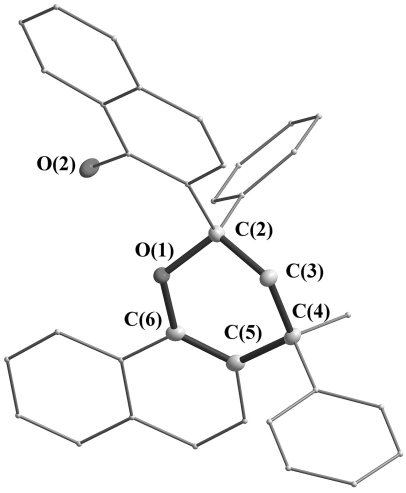


Figure 4. Molecular structure of compound **4**. Selected bond lengths [Å]: C-2–C-3 1.537(1), C-3–C-4 1.553(1), C-4–C-5 1.526(1), C-5–C-6 1.370(1), C-6–O-1, 1.385(1), O-1–C-2 1.461(1).

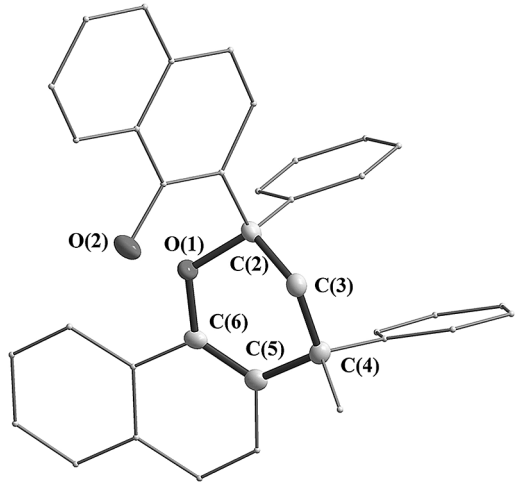


Figure 5. Molecular structure of compound **5**. Selected bond lengths [Å]: C-2–C-3 1.526(1), C-3–C-4 1.556(1), C-4–C-5 1.516(1), C-5–C-6 1.367(1), C-6–O-1 1.384(1), O-1–C-2 1.465(1).

with 2 mol-% of complex **2** at 90 °C in benzene, compound **3** gives **4** and **5** in 96% overall yield within 70 min (Figure 6). The mixture formed contained **4** and **5** in a molar ratio of 4:1. Heating of this mixture for 72 h led to the epimerization of **4** into **5** to give an almost equimolar mixture of **4** and **5** (Figure 7). Similar results were obtained using

Table 1. Crystal data and structure refinement details for **4** and **5**.

Compound	**4**	**5**
Formula	$C_{36}H_{28}O_2 \cdot C_6H_6$	$C_{36}H_{28}O_2$
M_w	570.69	492.58
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	17.7241(3)	16.6716(15)
b [Å]	10.61575(13)	9.9920(9)
c [Å]	16.6993(2)	15.1808(13)
β [°]	107.7804(15)	99.825(2)
V [Å]	2991.96(7)	2491.8(4)
Z	4	4
$\rho_{calcd.}$ [g m^{-3}]	1.267	1.313
μ [mm^{-1}]	0.076	0.080
$F(000)$	1208	1040
Crystal size [mm]	0.40 × 0.40 × 0.10	0.28 × 0.19 × 0.08
$\theta_{min}/\theta_{max}$ [°]	2.935/27.994	2.451/27.999
Index ranges	$-23 \le h \le 23$, $-14 \le k \le 14$, $-22 \le l \le 22$	$-22 \le h \le 22$, $-13 \le k \le 13$, $-20 \le l \le 20$
Total reflections	53989	28682
Unique reflections	7195	5999
R_{int}	0.0370	0.0608
GOF on F^2	1.008	1.034
Max/min transmission	1.0000/0.9967	0.9890/0.8852
Data/restraints/parameter	7195/0/402	5999/0/348
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0397, wR_2 = 0.1057	R_1 = 0.0486, wR_2 = 0.1098
R indices (all data)	R_1 = 0.0507, wR_2 = 0.1116	R_1 = 0.0774, wR_2 = 0.1182
Largest diff. peak/hole [e Å^{-3}]	0.363/–0.230	0.354 /–0.207

complex **1** as catalyst. In benzene at 90 °C, the conversion of compound **3** into products **4** and **5** was 94% after 5 h. Within 0.7 h of mixing complex **1** (2 mol-%) and compound **3**, diastereomers **4** and **5** were present in the reaction mixture in a 2:1 molar ratio. After 77 h, the ratio **4**/**5** had changed to 5:4 (Figure 8).

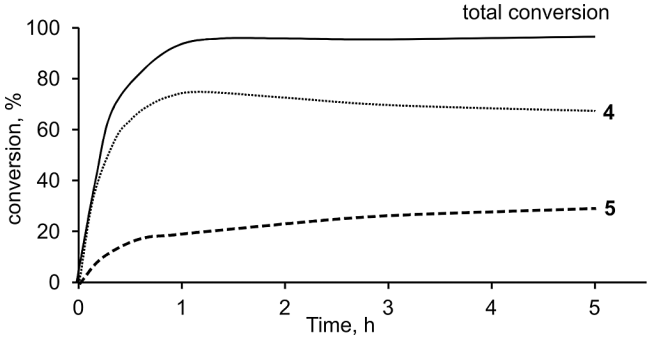


Figure 6. Kinetics of the formation of products **4** and **5** from compound **3** in benzene at 90 °C in the presence of 2 mol-% of complex **2**.

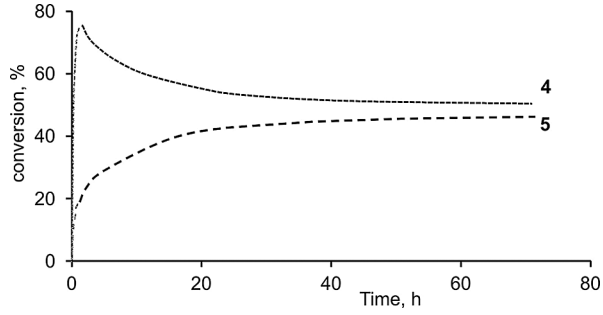


Figure 7. Kinetics of the epimerization of diastereomer **4** into diastereomer **5** at 90 °C in benzene in the presence 2 mol-% of complex **2**.

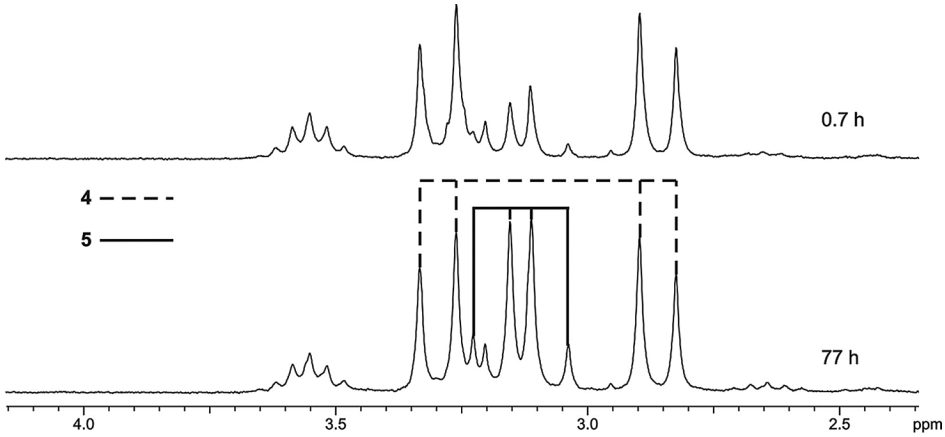
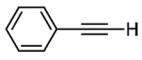
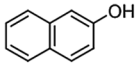
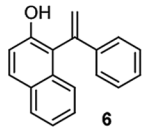
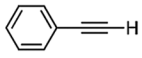
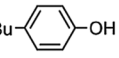
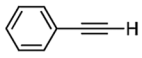
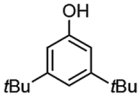
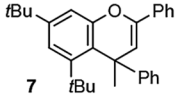
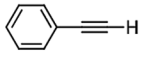
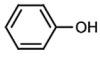
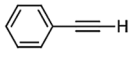
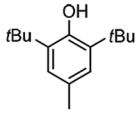
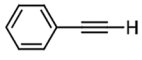
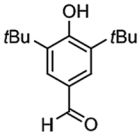
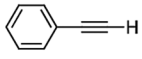
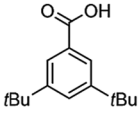
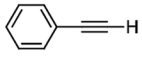
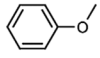
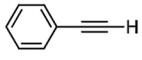
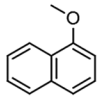
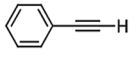
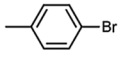
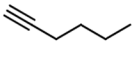
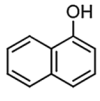
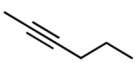
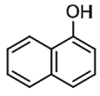


Figure 8. Extracts of the ^{1}H NMR spectra of mixtures of diastereomers **4** and **5** after 0.7 h (top) and 77 h (bottom) after mixing of complex **1** (2 mol-%) with compound **3** in benzene at 90 °C.

Obviously, **4** is the kinetically more favorable isomer, whereas diastereomer **5** is thermodynamically more stable. Also, the formation of **5** from **4** probably occurs through cleavage of the heterocycle in **4** to give the starting material (i.e., **3**). This was confirmed by the fact that compound **3** was always present in the reaction mixtures in a small amount (3–6%). Chromenes **4** and **5** are rather unique. Chromenes may show bistability that can be influenced by external stimuli.[11] Furthermore, they constitute an important class of scaffolds that are found in many natural products. Compounds related to **4** and **5** have been obtained using Au^{III} catalysts.[12] On the other hand, 1,3-disubstituted 3*H*-benzo[*f*]chromenes have been prepared by coupling of the three components naphthol, alkyne, and aromatic or aliphatic aldehyde in the presence of iron(III) hydrogensulfate[13] or gallium(III) chloride.[14]

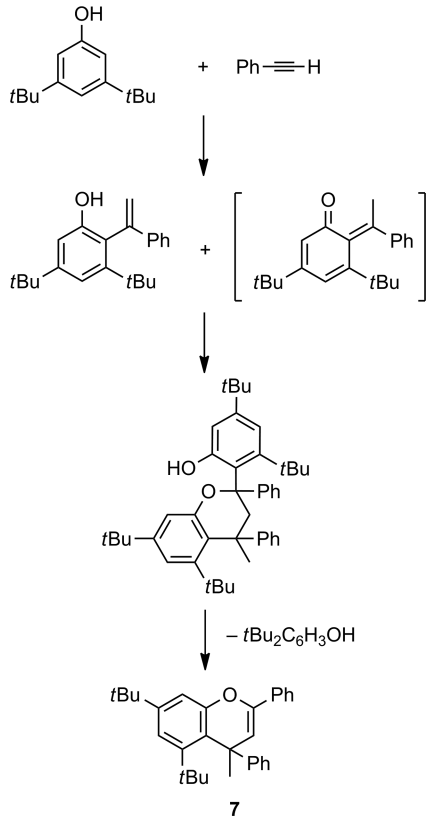
Table 2. Test of the catalytic activity of complexes **1** (Entries 11 and 12) and **2** (Entries 1–10) in the reactions of alkynes with aromatic compounds (NMR experiments, [D_6]benzene, 90 °C).

Entry	Alkyne	Arene	Product	Conv. [%] (time [h])
1			 **6**	99 (20)
2			mixture of products	96 (40)
3			 **7**	95 (46)
4			–	0 (24)
5			–	0 (24)
6			–	0 (24)
7			–	0 (24)
8			–	0 (24)
9			–	0 (24)
10			–	0 (24)
11			mixture of products	97 (58)
12			–	0 (25)

Thus, we have found that complexes **1** and **2** serve well as catalysts for the hydroarylation of phenylacetylene with 1-naphthol. In order to obtain more insight into the hydroarylation process, we tested complexes **1** and **2** as catalysts in the reactions of other aromatic compounds with phenylacetylene, 1-hexyne, and 2-hexyne. The results of these tests are summarized in Table 2.

We found that complex **2** catalyzes the reaction between phenylacetylene and 2-naphthol: the hydroarylation product (i.e., **6**) was obtained in high yield. Unlike product **3**, compound **6** is stable, and it did not undergo further conversion, even in the presence of the catalyst. The catalytic activity of compound **2** in the reaction between 2-naphthol and phenylacetylene is comparable with the activities of other catalysts reported for this reaction.[8,9,15]

According to NMR spectroscopy, phenylacetylene reacted with 4-*tert*-butylphenol to give, in the beginning, the hydroarylation product. Furthermore, similarly to the reaction of phenylacetylene with 1-naphthol, signals due to the nonequivalent protons of the CH_2 group appeared in the



Scheme 5. Reaction of 3,5-di-*tert*-butylphenol with phenylacetylene in the presence of complex **2**.

NMR spectrum. Unfortunately, we failed to isolate the individual products of this reaction. The reaction of 3,5-di-*tert*-butylphenol with phenylacetylene in the presence of complex **2** first gave the hydroarylation product and then resulted in the [4+2] cycloaddition product. However, in contrast to the reaction with 1-naphthol, the cycloaddition product eliminated 3,5-di-*tert*-butylphenol to give 4*H*-benzopyran **7** (Scheme 5), which was isolated by column chromatography and characterized by NMR spectroscopy.

The hydroarylation of phenylacetylene with phenol or benzoic acid in the presence of complex **2** did not proceed, probably due to the destruction of complex **2** by these reagents. Complex **2** did not catalyze the reactions between phenylacetylene and substrates that do not contain C–H bonds in a position *ortho* to the OH group (Table 1, Entries 5 and 6). In the presence of complex **2**, phenylacetylene was also unreactive towards anisole, 1-methoxynaphthol, and 4-bromotoluene. Furthermore, the internal alkyne 2-hexyne was inert towards 1-naphthol, whereas 1-hexyne reacted with 1-naphthol to give a mixture of products that could not be separated. Nevertheless, the NMR spectrum of the reaction mixture contained a set of signals that suggest the formation of the [4+2] cycloaddition product.

Conclusions

We have found that gallium complexes with the functionally labile (redox-active) bis-amido ligand dpp-bian serve well as catalysts for the hydroarylation of terminal alkynes, primarily phenylacetylene. The product of the reaction between phenylacetylene and 1-naphthol-2-(1-phenylvinyl)-naphthalen-1-ol (**3**), undergoes further catalytic transformation to give chiral chromenes. The hydroarylating reagents are limited to non-acidic aromatic derivatives and to substrates that do not have substituents in the position *ortho* to the OH group.

Experimental Section

General Remarks: Compounds **1** and **2** are sensitive to oxygen and moisture. Therefore, all manipulations involving their preparation or their use as catalysts were carried out under vacuum or under nitrogen, using glass ampoules, Schlenk flasks, and NMR tubes. Benzene (Vekos) and [D_6]benzene (Aldrich) were dried with sodium/benzophenone at ambient temperature and distilled under vacuum immediately before use into the reaction ampoule or into the NMR tube. The solvents light petroleum (OOO Novye Tekhnologii; boiling range 40–70 °C), ethyl acetate (Vekos), and *n*-hexane (Acros) were used as received. IR spectra were recorded with an FSM-1201 spectrometer. ^{1}H NMR spectra were recorded with Bruker DPX-200 and Bruker Avance III 400 spectrometers. 1-Naphthol (Khimreaktiv) was recrystallized from hexane and sublimed in vacuo. Phenylacetylene (Aldrich) was distilled at reduced pressure (79 °C/122 Torr). 1-Hexyne (Aldrich) and 2-hexyne (Aldrich) were used as received. Diimine dpp-bian,[16] and the complexes (dpp-bian)Ga–Ga(dpp-bian) (**1**)[17] and [dpp-bian-(PhC=CH)Ga–Ga(HC=CPh)dpp-bian] (**2**)[6a] were prepared according to literature procedures.

2-(1-Phenylvinyl)naphthalen-1-ol (3): Naphthalen-1-ol (0.432 g, 3 mmol), complex **2** (45 mg, 0.031 mmol), phenylacetylene (0.4 g, 3.9 mmol), and benzene (15 mL) were placed in a Schlenk flask (50 mL). The flask was filled with nitrogen (99.995%), and the mixture was heated at reflux at 45 °C. After 20 d, silica gel was added to the reaction mixture. The mixture was dried in vacuo, and purified by column chromatography (light petroleum/ethyl acetate, 9:1). Volatile products were evaporated from the extract at room temperature. Compound **3** (0.51 g, 70%) was isolated as a brown oily liquid. The ^{1}H NMR spectrum of isolated **3** corresponds to that reported in the literature.[9] ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.27 (d, J = 3.5 Hz, 1 H, CH arom), 7.80 (d, J = 3.1 Hz, 1 H, CH arom), 7.55–7.3 (m, 8 H, CH arom), 7.26 (s, 1 H, CH arom), 6.0 [d, J = 1.1 Hz, 1 H, HC=C(Ph)], 5.85 (s, 1 H, OH), 5.53 [d, J = 1.1 Hz, 1 H, HC=C(Ph)] ppm.

(2*R*,4*R*)/(2*S*,4*S*)-2-[4-Methyl-2,4-diphenyl-3,4-dihydro-2*H*-benzo[*h*]chromen-2-yl]naphthalen-1-ol (4): Phenylacetylene (0.8 g, 7.85 mmol) and compound **2** (85 mg, 6.0 mmol) were added to an ampoule containing naphthalen-1-ol (0.73 g, 5.06 mmol). Benzene (4 mL) was then added, and the ampule was sealed. The mixture was heated at 90 °C. After 16 h, silica gel was added to the resulting solution. The mixture was dried in vacuo, and then it was eluted with light petroleum/benzene (9:1). Volatile products were evaporated from the extract at ambient temperature. The residual solid was recrystallized from light petroleum/benzene (4:1) to give compound **4** (0.2 g, 16%) as pale yellow crystals. M.p. 129–131 °C. IR (Nujol): $\tilde{\nu}$ = 3429 (m), 3053 (w), 1962 (w), 1943 (w), 1813 (w), 1636 (w), 1600 (w), 1575 (m), 1510 (w), 1493 (m), 1460 (s), 1377 (s), 1342 (m), 1291 (m), 1261 (m), 1235 (w), 1218 (m), 1197 (m), 1159 (m), 1121 (m), 1079 (m), 1070 (m), 1061 (m), 1027 (m), 996 (w), 977 (m), 952 (m), 937 (w), 915 (w), 905 (w), 883 (m), 860 (w), 853 (w), 822 (w), 802 (s), 792 (m), 782 (w), 767 (m), 759 (m), 743 (s), 721 (s), 699 (s), 614 (w), 592 (w), 575 (m), 567 (m), 536 (w), 523 (w), 500 (w), 477 (w), 467 (w) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): δ = 8.50 (s, 1 H, OH), 8.49 (d, J = 6.0 Hz, 1 H, CH arom), 8.18 (d, J = 9.0 Hz, 1 H, CH arom), 7.86 (d, J = 7.8 Hz, 1 H, CH arom), 7.64 (m, 3 H, CH arom), 7.42 (m, 5 H, CH arom), 7.26 (m, 3 H, CH arom), 7.09 (m, 7 H, CH arom), 7.01 (d, J = 8.5 Hz, 1 H, CH arom), 3.43 (d, J = 14.5 Hz, 1 H, CH_2), 3.14 (d, J = 14.5 Hz, 1 H, CH_2), 1.51 (s, 3 H, CH_3) ppm. ^{13}C NMR (200 MHz, $CDCl_3$, 20 °C): δ = 30.0, 39.8, 49.3, 84.7, 118.7, 121.1, 121.6, 121.7, 122.5, 133.0, 124.2, 125.0, 125.5, 126.0, 126.1, 126.5, 126.5,126.6, 126.8, 126.9, 127.3, 127.5, 128.0, 128.4, 133.5, 133.9, 143.2, 146.5, 149.6, 150.6 ppm.

(2*S*,4*R*)/(2*R*,4*S*)-2-[4-Methyl-2,4-diphenyl-3,4-dihydro-2H-benzo[*h*]chromen-2-yl]naphthalen-1-ol (5): Compound **5** was prepared by a method similar to that described for **4**. After column chromatography, the product was crystallized from light petroleum/benzene (4:1) to give compound **5** (0.1 g, 8%) as colorless crystals. M.p. 200–202 °C. IR (Nujol): $\tilde{\nu}$ = 3470 (m), 3059 (w), 1962 (w), 1943 (w), 1813 (w), 1636 (w), 1600 (w), 1573 (m), 1509 (w), 1493 (m), 1460 (s), 1397 (w), 1377 (s), 1304 (w), 1283 (m), 1261 (m), 1235 (w), 1221 (m), 1200 (m), 1157 (m), 1121 (m), 1082 (m), 1063 (m), 1027 (w), 1007 (w), 971 (w), 956 (m), 935 (w), 909 (w), 879 (m), 866 (w), 807 (s), 786 (w), 762 (m), 748 (s), 722 (m), 700 (s), 677 (m), 617 (w), 604 (w), 576 (m), 558 (m), 526 (w), 513 (w), 493 (w), 468 (w) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): δ = 8.78 (s, 1 H, OH), 8.50 (d, J = 8.1 Hz, 1 H, CH arom), 8.31 (d, J = 5.2 Hz, 1 H, CH arom), 7.88 (d, J = 7.6 Hz, 1 H, CH arom), 7.73–6.75 (m, 19 H, CH arom), 3.46 (d, J = 8.0 Hz, 1 H, CH_2), 3.25 (d, J = 8.0 Hz, 1 H, CH_2), 1.82 (s, 3 H, CH_3) ppm. ^{13}C NMR (200 MHz, $CDCl_3$, 20 °C): δ = 32.5, 39.6, 48.2, 85.3, 119.1, 121.3, 121.6, 122.3, 122.8, 123.4, 124.4, 125.3, 125.4, 126.0, 126.4, 126.6, 126.6, 126.7, 126.9, 126.9, 127.1, 127.3, 127.8, 128.0, 133.6, 134.2, 140.6, 146.5, 148.7, 150.7 ppm.

2-(1-Phenylvinyl)naphthalen-1-ol (6): Under air, naphthalen-2-ol (0.14 g, 1.0 mmol) was placed in an NMR tube. Then, under vacuum, compound **2** (15 mg, 0.01 mmol), phenylacetylene (0.1 g, 1.0 mmol), and [D_6]benzene (0.5 mL) were added to this tube. The tube was sealed, and the mixture was heated at 90 °C. The formation of compound **6** was monitored by NMR spectroscopy. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.84–7.81 (m, 1 H, CH arom), 7.79–7.76 (m, 1 H, CH arom), 7.57–7.49 (m, 1 H, CH arom), 7.41–7.26 (m, 8 H, CH arom), 6.34 [d, J = 1.1 Hz, 1 H, HC=C(Ph)], 5.62 (s, 1 H, OH), 5.53 [d, J = 1.1 Hz, 1 H, HC=C(Ph)] ppm. The NMR spectrum listed above is identical with that reported in the literature.[9] After 20 h at 90 °C, the conversion of the reagents reached 99%.

5,7-(Di-*tert*-butyl)-4-methyl-2,4-diphenyl-4*H*-chromene (7): Under air, 3,5-di-*tert*-butylphenol (0.21 g, 1.0 mmol) was placed in an NMR tube. Then, under vacuum, compound **2** (15 mg, 0.01 mmol), phenylacetylene (0.1 g, 1.0 mmol) and [D_6]benzene (0.5 mL) were added to this tube. The tube was sealed, and the mixture was heated at 90 °C. The formation of compound **7** was monitored by NMR spectroscopy. According to the NMR spectroscopic data, the yield of compound **7** reached 95% after 46 h. Compound **7** (0.17 g, 80%) was isolated by column chromatography using light petroleum/benzene (9:1). ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): δ = 7.50 (d, J = 6.4 Hz, 2 H, CH arom), 7.30–7.15 (m, 8 H, CH arom), 6.96 (s, 1 H, CH arom), 6.90 (s, 1 H, CH arom), 5.95 (s, 1 H, CH), 1.78 (s, 3 H, CH_3), 1.29 (s, 9 H, CH_3), 0.82 (s, 9 H, CH_3) ppm.

Single-Crystal X-ray Structure Determination: The X-ray data for **4** and **5** were collected at 100 K with Agilent Xcalibur E and Bruker D8 QUEST diffractometers, respectively, with monochromated Mo-K_α radiation (λ = 0.71073 Å) using the ω-scan technique. The structures were solved by direct methods and were refined on F^2 using SHELXTL.[18] SCALE3 ABSPACK[19] (for **4**) and SADABS[20] (for **5**) were used to perform area-detector scaling and absorption corrections. All non-hydrogen atoms in **4** and **5** were found from Fourier syntheses of electron density, and were refined anisotropically. Hydrogen atoms were placed in calculated positions and were refined using the "riding model" with U_{iso}(H) = 1.2 U_{eq} of their parent atoms [or U_{iso}(H) = 1.5 U_{eq} for the hydrogen atoms in CH_3 groups]. The H atoms of the OH groups in **4** and **5** were located from Fourier synthesis and refined isotropically. A solvent molecule of benzene was found in the crystal of **4**. CCDC-1402892 (for **4**) and -1402893 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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