ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

Complexes of Donor–Acceptor Cyclopropanes with Tin, Titanium, and Gallium Chlorides — Mechanism Studies

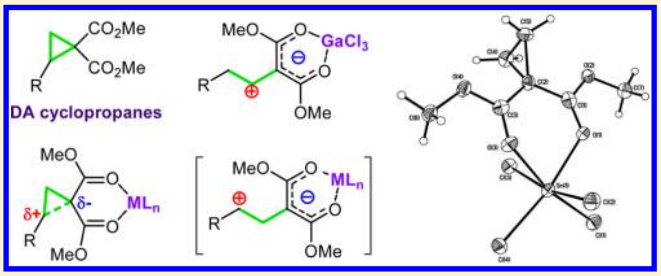
Roman A. Novikov,[†,‡] Dmitry O. Balakirev,[†] Vladimir P. Timofeev,[‡] and Yury V. Tomilov*[,†]

[†]N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation

[‡]V. A. Engelhardt Institute of Molecular Biology, Russian Academy of Sciences, 32 Vavilov st., 119991 Moscow, Russian Federation

Supporting Information

ABSTRACT: Hitherto unknown complexes of dimethyl cyclopropane-1,1-dicarboxylate with Lewis acids (Sn, Ti, and Ga chlorides) have been isolated and characterized. Their structures, which were previously assumed from theoretical considerations, have been confirmed, and the activating effect of Lewis acids on the cyclopropane ring has been shown experimentally. A single crystal of the complex with $SnCl_4$ has been obtained, and an X-ray diffraction study has been performed. Hitherto unknown complexes of donor–acceptor cyclopropanes with $GaCl_3$ belonging to a new type and having a 1,2-dipole (ylide) structure have been obtained and characterized. 1D and 2D NMR spectroscopy on ^{1}H, ^{13}C, ^{35}Cl, ^{71}Ga, and ^{119}Sn nuclei were used to study the structures of the complexes. Furthermore, DOSY diffusion NMR spectroscopy was used to determine the diffusion coefficient in solution and the molecular masses of the complexes. The data obtained enrich the picture of transformations of donor–acceptor cyclopropanes widely used in organic synthesis. The practical use of the gallium phenylcyclopropanedicarboxylate complex in a synthesis of polysubstituted cyclic structures in one synthetic stage has also been demonstrated.



INTRODUCTION

Donor–acceptor cyclopropanes (cyclopropanes with donor and acceptor substituents in vicinal positions) are now popular in contemporary organic synthesis as sources of 1,3-dipoles that are generated from them on treatment with Lewis acids.[1] The capability of donor–acceptor cyclopropanes to undergo [2 + 3]-, [3 + 3]-, and [3 + 4]-dipolar cycloaddition with various substrates[2] is now used to build five-, six-, and seven-membered heterocycles (Scheme 1); these reactions can be performed enantioselectively,[3] which makes them very attractive for applications in organic synthesis. More than 20 full syntheses of natural compounds have been carried out to date on the basis of donor–acceptor cyclopropanes.[4]

Aryl and sometimes alkyl, alkoxy, or amino groups are used as electron-donating substituents in cyclopropanes, whereas alkoxycarbonyls are used mainly as electron-withdrawing substituents. Tin(II) triflates and rare-earth-element triflates as well as chloroalanes are the most popular Lewis acids; gallium and indium compounds are less common.[1,2]

In view of the wide application of donor–acceptor cyclopropanes in organic synthesis, a study on the mechanisms of their opening and cycloaddition was carried out by computation methods, isotope labeling and changes in the chirality of optically active centers during the process.[1] Presumably, a complex of the Lewis acid with the donor–acceptor cyclopropane is first formed due to coordination to an electron-accepting group. As a result, polarization of a σ bond in the cyclopropane ring occurs, resulting in its opening with generation of a 1,3-dipolar intermediate, which then undergoes subsequent reactions.

However, complexes of Lewis acids with donor–acceptor cyclopropanes and their 1,3-zwitterionic intermediates are hypothetical structures, none of which was ever actually detected in a reaction mixture.[1]

RESULTS AND DISCUSSION

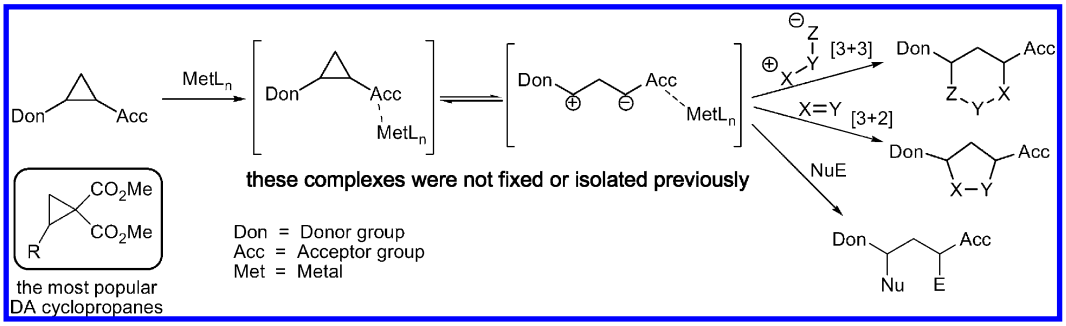
Complexes of Dimethyl Cyclopropane-1,1-dicarboxylate with $SnCl_4$, $TiCl_4$, and $GaCl_3$. Since no physicochemical data are available in the literature for complexes of donor–acceptor cyclopropanes with Lewis acids, we performed a series of experiments in order to detect and isolate intermediate complexes. The study was started from nonsubstituted dimethyl cyclopropane-1,1-dicarboxylate (**1**). This cyclopropane is among the least reactive species in the series of donor–acceptor cyclopropanes. It was therefore expected that its complexes with Lewis acids would be most stable for observation by physicochemical methods. Tin, titanium, and gallium chlorides that have a considerable Lewis acidity were chosen as the Lewis acids.

It was found that mixing of cyclopropanedicarboxylate **1** with the above metal chlorides in dichloromethane at room

Received: November 8, 2012

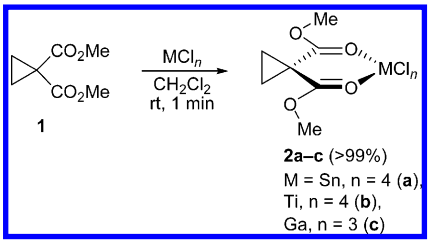
   dx.doi.org/10.1021/om301072v | Organometallics XXXX, XXX, XXX–XXX

Scheme 1. Donor–Acceptor Cyclopropanes in Modern Organic Synthesis



temperature gave the stable complexes **2a–c** (Scheme 2) in a few minutes. These complexes separated from the solutions due

Scheme 2. Reactions of Cyclopropane-1,1-dicarboxylate 1 with Sn, Ti, and Ga Chlorides



to low solubility in CH_2Cl_2. The Sn and Ti complexes **2a,b** precipitated as colorless crystals, whereas the complex with $GaCl_3$ (**2c**) was a colorless, heavy, thick oil resembling ionic liquids.

Complexes **2a–c** were found to be sufficiently stable compounds that were almost not hydrolyzed in the air. Retention of the cyclopropane ring was observed in all complexes **2a–c**. This ring was found to be incapable of opening, even in the presence of rather strong Lewis acids. The complexes obtained are insoluble in low-polarity organic solvents, such as alkanes, benzene, and chloroform, whereas in polar solvents (ether, ethyl acetate, acetone, methanol, etc.) they undergo ligand exchange, releasing the original molecule of cyclopropane **1**. Dichloromethane is among the acceptable solvents in which complexes **2a–c** are at least slightly soluble.

We succeeded in performing an X-ray diffraction analysis of tin complex **2a**. Recrystallization of this complex was found to be impossible due to its low solubility; thus, we were forced to use the crystals obtained during the synthesis upon fast mixing of solutions of cyclopropane **1** and tin tetrachloride in CH_2Cl_2. As a result, complex **2a** was obtained as large monoclinic crystals up to 10 mm long.

X-ray diffraction analysis of complex **2a** showed that the cyclopropane ring is retained, while the tin atom is coordinated to the sp^2 oxygen atoms of the two ester groups. The coordination sphere of tin is nearly octahedral. The crystal structure of **2a** involves the intermolecular contact Cl(1)···Cl(4) = 3.480 Å and hydrogen bond Cl(2)···H(4b) = 2.86 Å, which apparently strengthen the crystal lattice and govern the low solubility of the complex (Figures 1 and 2).

In comparison to the cyclopropane-1,1-dicarboxylic acid molecule (**3**),[5] all the bonds in the cyclopropane ring in complex **2a** are elongated (Table 1). The maximum elongation is observed in C–CH_2 bonds, just as was assumed theoretically for complexes of this type.[1]

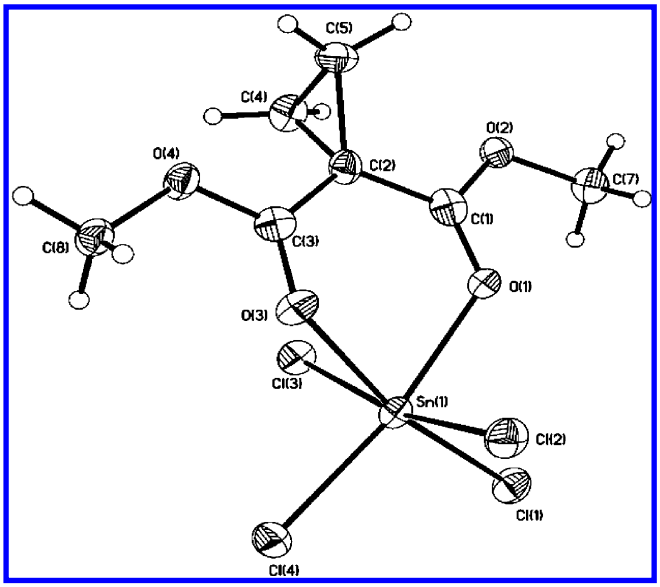


Figure 1. ORTEP diagram of **2a**, with thermal ellipsoids given at the 50% probability level.

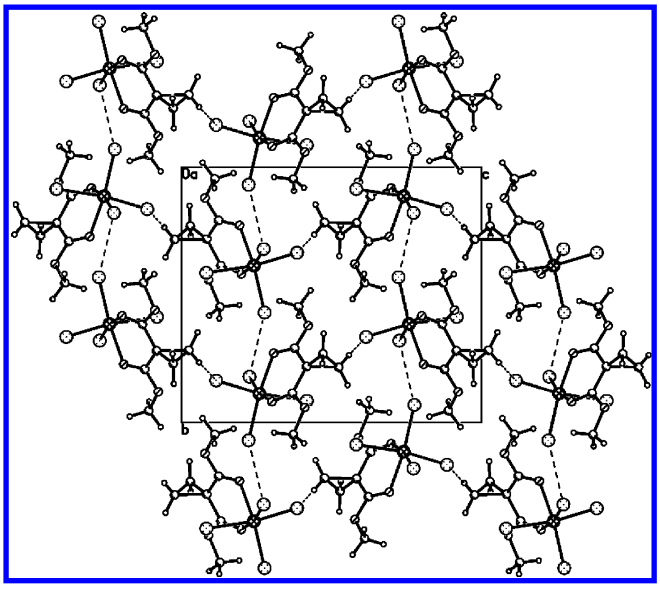


Figure 2. Unit cell of **2a** showing the intermolecular contact Cl(1)···Cl(4) = 3.480 Å and hydrogen bond Cl(2)···H(4b) = 2.86 Å.

The elongation of the C–CH_2 bond of the cyclopropane ring upon complex formation is due to the fact that, as a strong Lewis acid, the metal chloride withdraws electron density from the cyclopropane ring, which results in polarization of the σ

dx.doi.org/10.1021/om301072v | *Organometallics* XXXX, XXX, XXX–XXX

Table 1. Comparison of Bond Lengths in Molecule 2a and Cyclopropane-1,1-dicarboxylic Acid (3)[5] According to the Data of the X-ray Analysis

	bond length, Å		
bond	**2a**	**3**[a]	**3′**[a]
H_2C-CH_2	1.478	1.456	1.467
H_2C-C	1.545, 1.564	1.531, 1.535	1.531, 1.540
C−CO	1.469, 1.491	1.483, 1.485	1.483, 1.485
C=O	1.219, 1.245	1.214, 1.218	1.217, 1.218
Sn−O	2.165, 2.172		
Sn−Cl	2.349, 2.351, 2.367, 2.393		

[a]A cell contains two crystallographically independent molecules.

bond in the three-membered ring and hence causes its weakening and elongation (Figure 3). In this case, the C−

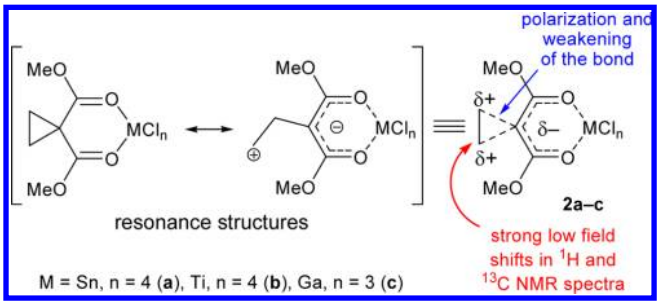


Figure 3. Structure of the complexes **2a−c**.

CH_2 bond undergoes the strongest elongation. As a result, the cyclopropane ring becomes involved in a conjugated system of a kind, which can be represented by limiting resonance structures, one with an intact cyclopropane ring and one with an open one (see Figure 3).

In reality, there is no σ-bond cleavage in the three-membered ring if there are no additional electron-donating substituents on the cyclopropane ring. However, owing to coordination with a Lewis acid, the C−C bond that has vicinal donor and acceptor substituents is polarized noticeably and cleaved by suitable substrates.[1]

Polarization of the σ bond in the cyclopropane ring and charge distribution in the molecules of complexes **2a−c** can be judged by the chemical shifts in the ^{1}H and ^{13}C NMR spectra in comparison with those of the original cyclopropanedicarboxylate **1**. Cumulated data on the chemical shifts are presented in Table 2.

As expected, the ^{1}H and ^{13}C NMR spectra are characterized by a downfield shift of all ester group signals, which normally takes place in the case of coordination of the metal atom to the oxygen atoms of these groups.[6] However, the strongest downfield shift is observed for signals of the CH_2 groups of the cyclopropane ring ($\Delta\delta$ 0.8−2.3 ppm in the ^{1}H NMR spectra and 12−19 ppm in the ^{13}C NMR spectra), which is due to a considerable increase in the partial positive charge[6] on the CH_2 groups of the three-membered ring due to involvement of the latter in conjugation with the ester groups and the metal atom (Figure 3). In this case, the ^{13}C NMR signal of the quaternary carbon atom in the cyclopropane ring remains almost unchanged.

As one can see from Table 2, the chemical shifts of complexes **2a−c**, in both the ^{1}H and ^{13}C NMR spectra, change synchronously in accordance with the nature of the metal atom in the complex. In fact, it is possible to build a qualitative dependence of the chemical shift (and hence the δ^+ on the CH_2 group) on the type the metal atom. The observed effect increases in the series Sn < Ti < Ga: i.e., of the Lewis acids studied, $GaCl_3$ should activate the cyclopropane ring most strongly, in agreement with the experimental observations.[1,7,8] A similar trend is observed for the signal width: it is the largest for gallium complexes (evidently due to dynamic processes). The liquid gallium complex **2c** in pure form shows much larger downfield shifts and line widths in the ^{1}H NMR spectrum in comparison with its solution, which may be explained by additional intermolecular interactions.

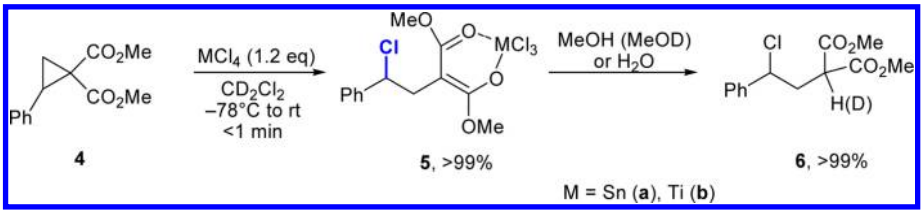
Table 2. Multinuclear NMR Spectra (CD_2Cl_2) of Cyclopropane 1 and Its Complexes 2a−c

		^{1}H NMR		^{13}C NMR				multinuclear NMR		
compd	data	CH_2	OCH_3	CH_2	C	OCH_3	CO	^{119}Sn	^{71}Ga	^{35}Cl
1	δ, ppm	**1.45**	**3.74**	**16.4**	**27.8**	**52.4**	**170.0**			
	$W_{1/2}$, Hz	0.8	0.8							
$SnCl_4$	δ, ppm							**−151.6**		**220**
	$W_{1/2}$, Hz							380		6900
$GaCl_3$[a]	δ, ppm								**228**	**220**
	$W_{1/2}$, Hz								12600	5600
2a (M = Sn)	δ, ppm	**2.24**	**4.02**	**28.5**	**28.5**	**58.3**	**178.6**	**−591**		
	$\Delta\delta$, ppm	+0.79	+0.28	+12.1	+0.7	+5.9	+8.6	−439		
	$W_{1/2}$, Hz	2.2	1.6					1200		
2b (M = Ti)	δ, ppm	**2.30**	**4.06**	**28.3**	**28.6**	**58.4**	**178.8**			
	$\Delta\delta$, ppm	+0.85	+0.32	+11.9	+0.8	+6.0	+8.8			
	$W_{1/2}$, Hz	12.8	1.9	br	br	br	br			
2c (M = Ga)	δ, ppm	**2.65**	**4.1**						**252**	
(CD_2Cl_2)	$\Delta\delta$, ppm	+1.2	+0.4						+24	
	$W_{1/2}$, Hz	75	60						2300	
2c (M = Ga, neat)	δ, ppm	**3.7**	**5.1**	**35.7**	**30.5**	**62.4**	**183.4**		**252**	**220**
	$\Delta\delta$, ppm	+2.3	+1.4	+19.3	+2.7	+10.0	+13.4		+24	0
	$W_{1/2}$, Hz	400	400	br	br	br	br		2300	6100

[a]Gallium chloride in solution exists as the dimer Ga_2Cl_6.

dx.doi.org/10.1021/om301072v | *Organometallics* XXXX, XXX, XXX−XXX

Scheme 3. Reactions of 2-Phenylcyclopropane-1,1-dicarboxylate 4 with $SnCl_4$ and $TiCl_4$



Multinuclear NMR spectra of complexes **2a**,**c** also show strong shifts of the signals of the metal atoms in comparison with the pure metal chlorides. In fact, the ^{119}Sn NMR spectra of complex **2a** show an upfield shift by 439 ppm, whereas the ^{71}Ga NMR spectra of complex **2c** show a downfield shift by 24 ppm. These shifts are in good agreement with the literature data concerning coordination of tin and gallium chlorides with oxygen-containing ligands.[9,10] On the other hand, no changes occur in the ^{35}Cl NMR spectra.

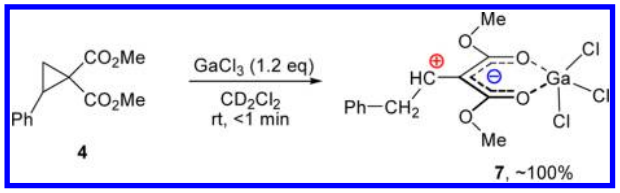
Thus, we isolated and characterized hitherto unknown complexes of dimethyl cyclopropane-1,1-dicarboxylate with Lewis acids, confirmed their structures previously assumed theoretically, and experimentally showed the activating effect of Lewis acids on the cyclopropane ring.

Complexes of 2-Phenylcyclopropane-1,1-dicarboxylate with $GaCl_3$. After the studies with dimethyl cyclopropane-1,1-dicarboxylate, we studied the complexation of 2-phenylcyclopropane-1,1-dicarboxylate **4** with the same Lewis acids (tin, titanium, and gallium chlorides). However, cyclopropane **4** was found to be much more reactive than its nonsubstituted analogue,[1] and its complexes with Lewis acids similar to **2a**–**c** were extremely unstable and very quickly underwent further transformations with cyclopropane ring opening.

In fact, the reaction of cyclopropanedicarboxylate **4** with $SnCl_4$ or $TiCl_4$ resulted in fast cyclopropane ring opening in the complex formed initially upon exposure to the chloride anion eliminated from the Lewis acid. The reaction gave enolates **5**, which on exposure to methanol or water were converted to substituted malonates **6** (Scheme 3).[7]

Gallium trichloride behaves differently. It exists as a dimer in dichloromethane solutions, and it is not a chloride anion donor in this form,[7] unlike titanium and tin chlorides. However, even in this case, we failed to detect a primary complex of $GaCl_3$ with cyclopropane **4** with retention of the three-membered ring. On the other hand, the complex formed with cyclopropane ring opening was found to be sufficiently stable. In fact, the reaction of phenylcyclopropanedicarboxylate **4** with an equimolar amount of gallium trichloride in dichloromethane (c < 0.15 mol/L) at room temperature occurred almost instantaneously in quantitative yield to give gallium complex **7** (Scheme 4) as an orange solution (it is fairly well soluble in CH_2Cl_2, unlike gallium complex **2c**). The complex obtained in this way decomposed almost completely in 6 h at 20 °C in solution.

Scheme 4. Reaction of 2-Phenylcyclopropane-1,1-dicarboxylate 4 with $GaCl_3$

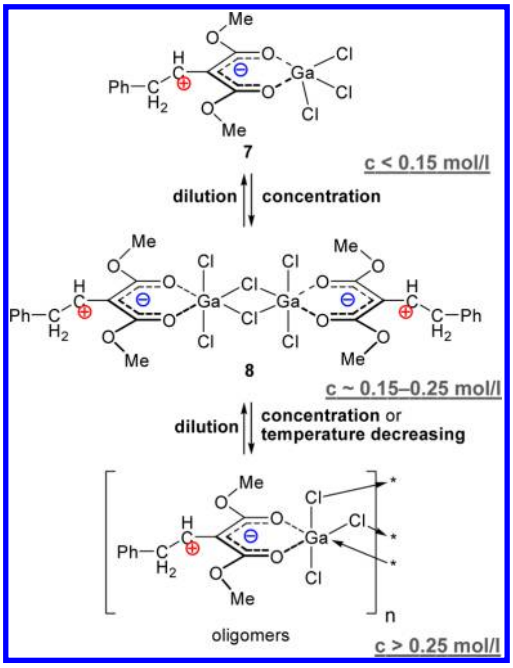


When the solution was cooled below 0 °C, the complex abruptly lost solubility and formed a deposit of a heavy thick oil. It is interesting to note that this deposit no longer dissolved in CH_2Cl_2 upon warming, which is apparently indicative of irreversible polymerization. Owing to this, it did not appear possible to work with gallium complex **7** at low temperatures. Therefore, all necessary experiments for detection of intermediates by NMR spectroscopy and studies of their subsequent transformations were carried out at room temperature under dry argon and with dehydrated solvents.

The processes occurring during the formation of gallium complexes with cyclopropanedicarboxylate **4** were studied by 1D and 2D NMR spectroscopy, including the DOSY technique,[12] allowing the diffusion of components in a solution to be analyzed. It was found that monomeric complex **7** with a pentacoordinate gallium atom mostly exists in CD_2Cl_2 solution at concentrations below 0.15 M, whereas dimeric complex **8**, which is formed owing to two additional Ga–Cl bridging bonds[11] by analogy with the Ga_2Cl_6 dimer (Scheme 5), predominates at concentrations in the range of 0.15–0.25 M. Oligomeric complexes start to predominate upon subsequent increase in the complex concentration in solution.

DOSY diffusion spectroscopy is a well-proven NMR approach that allows one to analyze various chemical systems and mixtures without preliminary separation.[12] Diffusion coefficients are related to the speed of molecular motions in solution and depend on the size of dissolved compounds. The

Scheme 5. Complexes of 4 with $GaCl_3$ at Various Concentrations



dx.doi.org/10.1021/om301072v | Organometallics XXXX, XXX, XXX–XXX

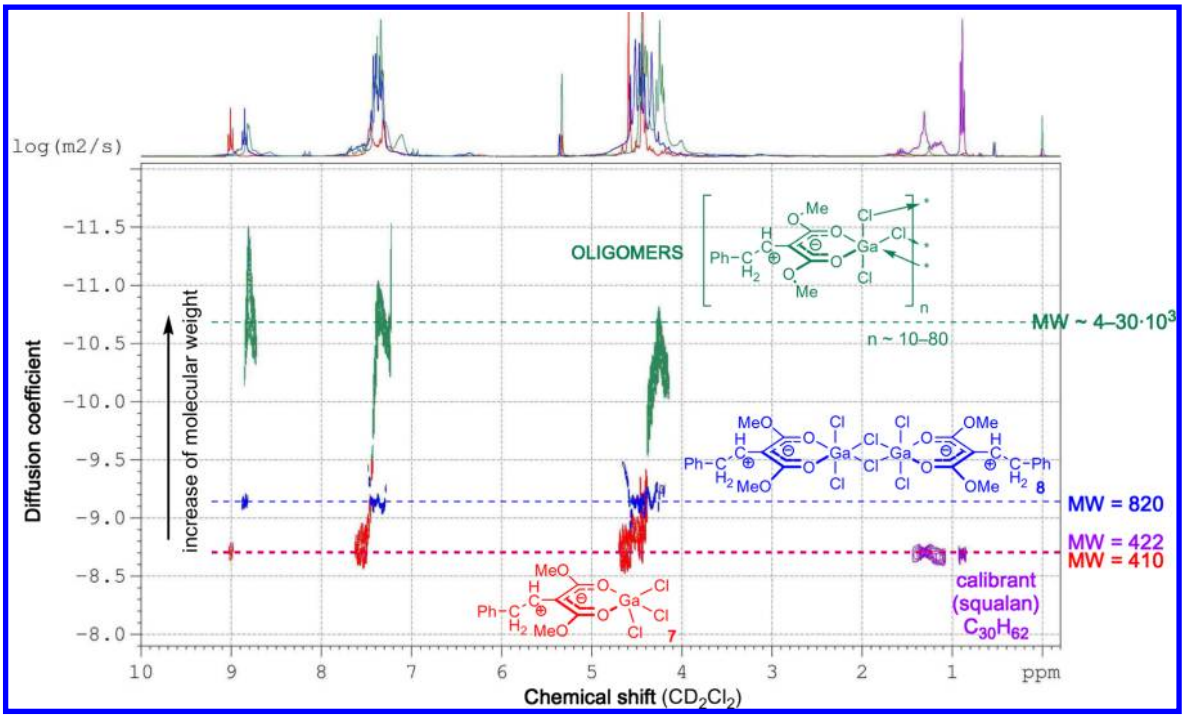


Figure 4. 2D ^{1}H DOSY NMR spectra processed by monoexponential fitting for cyclopropane **4** Ga complexes with calibrant (squalane). Conditions: CD_2Cl_2, 0.15–0.25 mol/L, 32 °C, LEDBPP pulse sequence, Δ = 100 ms, T_e = 5 ms. The figure shows several spectra recorded under the same conditions and superimposed on each other. Due to the small variation in the viscosities of the solutions arising from differences in the solute concentrations used, the diffusion coefficient was brought to the same value with respect to the calibrant, which is not quite correct. Each component in the spectra is shown by a horizontal dashed line marked with different colors: **7**, red; **8**, blue; oligomers. green; squalane, violet.

diffusion coefficient for a molecule represented by a rigid sphere is inversely proportional to the sixth power of hydrodynamic radius of the sphere according to the Stokes–Einstein equation. It may be considered in this case that in the first approximation (in the absence of interaction of solute molecules with the solvent), diffusion of molecules only depends on their molecular masses; hence, one can estimate the solute molecular masses rather precisely by measuring the diffusion coefficient.[12]

Since the diffusion coefficient strongly depends on the solution viscosity, all DOSY experiments were carried out under nearly the same conditions (solvent, concentration, temperature, and pulse sequence parameters). In order to identify the nature of gallium complexes formed, diffusion coefficients were measured by 2D ^{1}H DOSY NMR using the LEDBPP pulse sequence[13] in the presence of an internal calibrant (squalane,[14] $C_{30}H_{62}$).

The calibrant had to meet a number of stringent requirements. In particular, its molecular mass had to be close to that of the compound being studied (in this case, complex **7**), it had to be inert toward the other solution components, and the signals of the calibrant in the ^{1}H spectrum should not overlap the signals of the complexes of interest. Saturated hydrocarbons satisfy our requirements quite well; thus, we used squalane ($C_{30}H_{62}$, a hydrogenation product of natural squalene).[14] According to DOSY data, though the chemical nature of the calibrant and the complexes of interest differ, it has nearly the same diffusion coefficient as monomeric complex **6**, which unambiguously confirms that the composition of the latter is **3**:$GaCl_3$ = 1:1.

Using 2D ^{1}H DOSY NMR spectra, we were able to distinguish unambiguously monomeric (**7**), dimeric (**8**), and oligomeric complexes of donor–acceptor cyclopropanes and estimate the concentration ranges of their existence (Figure 4). One can also see that the monomeric and dimeric complexes have a narrow scatter of diffusion coefficients (as expected for individual stoichiometric compounds), whereas oligomers have a very wide scatter of diffusion coefficients and comprise a set of compounds with various molecular masses and degrees of oligomerization. The use of a special mathematical algorithm (SCORE[15]) for DOSY processing along with DOSYToolbox software[15] allowed us to obtain signals of separate components in the form of 1D or 2D images even for mixtures of complexes where the majority of signals totally overlap (see the Supporting Information).

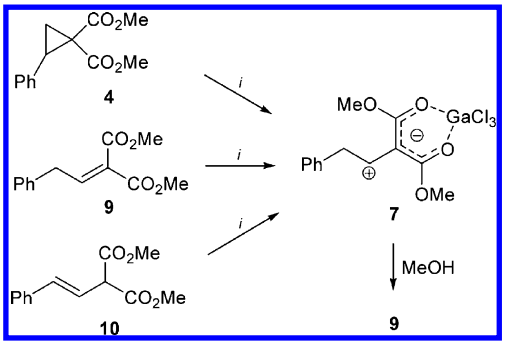
On the basis of the known molecular masses of the monomeric and dimeric gallium complexes and the calibrant, we determined the molecular masses of oligomeric complexes and the degree of oligimerization. The calculation was carried out under the assumption that the relationship between the logarithms of the diffusion coefficient and the molecular mass is nearly linear.[12,14] It was found that oligomeric complexes have molecular masses in the range of 4000–30000 D, which corresponds to ~10–80 molecules of the respective monomeric complex.

Thus, DOSY NMR spectroscopy proved to be quite promising for studying the composition and structure of gallium complexes of donor–acceptor cyclopropanes that were impossible to isolate in pure form, even at reduced temperatures.

It is interesting to note that complex **7** was formed not only from donor–acceptor cyclopropane **4**. Reactions of its isomers, viz., unsaturated compounds **9** and **10**, also gave this compound. Both reactions occurred under the same conditions as for cyclopropane **4** (Scheme 6). Decomposition of gallium complex **7** with methanol gave benzylidenemalonate **9**, which

dx.doi.org/10.1021/om301072v | *Organometallics* XXXX, XXX, XXX–XXX

Scheme 6. Different Formation Pathways of the Ga Complex 7[a]



[a]Reaction conditions: (*i*) $GaCl_3$, CD_2Cl_2, 25 °C, 1 min.

additionally confirms the structure of this complex. It should also be noted that dimethyl (2-phenylethyl)malonate, a saturated analogue of compounds **9** and **10**, almost does not undergo complexation with $GaCl_3$.

Thus, gallium complexes **7** and **8** have a 1,2-dipole structure (ylide structure) that was not mentioned before for assumed complexes of donor–acceptor cyclopropanes. The structure of complex **7** was unambiguously confirmed by 1D and 2D NMR spectroscopy on ^{1}H, ^{13}C, ^{35}Cl, ^{69}Ga, and ^{71}Ga nuclei with the use of the two-dimensional correlation techniques COSY, NOESY, HSQC, and HMBC. The ^{1}H NMR spectra show an isolated acyclic system $CHCH_2$ remaining from the cyclopropane ring, in which the CH moiety has a very strong downfield chemical shift (δ_H 9.00 ppm) that approaches those of benzyl cations,[16] indicating that a considerable positive charge is localized on it. However, the methine moiety (CH) in the structure of this complex is directly bound to the malonyl group, as suggested by the couplings in the 2D $^{1}H,^{13}C$-HMBC NMR spectrum that rule out the "classical" 1,3-dipole structure **I** (Figure 5). At the same time, complex **7** was found to rather

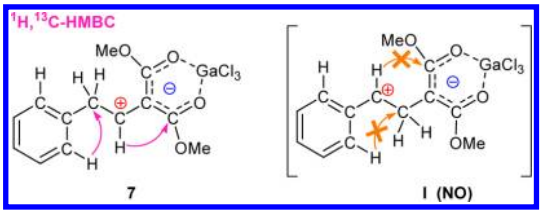


Figure 5. Structure of Ga-complex **7**.

stable. According to combined 1D, 2D, and DOSY NMR spectroscopic data, no dynamic processes occur in solution, except for the concentration-dependent monomer–dimer–oligomer transformations noted above. Furthermore, the NMR spectra do not manifest signals of the free ligand and gallium trichloride, as they are irreversibly bound to complex **7**.

Comparison of ^{1}H and ^{13}C NMR spectra of complex **7** and of the corresponding alkene **9** has shown that transition of the latter to complex **7** is accompanied by a strong downfield shift of the CH moiety ($\Delta\delta_H$ 1.88 and $\Delta\delta_C$ 38.3) in both the ^{1}H and ^{13}C NMR spectra. We should also note a downfield shift of the carbonyl and methoxy C atoms of the ester groups by about 10 ppm, which characterizes $GaCl_3$ coordination to these groups. However, conversely, two signals in the ^{13}C NMR spectrum of complex **7** shifted upfield. In fact, the signal of the ipso C atom of the phenyl substituent shifted by 3 ppm, whereas the signal of the quaternary C atom in the malonyl moiety shifted upfield by 13.0 ppm (Figure 6). Judging by the combination of the observed signals, the methylidenemalonate moiety in gallium complex **7** is, in fact, rather similar to the ylide structure proposed.

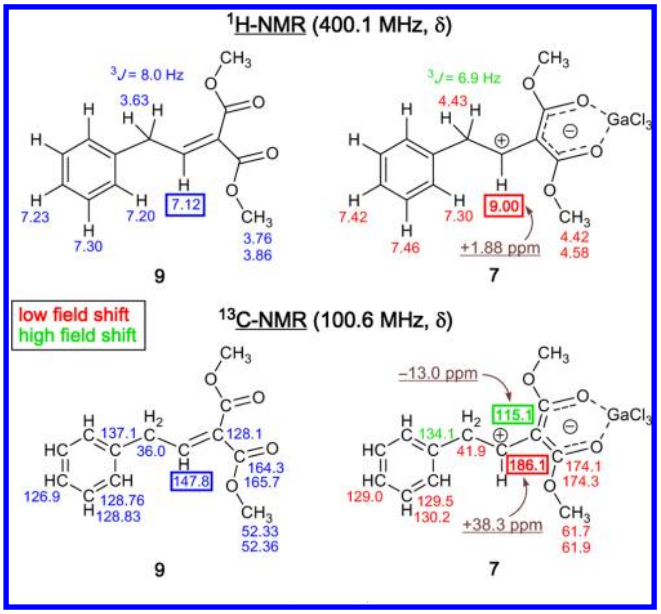


Figure 6. Chemical shifts of the signals in ^{1}H and ^{13}C NMR spectra of alkene **9** and complex **7**.

In the ^{71}Ga NMR spectra, transition from gallium trichloride to complex **7** results in a downfield shift of the signal by 54 ppm accompanied by a slight signal broadening, which is in good agreement with literature data and agrees with gallium coordination to two oxygen atoms (Figure 7).[9] After

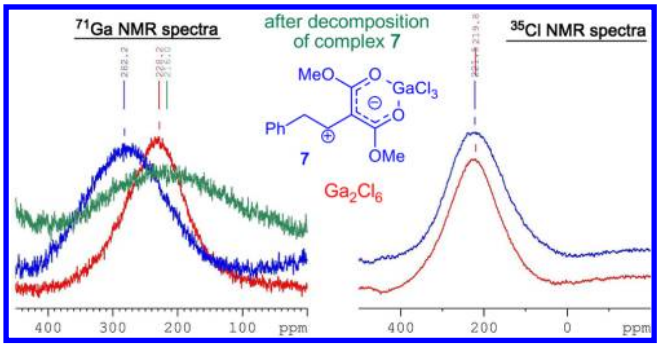


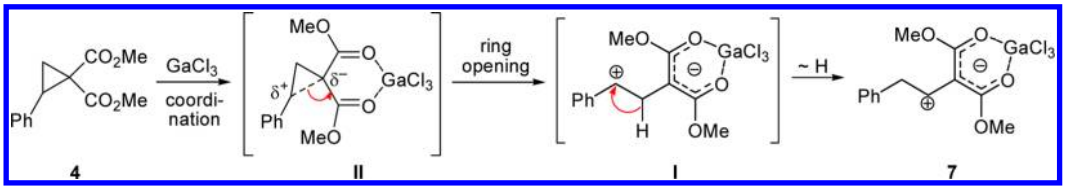
Figure 7. ^{71}Ga and ^{35}Cl NMR spectra of complex **7** compared with those of Ga_2Cl_6.

decomposition of complex **7**, the gallium signal shifts back upfield in the course of time and broadens noticeably. Conversely, no changes occur in the ^{35}Cl NMR spectra: all the chlorine atoms in complex **7** are still strongly bound to the gallium atoms and are not released to solution.

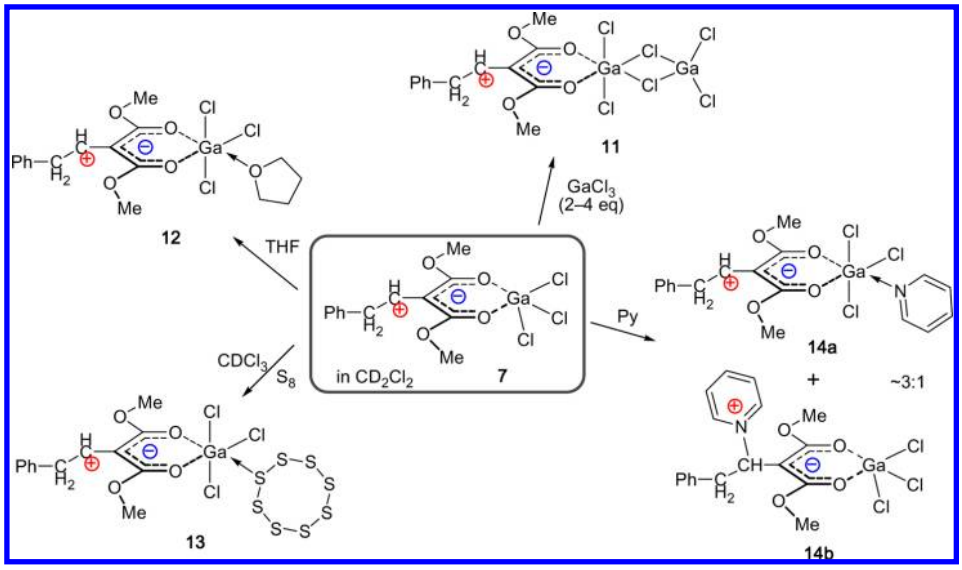
The ylide structure of complex **7** with localized charges allows certain experimental facts to be explained in addition. In fact, the organic ligand in complex **7** has a negative charge, which makes it a much stronger ligand than, for example, (2-phenylethyl)malonate. On the other hand, compounds with separated charges and with no steric substituents, as is the case in complex **7**, show high reactivity and undergo further

dx.doi.org/10.1021/om301072v | *Organometallics* XXXX, XXX, XXX–XXX

Scheme 7. Mechanism of the Formation of Ga Complex 7



Scheme 8. Addition of Different Nucleophiles to Ga Complex 7



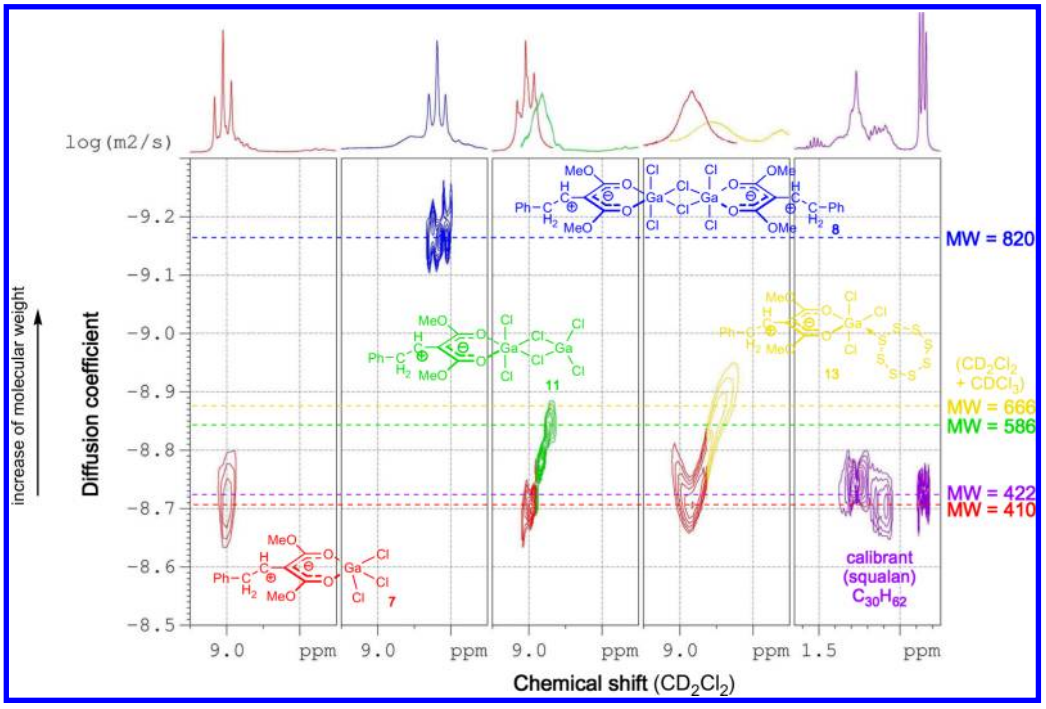


Figure 8. 2D ^{1}H DOSY NMR spectra processed by monoexponential fitting for Ga complexes **7**, **8**, **11**, and **13** with the calibrant (squalane). Conditions: CD_2Cl_2, 0.15−0.20 mol/L, 32 °C, LEDBPP pulse sequence, Δ = 100 ms, T_e = 5 ms (all spectra were recorded under the same conditions). The spectrum of complex **13** was recorded in a ~1/1 mixture of $CDCl_3$ and CD_2Cl_2. Due to small variations in the viscosities of the solutions, the diffusion coefficient was brought to the same value with respect to the calibrant, which is not quite correct. Each component in the spectra is shown by a horizontal dashed line marked with different colors: **7**, red; **8**, blue; **11**, green; **13**, yellow; squalane, violet. The 1D projections of the components were separated from the DOSY spectra of appropriate mixtures using the SCORE algorithm.

transformations as a 1,2-dipole (see Scheme 9). As already noted, the ^{71}Ga NMR spectra of complex **7** show a downfield shift of the signal by 54 ppm in comparison with Ga_2Cl_6, whereas a similar shift in related gallium complex **2c** is as small

dx.doi.org/10.1021/om301072v | *Organometallics* XXXX, XXX, XXX−XXX

as 24 ppm. This effect can be explained by the existence of additional electron density on the malonyl moiety in complex **7**, which, according to literature data,[9] additionally shifts the ^{71}Ga signal downfield.

According to the data obtained, the following mechanism of formation of gallium complex **7** can be assumed. First, the reaction of cyclopropanedicarboxylate **4** with $GaCl_3$ results in coordination of the latter to ester groups to give the primary complex **II**, which is analogous to gallium complex **2c**. The presence of a phenyl substituent activates the cyclopropane ring. As a result, this complex is quickly transformed to 1,3-dipolar complex **I**, which in turn also quickly undergoes migration of a hydride anion to give the detectable ylide complex **7** (Scheme 7). Unfortunately, attempts at low-temperature detection of complexes **II** and **I** failed due to the reasons considered above. However, their involvement in various transformations seems rather reasonable.

As noted above, the gallium atom in complex **7** is pentacoordinate and can add more ligands:[11] in particular, to give dimeric complex **8**. It was found that not only another molecule of complex **7** but also gallium trichloride itself can act as a nucleophile. In fact, the reaction of cyclopropanedicarboxylate **4** with excess $GaCl_3$ results in addition of the latter as a ligand to give complex **11** with two new Ga−Cl bridging bonds (Scheme 8). However, the resulting binuclear complex was found to be even less stable than complex **8**; even with excess $GaCl_3$, complex **11** is in equilibrium with mononuclear complex **7** and its content in solution does not exceed 50% according to NMR data. What is more, complex **11** was completely decomposed in 30 min, whereas complex **7** existed for another several hours.

The composition of complex **11** was confirmed by ^{1}H DOSY NMR spectroscopy. Though its signals overlapped considerably with the signals of original complex **7**, it is clear that it fits the ratio ligand:$GaCl_3$ = 1:2 according to the molecular mass. Furthermore, its molecular mass is larger than that of mononuclear complex **7** and smaller than that of dimeric complex **8** (Figure 8). Considering that this complex (DOSY signal) appears only if excess $GaCl_3$ is present and that, according to ^{1}H and ^{13}C NMR data, the frame and structure of the organic ligand in complex **11** are completely the same as those in complex **7**, it becomes obvious that it is a product of addition of a second $GaCl_3$ molecule to complex **7**.

Complex **7** also readily reacted with other nucleophilic ligands, such as tetrahydrofuran, elementary sulfur, and pyridine. In all the cases, the ligand was coordinated to the gallium atom to create a six-coordinate environment of the latter and to give complexes **12**−**14**, respectively (Scheme 8).

The structures of complexes **12**−**14** were also confirmed by a combination of 1D and 2D ^{1}H and ^{13}C NMR techniques, as well as by DOSY diffusion spectroscopy. In fact, 2D ^{1}H DOSY NMR spectra recorded using squalane as the internal calibrant showed unambiguously that the molecular masses of complexes **12**−**14** were higher than that of the original complex but lower than that of the dimeric complex **8**. The structures of the organic ligands in the complexes remain unchanged, as indicated by only small changes in the chemical shifts. Hydrolysis of complexes **11**−**14** with methanol gave the same product, viz., benzylidenemalonate **9**, which also confirms the structures of the complexes.

The insignificance of changes in the chemical shifts of the corresponding signals in the ^{1}H and ^{13}C NMR spectra of complexes **11**−**14** in comparison with those for complex **7** allows us to state that they all retain their ylide structure. It is interesting to note that, of all the gallium complexes observed, complex **7** has the largest downfield shift of the CH moiety carrying a positive charge. This agrees with the fact that the stronger the positive charge localized on the CH moiety, the larger its downfield shift in the spectra. Since, in comparison with complex **7**, each of the complexes **8** and **11**−**14** contains additional ligands that donate electron density to the organic moiety of the complex, the positive charge on the CH moiety decreases accordingly, thus causing a reverse upfield shift of the signal (Table 3).

Table 3. Chemical Shifts for the CH Fragment in NMR Spectra of Ga Complexes

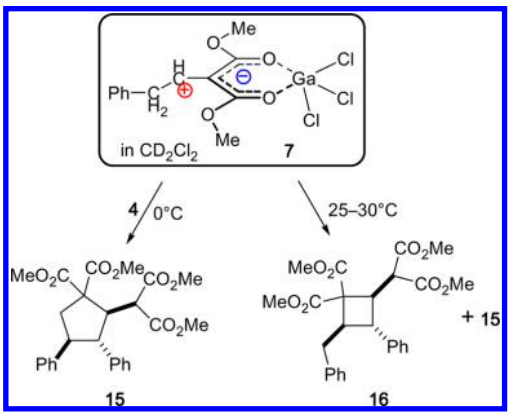
	^{1}H NMR (CH)		
complex	δ, ppm (t)	^3J, Hz	t_{decomp}, h (estimated)
9·$GaCl_3$ (**7**)	9.00	6.9	6
[**9**·$GaCl_3$]$_2$ (**8**)	8.84	6.8	3−4
[**9**·$GaCl_3$]$_n$	8.80 (br m)		<3
9·Ga_2Cl_6 (**11**)	8.97 (br)	∼6.9	0.5
9·$GaCl_3$·THF (**12**)	8.52 (br)	∼7.1	0.1
9·$GaCl_3$·S_8 (**13**)	8.88	6.8	3
9·$GaCl_3$·Pyr (**14a**)	8.69	6.7	0.3
9·Pyr·$GaCl_3$ (**14b**)	5.93	7.6	0.2

As a result, we succeeded in synthesizing hitherto unknown complexes of a new type with a 1,2-dipole structure (ylide structure) formed by donor−acceptor cyclopropanes and Lewis acids and thoroughly studied their structure and reactivity. These data certainly enrich the understanding of the mechanism of reactions involving donor−acceptor cyclopropanes, at least those that occur in the presence of gallium trichloride, which were previously explained via the "classical" 1,3-dipole.[1,7,8]

For example, we recently implemented a dimerization of donor−acceptor cyclopropanes to polysubstituted cyclopentanes **15** in the presence of catalytic amounts of gallium trichloride.[7] At that time, the mechanism of the reaction was unknown. Taking the new data into consideration, it becomes clear that this process occurs via ylide complex **7**. We have also shown that heating of gallium complex **7** partially gives cyclobutane structure **16**, in which one molecule of complex **7** directly participates as a 1,2-dipole (Scheme 9).

Thus, the use of complex **7** enables a one-stage synthesis of complex polysubstituted cyclic structures from readily available

Scheme 9. Possible Transformations of Ga Complex 7



dx.doi.org/10.1021/om301072v | Organometallics XXXX, XXX, XXX−XXX

donor−acceptor cyclopropanes. Moreover, the use of additional ligands will expand its applicability in organic synthesis.

3. CONCLUSION

We have isolated and characterized for the first time complexes of dimethyl cyclopropane-1,1-dicarboxylate with Lewis acids, confirmed their structures that were previously assumed theoretically, and experimentally showed the activating effect of Lewis acids on the cyclopropane ring. A single crystal of the complex **1**·$SnCl_4$ has been grown, and an X-ray diffraction study has been carried out. We have synthesized hitherto unknown complexes of a new type with 1,2-dipole structure (ylide structure) formed by donor−acceptor cyclopropanes and gallium trichloride and thoroughly studied their structures and reactivities. The data obtained provide a new understanding of the mechanisms of reactions of donor−acceptor cyclopropanes on treatment with Lewis acids, in particular $GaCl_3$. A practical use of the gallium phenylcyclopropanedicarboxylate complex in organic synthesis to obtain polysubstituted cyclic structures in one synthetic stage has been demonstrated as an example.

4. EXPERIMENTAL SECTION

General Experimental Details. All reagents and solvents used were commercial grade chemicals (>99.5%) without additional purification. All operations with metal chlorides and their complexes were carried out under a dry argon atmosphere. TLC analysis was performed on Silufol chromatographic plates. For preparative chromatography, silica gel 60 (0.040−0.063 mm) was used. ^{1}H and ^{13}C NMR spectra were recorded on 400 MHz (400.1 and 100.6 MHz, respectively) and 300 MHz (300.1 and 75.5 MHz, respectively) spectrometers in CD_2Cl_2 and $CDCl_3$ containing 0.05% Me_4Si as the internal standard. Assignments of ^{1}H and ^{13}C signals were made with the aid of 2D COSY, TOCSY, NOESY, HSQC, and HMBC spectra where necessary. Some chemical shifts in ^{1}H and ^{13}C NMR spectra, due to the impossibility of direct detection, were taken from the corresponding two-dimensional spectra. ^{35}Cl, ^{71}Ga, and ^{119}Sn NMR spectra were recorded on a 400 MHz spectrometer (39.2, 122.0, and 149.2 MHz, respectively) in CD_2Cl_2; standards were NaCl and $Ga(NO_3)_3$ solutions in water and Me_4Sn with the addition of C_6D_6, respectively. Monitoring of the reactions in NMR tubes was carried out in CD_2Cl_2 solution containing 0.05% Me_4Si as the internal standard. Measurements of the diffusion coefficients were performed using 2D ^{1}H DOSY NMR spectroscopy (diffusion ordered spectroscopy)[12] in CD_2Cl_2 and $CDCl_3$ solutions on a 300 MHz spectrometer (300.1 MHz for ^{1}H). A BPP-LED pulse sequence[13] was used with Δ = 100 ms and T_e = 5 ms. The DOSY spectra were processed by monoexponential fitting and the SCORE algorithm using Bruker TopSpin and DOSYToolbox software.[15] Squalane ($C_{30}H_{62}$, mol wt 422) was used as the internal calibrant of the molecular weight in DOSY spectra in ∼1:1 molar ratio to the studied complexes. IR spectra were obtained on a FT-IR spectrometer in $CHCl_3$ solution (1%). Mass spectra were recorded using electron impact ionization (EI, 70 eV, direct inlet probe). High-resolution mass spectra were obtained using simultaneous electospray (ESI). The elemental compositions were determined on a Perkin-Elmer Series II 2400 CHN analyzer. X-ray crystallographic data for complex **2a** were obtained on a "Bruker 1K SMART CCD" diffractometer (Mo Kα radiation) at 100 K. The starting arrays of measured intensities were processed using the APEX2 program.[17] The structure was solved by direct methods and refined by full-matrix least squares in the anisotropic approximation for non-hydrogen atoms on F^2_{hkl}. Hydrogen atoms were placed in geometrically calculated positions.

Complex $(CH_2)_2C(CO_2Me)_2$·$SnCl_4$ (2a). *Method A.* A solution of $SnCl_4$ (329 mg, 1.26 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise over 5 min under an argon atmosphere to a solution of cyclopropane **1** (200 mg, 1.26 mmol) in dry CH_2Cl_2 (2.5 mL), and the mixture was stirred at room temperature for 10 min. Then the reaction mixture was concentrated under vacuum to 0.5 mL volume. The precipitate that formed was filtered on a Schott filter and was dried under vacuum to afford complex **2a** (515 mg, 97%) as a colorless powder: mp 138−140 °C dec.

Method B (Growth of Crystals for X-ray Analysis). A solution of $SnCl_4$ (329 mg, 1.26 mmol) in CH_2Cl_2 (0.5 mL) was added in one portion under an argon atmosphere at room temperature without stirring to a solution of cyclopropane **1** (200 mg, 1.26 mmol) in dry CH_2Cl_2 (2.5 mL). After 1 min complex **2a** began to precipitate from the solution as colorless crystals. The reaction mixture was kept at room temperature for 10 min without stirring until the end of the precipitation of crystals. The precipitate that formed was filtered on a Schott filter, washed with CH_2Cl_2 (2 × 2 mL), and dried under vacuum. Complex **2a** (450 mg, 85%) was obtained as large colorless monoclinic crystals.

Anal. Calcd for $C_7H_{10}Cl_4O_4Sn$: C, 20.08; H, 2.41. Found: C, 20.01; H, 2.27. IR (KBr): ν 3116, 3029, 2958, 2853, 1728 br (C═O), 1639, 1561, 1442, 1357, 1340, 1222, 1199, 1139 cm^{-1}. ^{1}H NMR (400.1 MHz, CD_2Cl_2): δ 2.24 (s, 4H, $2CH_2$, $W_{1/2}$ = 2.2 Hz), 4.02 (s, 6H, $2OCH_3$, $W_{1/2}$ = 1.6 Hz). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 28.5 (C and $2CH_2$), 58.3 ($2OCH_3$), 178.6 (2COO). ^{119}Sn NMR (149.2 MHz, CD_2Cl_2): δ −591 (s, $W_{1/2}$ = 1200 Hz). MS (m/z, %): 260 (8, $^{120}Sn^{35}Cl_4^+$), 225 (54, $^{120}Sn^{35}Cl_3^+$), 190 (2, $^{120}Sn^{35}Cl_2^+$), 158 (8, $C_7H_{10}O_4^+$), 155 (8, $^{120}Sn^{35}Cl^+$), 127 (100, $C_7H_{10}O_4$ − OMe^+), 120 (9, $^{120}Sn^+$), 100 (28, $C_7H_{10}O_4$ − CO_2Me + H^+), 98 (30), 95 (33), 68 (33), 59 (80), 39 (39).

Selected geometric parameters for **2a** (from X-ray analysis data): monoclinic crystals, a = 7.3546(11) Å, b = 12.4212(19) Å, c = 14.965(2) Å, V = 1330.5(3) Å^3, d_{calc} = 2.090 g cm^{-3}, space group $P2_1/c$. Bond lengths (Å): Sn(1)−O(1), 2.165; Sn(1)−O(3), 2.172; Sn(1)−Cl(1), 2.349; Sn(1)−Cl(4), 2.351; Sn(1)−Cl(2), 2.367; Sn(1)−Cl(3), 2.393; O(1)−C(1), 1.219; O(3)−C(3), 1.245; C(1)−C(2), 1.491; C(2)−C(3), 1.469; C(2)−C(5), 1.545; C(2)−C(4), 1.564; C(4)−C(5), 1.478. Angles (deg): O(1)−Sn(1)−O(3), 78.5; O(1)−Sn(1)−Cl(1), 88.6; O(3)−Sn(1)−Cl(1), 166.8; Cl(1)−Sn(1)−Cl(4), 101.5; Cl(1)−Sn(1)−Cl(2), 95.7. Intermolecular contacts (Å): Cl(1)···Cl(4), 3.480; Cl(2)···H(4b), 2.86.

Complex $(CH_2)_2C(CO_2Me)_2$·$TiCl_4$ (2b). A solution of $TiCl_4$ (239 mg, 1.26 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise over 1 min under an argon atmosphere to a solution of cyclopropane **1** (200 mg, 1.26 mmol) in dry CH_2Cl_2 (2.5 mL), and the mixture was stirred at a room temperature for 15 min. Then the reaction mixture was concentrated under vacuum to 0.5 mL volume. The precipitate formed was filtered on a Schott filter and was dried under vacuum to afford complex **2b** (403 mg, 92%) as light yellow crystals: mp 100−102 °C dec.

Anal. Calcd for $C_7H_{10}Cl_4O_4Ti$: C, 24.17; H, 2.90. Found: C, 23.51; H, 3.07. IR (KBr): ν 2959, 1737 br (C═O), 1629, 1439, 1321, 1308, 1246, 1219, 1200, 1150 cm^{-1}. ^{1}H NMR (400.1 MHz, CD_2Cl_2): δ 2.30 (s, 4H, $2CH_2$, $W_{1/2}$ = 12.8 Hz), 4.06 (s, 6H, $2OCH_3$, $W_{1/2}$ = 1.9 Hz). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 28.3 (br.s, $2CH_2$), 28.6 (br s, C), 58.4 (br s, $2OCH_3$), 178.8 (br.s, 2COO). MS (m/z, %): 190 (1, $^{48}Ti^{35}Cl_3^{37}Cl^+$), 158 (1, $C_7H_{10}O_4^+$), 155 (2, $^{48}Ti^{35}Cl_2^{37}Cl^+$), 127 (12, $C_7H_{10}O_4$ − OMe^+), 118 (1, $^{48}Ti^{35}Cl_2^+$), 100 (15, $C_7H_{10}O_4$ − CO_2Me + H^+), 69 (13), 59 (23), 36 (100).

Complex $(CH_2)_2C(CO_2Me)_2$·$GaCl_3$ (2c). Solid $GaCl_3$ (222 mg, 1.26 mmol) was added in one portion under an argon atmosphere with stirring to a solution of cyclopropane **1** (200 mg, 1.26 mmol) in dry CH_2Cl_2 (2.5 mL), and the mixture was kept at room temperature for 15 min without stirring. Complex **2c** drops out as a thick, heavy, oily precipitate, which was separated by decantation. Complex **2c** obtained by this method (420 mg, 99%) is nearly pure by NMR data but contains traces of CH_2Cl_2 and is a colorless, thick, heavy oil. Complex **2c** can be additionally dried under vacuum to give a white semisolid powder: mp 54−59 °C.

Anal. Calcd for $C_7H_{10}Cl_3GaO_4$: C, 25.16; H, 3.02. Found: C, 24.59; H, 3.07. IR (KBr): ν 3009, 2957, 2855, 1739 br (C═O), 1615, 1444, 1364, 1229, 1197, 1132 cm^{-1}. ^{1}H NMR (400.1 MHz, CD_2Cl_2): δ 2.65 (s, 4H, $2CH_2$, $W_{1/2}$ = 75 Hz), 4.1 (s, 6H, $2OCH_3$, $W_{1/2}$ = 60 Hz). ^{71}Ga

dx.doi.org/10.1021/om301072v | Organometallics XXXX, XXX, XXX−XXX

NMR (122.0 MHz, CD_2Cl_2): δ 252 (s, $W_{1/2}$ = 2300 Hz). ^{1}H NMR (400.1 MHz, neat): δ 3.7 (s, 4H, $2CH_2$, $W_{1/2}$ = 400 Hz), 5.1 (s, 6H, $2OCH_3$, $W_{1/2}$ = 400 Hz). ^{13}C NMR (100.6 MHz, neat): δ 30.5 (br.s, C), 35.7 (br.s, $2CH_2$), 62.4 (br.s, $2OCH_3$), 183.4 (br.s, 2COO). ^{71}Ga NMR (122.0 MHz, neat): δ 252 (s, $W_{1/2}$ = 2300 Hz). MS (m/z, %): 176 (17, $^{69}Ga^{35}Cl_2{}^{37}Cl^+$ and $^{71}Ga^{35}Cl_3{}^+$), 158 (3, $C_7H_{10}O_4{}^+$), 141 (76, $^{69}Ga^{35}Cl^{37}Cl^+$ and $^{71}Ga^{35}Cl_2{}^+$), 127 (41, $C_7H_{10}O_4$ − OMe^+), 106 (11, $^{69}Ga^{37}Cl^+$ and $^{71}Ga^{35}Cl^+$), 100 (21, $C_7H_{10}O_4$ − CO_2Me + H^+), 59 (50), 59 (51), 50 (100), 44 (79), 36 (55), 29 (48).

Dimethyl 2-(2-Chloro-2-phenylethyl)malonate (6) and Its 2-Deuterium Analogue. *Method A.* A solution of $SnCl_4$ (221 mg, 0.85 mmol) in dry CH_2Cl_2 (0.5 mL) was added under an argon atmosphere to a solution of cyclopropane **4** (200 mg, 0.85 mmol) in CH_2Cl_2 (5 mL), and the mixture was stirred at room temperature for 5 min to give a pure solution of the Sn-enolate **5**. Then an aqueous solution of HCl (5%) (or DCl (5%) in D_2O) was added until pH 3 was achieved and the reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed in vacuo to afford compound **6** (230 mg, 99%) as a colorless oil. ^{1}H and ^{13}C NMR spectra correspond to literature data.[18]

Method B. A solution of $TiCl_4$ (161 mg, 0.85 mmol) in dry CH_2Cl_2 (0.5 mL) was added under an argon atmosphere to a solution of cyclopropane **4** (200 mg, 0.85 mmol) in CH_2Cl_2 (5 mL), and the mixture was stirred at room temperature for 5 min to give a pure solution of the Ti-enolate **5**. Then an aqueous solution of HCl (5%) (or DCl (5%) in D_2O) was added until pH 3 was achieved and the reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed in vacuo to afford compound **6** (227 mg, 98%) as a colorless oil. ^{1}H and ^{13}C NMR spectra correspond to literature data.[18]

Complex $PhCH_2CH^+C^-(CO_2Me)_2{\cdot}GaCl_3$ (7). *Method A (Preparative Synthesis).* Solid $GaCl_3$ (165 mg, 0.94 mmol, 1.1 equiv) was added in one portion under an argon atmosphere at 5 °C with stirring to a solution of cyclopropane **4** (200 mg, 0.85 mmol) in CH_2Cl_2 (6 mL), and the mixture was stirred at the same temperature for 1 min. Complex **7** (~99%) was obtained as a solution in CH_2Cl_2, which is nearly pure by NMR data. The prepared solution of complex **7** was immediately used for further syntheses.

Method B (NMR Studies). The reaction was carried out in NMR tube under an argon atmosphere. The solution was purged with an argon flow before the reaction was started. Solid $GaCl_3$ (14 mg, 0.077 mmol, 1.2 equiv) was added in one portion at 32 °C to a solution of cyclopropane **4** (15 mg, 0.064 mmol) in dry CD_2Cl_2 (0.5 mL), and the mixture was shaken for 0.5 min. The nearly pure complex **7** (~99%) was obtained as a solution in CD_2Cl_2. The necessary NMR experiments were made immediately after synthesis of gallium complex. For recording of 2D ^{1}H DOSY NMR spectra with calibrant for diffusion coefficient measurements squalane $C_{30}H_{62}$ (~15 mg, 0.036 mmol) was added to the reaction mixture. Complex **7** significantly decomposes in solution after several hours at room temperature. When the solution was cooled, **7** rapidly oligomerized and decomposed; attempts to isolate this complex failed.

^{1}H NMR (400.1 MHz, CD_2Cl_2): δ 4.42 and 4.58 (both s, 2 × 3H, $2OCH_3$), 4.43 (d, 2H, CH_2, ^3J = 6.9 Hz), 7.30 (m, 2H, 2 *o*-CH), 7.42 (m, 1H, *p*-CH), 7.46 (m, 2H, 2 *m*-CH), 9.00 (t, 1H, CH^+, ^3J = 6.9 Hz). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 41.9 (CH_2), 61.7 and 61.9 ($2OCH_3$), 115.1 (C^-), 129.0 (*p*-CH), 129.5 and 130.2 (2 *o*-CH and 2 *m*-CH), 134.1 (*i*-C), 174.1 and 174.3 (2COO), 186.1 (CH^+). ^{35}Cl NMR (39.2 MHz, CD_2Cl_2): δ −221 (s, $W_{1/2}$ = 6500 Hz). ^{71}Ga NMR (122.0 MHz, CD_2Cl_2): δ 282 (s, $W_{1/2}$ = 2300 Hz).

Method C. The reaction was carried out in an NMR tube under an argon atmosphere. The solution was purged with argon flow before the reaction was started. Solid $GaCl_3$ (14 mg, 0.077 mmol, 1.2 equiv) was added in one portion at 32 °C to a solution of benzylidenemalonate **9** (15 mg, 0.064 mmol) in dry CD_2Cl_2 (0.5 mL), and the mixture was shaken for 0.5 min. Complex **7** (~99%) was obtained as a solution in CH_2Cl_2, which was nearly pure by NMR data.

Method D. The reaction was carried out in an NMR tube under an argon atmosphere. The solution was purged with an argon flow before the reaction was started. Solid $GaCl_3$ (14 mg, 0.077 mmol, 1.2 equiv) was added in one portion at 32 °C to a solution of styrylmalonate **10** (15 mg, 0.064 mmol) in dry CD_2Cl_2 (0.5 mL), and the mixture was shaken for 0.5 min. Complex **7** (~99%) was obtained as a solution in CH_2Cl_2, which was nearly pure by NMR data.

Complex $[PhCH_2CH^+C^-(CO_2Me)_2{\cdot}GaCl_3]_2$ (8). The reaction was carried out in an NMR tube under an argon atmosphere. The solution was purged with argon flow before the reaction was started. Solid $GaCl_3$ (28 mg, 0.16 mmol, 1.2 equiv) was added in one portion at 32 °C to a solution of cyclopropane **4** (30 mg, 0.13 mmol) in dry CD_2Cl_2 (0.5 mL) and the mixture was shaken for 0.5 min. The necessary NMR experiments were made immediately after synthesis of the gallium complex. For recording of 2D ^{1}H DOSY NMR spectra with calibrant for diffusion coefficient measurements squalane $C_{30}H_{62}$ (~15 mg, 0.036 mmol) was added to the reaction mixture. According to the ^{1}H DOSY data the resulting solution contains mainly binuclear complex **8** with a small amounts of monomeric complex **7** and oligomeric complexes. Complex **8** significantly decomposed in solution after several hours at room temperature. When the solution was cooled, **8** rapidly oligomerized and decomposed; attempts to isolate this complex failed.

^{1}H NMR (400.1 MHz, CD_2Cl_2): δ 4.26 and 4.45 (both s, 2 × 3H, $2OCH_3$), 4.39 (d, 2H, CH_2, ^3J = 6.8 Hz), 7.24−7.45 (m, 5H, Ph), 8.84 (t, 1H, CH^+, ^3J = 6.8 Hz). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 42.2 (CH_2), 61.2 and 61.6 ($2OCH_3$), 116.8 (C^-), 129.5 (*p*-CH), 130.5 and 130.8 (2 *o*-CH and 2 *m*-CH), 136.2 (*i*-C), 174.7 and 174.9 (2COO), 184.0 (CH^+).

Oligomeric Complexes $[PhCH_2CH^+C^-(CO_2Me)_2{\cdot}GaCl_3]_n$. The reaction was carried out in an NMR tube under an argon atmosphere. The solution was purged with an argon flow before the reaction was started. Solid $GaCl_3$ (59 mg, 0.34 mmol, 1.2 equiv) was added in one portion at 32 °C to a solution of cyclopropane **4** (65 mg, 0.28 mmol) in dry CD_2Cl_2 (0.5 mL), and the mixture was shaken for 0.5 min. The necessary NMR experiments were made immediately after synthesis of the gallium complex. For recording of 2D ^{1}H DOSY NMR spectra with calibrant for diffusion coefficient measurements squalane $C_{30}H_{62}$ (~15 mg, 0.036 mmol) was added to the reaction mixture. According to the ^{1}H DOSY data the resulting solution contains mainly oligomeric gallium complexes with small amounts of binuclear complex **8**. The oligomeric complex significantly decomposed in solution after several hours at room temperature. When the solution was cooled, the oligomer rapidly decomposed; attempts to isolate this complex failed.

^{1}H NMR (400.1 MHz, CD_2Cl_2): δ 4.35 (br s, 6H, $2OCH_3$), 4.35 (br m, 2H, CH_2), 7.10−7.40 (br m, 5H, Ph), 8.80 (br m, 1H, CH^+).

Complex $PhCH_2CH^+C^-(CO_2Me)_2{\cdot}Ga_2Cl_6$ (11). The reaction was carried out in an NMR tube under an argon atmosphere. The solution was purged with an argon flow before the reaction was started. Solid $GaCl_3$ (75 mg, 0.44 mmol, 4 equiv) was added in one portion at 32 °C to a solution of cyclopropane **4** (25 mg, 0.11 mmol) in dry CD_2Cl_2 (0.5 mL), and the mixture was shaken for 0.5 min. The necessary NMR experiments were carried out immediately after synthesis of the gallium complex. According to the ^{1}H DOSY data the resulting solution contains a mixture of binuclear complex **11** with mononuclear complex **7** in about an equimolar ratio. The binuclear complex **11** is much less stable than complex **7** and completely decomposes in solution in less than 0.5 h, while complex **7** remains in solution.

^{1}H NMR (400.1 MHz, CD_2Cl_2): δ 4.38 and 4.53 (both s, 2 × 3H, $2OCH_3$), 4.37 (br d, 2H, CH_2, $^3J \approx$ 6.9 Hz), 7.10−7.50 (br m, 5H, Ph), 8.97 (br t, 1H, CH^+, $^3J \approx$ 6.9 Hz). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 41.5 (CH_2), 63.4 and 63.6 ($2OCH_3$), 110.8 (C^-), 132.5 and 133.5 (5CH, Ph), 142.4 (*i*-C), 174.5 (2COO), 182.4 (CH^+).

Complex $PhCH_2CH^+C^-(CO_2Me)_2{\cdot}GaCl_3{\cdot}THF$ (12). The reaction was carried out in an NMR tube under an argon atmosphere. The solution was purged with an argon flow before the reaction was started. Solid $GaCl_3$ (30 mg, 0.17 mmol, 1.5 equiv) was added in one portion at 32 °C to a solution of cyclopropane **4** (25 mg, 0.11 mmol) in dry CD_2Cl_2 (0.4 mL); after that a solution of THF (8 mg, 0.11 mmol) in CD_2Cl_2 (0.1 mL) was added and the mixture was shaken. The necessary NMR experiments were carried out immediately after synthesis of the gallium complex. According to the NMR data the resulting solution contains complex **12** with products of destruction.

dx.doi.org/10.1021/om301072v | *Organometallics* XXXX, XXX, XXX−XXX

Complex **12** is highly unstable and completely decomposes in solution in less than 10 min.

^{1}H NMR (400.1 MHz, CD_2Cl_2): δ 2.17 (m, 4H, CH_2, THF), 4.27 (br d, 2H, CH_2, $^3J \approx 7.1$ Hz), 4.36 (m, 4H, CH_2O, THF), 8.52 (br t, 1H, CH^+, $^3J \approx 7.1$ Hz), other signals overlap with the signals of products of destruction. ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 26.7 (CH_2, THF), 41.3 (CH_2), 75.1 (CH_2O, THF), 178.5 (CH^+), other signals overlap with the signals of products of destruction.

Complex $PhCH_2CH^+C^-(CO_2Me)_2{\cdot}GaCl_3{\cdot}S_8$ (13). The reaction was carried out in an NMR tube under an argon atmosphere. The solution was purged with an argon flow before the reaction was started. Solid $GaCl_3$ (29 mg, 0.17 mmol, 1.5 equiv) was added in one portion at 32 °C to a solution of cyclopropane **4** (25 mg, 0.11 mmol) and molecular sulfur (28 mg, 0.11 mmol) in dry $CDCl_3$ (0.5 mL), and the mixture was shaken for 0.5 min. The necessary NMR experiments were carried out immediately after synthesis of the gallium complex. According to the NMR data the resulting solution contains a mixture of complex **13** with complex **7** in about an equimolar ratio. Conversion is not complete because of the poor solubility of sulfur in chloroform. Complex **13** significantly decomposes in solution after several hours at room temperature.

^{1}H NMR (300.1 MHz, CD_2Cl_2): δ 4.62 (d, 2H, CH_2, ^3J = 6.8 Hz), 8.88 (t, 1H, CH^+, ^3J = 6.8 Hz), other signals overlap with the signals of products of destruction and signals of complex **7**.

Complexes $PhCH_2CH^+C^-(CO_2Me)_2{\cdot}GaCl_3{\cdot}Py$ (14a) and $PhCH_2CH(Py^+)C^-(CO_2Me)_2{\cdot}GaCl_3$ (14b). The reaction was carried out in an NMR tube under an argon atmosphere. The solution was purged with an argon flow before the reaction was started. Solid $GaCl_3$ (30 mg, 0.17 mmol, 1.5 equiv) was added in one portion at 32 °C to a solution of cyclopropane **4** (25 mg, 0.11 mmol) in dry CD_2Cl_2 (0.4 mL); after that a solution of pyridine (9 mg, 0.11 mmol) in CD_2Cl_2 (0.1 mL) was added and the mixture was shaken. The necessary NMR experiments were carried out immediately after synthesis of the gallium complex. According to the NMR data the resulting solution contains complexes **14a** and **14b** in about a 3:1 molar ratio with products of destruction. Complexes **14** are highly unstable and completely decompose in solution in less than 15 min.

Data for complex **14a** are as follows. ^{1}H NMR (400.1 MHz, CD_2Cl_2): δ 4.15 and 4.34 (both s, 2 × 3H, $2OCH_3$), 4.36 (d, 2H, CH_2, ^3J = 6.7 Hz), 7.05–7.45 (m, 5H, Ph), 8.13 (br dd, 2H, H(3), Py, ^3J = 7.9 and 5.3 Hz), 8.66 (tt, 1H, H(4), Py, ^3J = 7.9 Hz, ^3J = 1.4 Hz), 8.69 (t, 1H, CH^+, ^3J = 6.7 Hz), 8.78 (br d, 2H, H(2), Py, ^3J = 5.3 Hz). ^{13}C (100.6 MHz, CD_2Cl_2): δ 39.6 (CH_2), 58.7 and 59.0 ($2OCH_3$), 124.9–131.6 (5CH, Ph), 127.9 (2 CH(3), Py), 140.5 (2 CH(2), Py), 148.1 (CH(4), Py), 171.8 and 172.5 (2COO), 178.3 (CH^+), other signals could not be detected due to the instability of the complex.

Data for complex **14b** are as follows. ^{1}H NMR (400.1 MHz, CD_2Cl_2): δ 3.69 (d, 2H, CH_2, ^3J = 7.6 Hz), 5.93 (t, 1H, CHN, ^3J = 7.6 Hz), 7.05–7.45 (m, 5H, Ph), 7.98 (br dd, 2H, H(3), Py, ^3J = 7.0 and 6.4 Hz), 8.39 (br t, 1H, H(4), Py, ^3J = 7.0 Hz), 8.62 (br d, 2H, H(2), Py, ^3J = 6.4 Hz), other signals overlap with signals of complex **14a** and products of destruction. ^{13}C (100.6 MHz, CD_2Cl_2): δ 39.4 (CH_2), 71.8 (CHN), 128.4 (2 CH(3), Py), 142.5 (2 CH(2), Py), 148.2 (CH(4), Py), other signals could not be detected due to the instability of the complex.

(2*R,3*R**)-Dimethyl 2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-3,4-diphenylcyclopentane-1,1-dicarboxylate (15).** Solid $GaCl_3$ (83 mg, 0.47 mmol, 1.1 equiv) was added in one portion under an argon atmosphere at 0–5 °C with stirring to a solution of cyclopropane **4** (100 mg, 0.43 mmol) in dry CH_2Cl_2 (3 mL), and the mixture was stirred at the same temperature for 1 min. The nearly pure complex **7** (~99%) was obtained as a solution in CH_2Cl_2. A solution of cyclopropane **4** (100 mg, 0.43 mmol, 1 equiv) in dry CH_2Cl_2 (3 mL) was immediately added to a prepared solution of complex **7** at 0–5 °C, and the reaction mixture was stirred at the same temperature for 30 min. After that an aqueous solution of HCl (5%) was added until pH 3 was achieved and the reaction mixture was extracted with dichloromethane (3 × 10 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (benzene–EtOAc, 20:1) to afford compound **15** (165 mg, 83%) as a colorless oil (~2:1 mixture of two diastereomers). The product obtained can be additionally separated on a Silufol chromatographic plate (20 × 20 cm) with benzene–EtOAc (10:1) as eluent to afford the pure isomers. ^{1}H and ^{13}C NMR spectra correspond to the literature data.[7]

(2*R,3*R**,4*R**)-Dimethyl 2-Benzyl-4-(1,3-dimethoxy-1,3-dioxopropan-2-yl)-3-phenylcyclobutane-1,1-dicarboxylate (16).** Solid $GaCl_3$ (83 mg, 0.47 mmol, 1.1 equiv) was added in one portion under an argon atmosphere at 0–5 °C with stirring to a solution of cyclopropane **4** (100 mg, 0.43 mmol) in dry CH_2Cl_2 (3 mL), and the mixture was stirred at the same temperature for 1 min. The nearly pure complex **7** (~99%) was obtained as a solution in CH_2Cl_2. A prepared solution of complex **7** was heated at 25–30 °C for 3 h. After that, an aqueous solution of HCl (5%) was added until pH 3 was achieved and the reaction mixture was extracted with dichloromethane (3 × 10 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (benzene–EtOAc, 20:1) to afford a mixture (45 mg, 45%) of compound **15** (~30% by NMR data, about 2:1 mixture of two diastereomers) and compound **16** (~15% by NMR data, single diastereomer) as a colorless oil; attempts to separate this mixture by chromatography failed. IR ($CHCl_3$): ν 3055, 2988, 2955, 1734 br (C=O), 1601, 1550, 1496, 1436, 1423 cm^{-1}. MS (*m*/*z*, %): 468 (3, M^+), 437 (1, M^+-OCH_3), 376 (1), 336 (28), 276 (35), 245 (14), 217 (28), 203 (21), 171 (21), 145 (24), 115 (908), 91 (60), 77 (33), 59 (100), 51 (24), 39 (14). HRMS calcd for $C_{26}H_{28}O_8$: *M* + *H*, 469.1857; *M* + *Na*, 491.1676; *M* + *K*, 507.1416. Found: *m*/*z* 469.1649, 491.1672, 507.1422. Data for compound **16** are as follows. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 2.56 (ddd, 1H, CH(2), ^3J = 11.0, 10.0, and 4.5 Hz), 2.80 (dd, 1H, CH_2(a), ^2J = 16.5, ^3J = 4.5 Hz), 3.09 (dd, 1H, CH(3), ^3J = 11.0 and 7.0 Hz), 3.10 (dd, 1H, CH_2(b), ^2J = 16.5, ^3J = 10.0 Hz), 3.33 (dd, 1H, CH(4), ^3J = 7.0 and 3.0 Hz), 3.51, 3.79, 3.84, and 3.86 (all s, 4 × 3H, $4OCH_3$), 3.92 (d, 1H, CH(2′), ^3J = 3.0 Hz), 7.05–7.23 (m, 10H, 2 Ph). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 29.0 (CH_2), 43.9 (CH(4)), 44.3 (CH(2′)), 52.1, 52.2, 52.6, and 53.1 ($4OCH_3$), 51.9 (CH(2)), 55.2 (CH(3)), 58.5 (C(1)), 126.4 and 127.3 (2 *p*-C), 127.4, 127.8, 128.7, and 128.9 (2 × 2 *o*-C and 2 × 2 *m*-C), 141.5 and 141.6 (2 *i*-C), 168.7, 168.8, 169.0, and 172.2 (4COO).

■ ASSOCIATED CONTENT

Supporting Information

Figures, tables, and a CIF file giving NMR spectra for all new compounds and crystallographic data and refinement parameters of complex **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel/fax: +7 499 135 6390. E-mail: tom@ioc.ac.ru.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This study was financially supported by the Russian Federation President Council for Grants (Program for the State Support of Leading Scientific Schools of RF, Grant NSh-604.2012.3) and by the Division of Chemistry, Materials Science of the Russian Academy of Sciences (Programme for Basic Research "Theoretical and Experimental Study of the Nature of Chemical Bond and Mechanisms of the Most Important Reactions and Processes") and the Program "Molecular and cell Biology" of the Presidium of the Russian Academy of Sciences.

■ REFERENCES

(1) For reviews of donor–acceptor cyclopropanes, see: (a) Reissig, H. U.; Zimmer, R. *Chem. Rev.* **2003**, *103*, 1151. (b) Yu, M.; Pagenkopf,

B. L. *Tetrahedron* **2005**, *61*, 321. (c) De Simone, F.; Waser, J. *Synthesis* **2009**, *20*, 3353. (d) Campbell, M. J.; Johnson, J. S.; Parsons, A. T.; Pohlhaus, P. D.; Sanders, S. D. *J. Org. Chem.* **2010**, *75*, 6317. (e) Mel'nikov, M. Ya.; Budynina, E. M.; Ivanova, O. A.; Trushkov, I. V. *Mendeleev Commun.* **2011**, *21*, 293.

(2) For some examples of the reactions of donor−acceptor cyclopropanes, see the following. With alkenes: (a) Beal, R. B.; Dombroski, M. A.; Snider, B. B. *J. Org. Chem.* **1986**, *51*, 4391. (b) Shimada, S.; Hashimoto, Y.; Sudo, A.; Hasegawa, M.; Saigo, K. *J. Org. Chem.* **1992**, *57*, 7126. With allenes: (c) Yadav, V. K.; Sriramurthy, V. *Org. Lett.* **2004**, *6*, 4495. With acetylenes: (d) Yadav, V. K.; Sriramurthy, V. *Angew. Chem.* **2004**, *116*, 2723. With aldehydes: (e) Pohlhaus, P. D.; Johnson, J. S. *J. Org. Chem.* **2005**, *70*, 1057. (f) Min, S.; Yang, Y. H.; Bo, X. *Tetrahedron* **2005**, *61*, 1893. (g) Bernard, A. M.; Frongia, A.; Piras, P. P.; Secci, F.; Spiga, M. *Org. Lett.* **2005**, *7*, 4565. With amines: (h) Ying, H.; Qin, F.; Wanquan, T.; Chaoguo, Y. *Chin. J. Chem.* **2012**, *30*, 1867. With heterocumulenes: (i) Graziano, M. L.; Iesce, M. R. *J. Chem. Res.* **1987**, *11*, 362. (j) Goldberg, A. F. G.; O'Connor, N. R.; Craig, R. A.; Stoltz, B. M. *Org. Lett.* **2012**, *14*, 5314. With imines: (k) Carson, C. A.; Kerr, M. A. *J. Org. Chem.* **2005**, *70*, 8242. (l) Wurz, R. P.; Charette, A. B. *Org. Lett.* **2005**, *7*, 2313. (m) Saigo, K.; Shimada, S.; Hasegawa, M. *Chem. Lett.* **1990**, 905. With pyrazolines: (n) Tomilov, Yu. V.; Novikov, R. A.; Nefedov, O. M. *Tetrahedron* **2010**, *66*, 9151. (o) Novikov, R. A.; Shulishov, E. V.; Tomilov, Yu. V. *Mendeleev Commun.* **2012**, *22*, 87. With diazenes: (p) Graziano, M. L.; Iesce, M. R.; Cermola, F. *J. Chem. Res.* **1996**, *27*, 82. With nitriles: (q) Yu, M.; Lynch, V.; Pagenkopf, B. L. *Org. Lett.* **2001**, *3*, 2563. (r) Yu, M.; Pagenkopf, B. L. *J. Am. Chem. Soc.* **2003**, *125*, 8122. With α,β-unsaturated ketones: (s) Liu, L.; Montgomery, J. J. *Org. Lett.* **2007**, *9*, 3885. With azomethinimines: (t) Perreault, C.; Goudreau, S. R.; Zimmer, L. E.; Charette, A. B. *Org. Lett.* **2008**, *10*, 689. With nitrones: (u) Cardona, F.; Goti, A. *Angew. Chem.* **2005**, *117*, 8042. (v) Sibi, M. P.; Ma, Z. H.; Jasperse, C. P. *J. Am. Chem. Soc.* **2005**, *127*, 5764. (w) Ganton, M. D.; Kerr, M. A. *J. Org. Chem.* **2004**, *69*, 8554. With dienes: (x) Ivanova, O. A.; Budynina, E. M.; Grishin, Y. K.; Trushkov, I. V.; Verteletskii, P. V. *Angew. Chem., Int. Ed.* **2008**, *47*, 1107. (y) Ivanova, O. A.; Budynina, E. M.; Grishin, Y. K.; Trushkov, I. V.; Verteletskii, P. V. *Eur. J. Org. Chem.* **2008**, 5329. Dimerization reactions: (z) Novikov, R. A.; Korolev, V. A.; Timofeev, V. P.; Tomilov, Yu. V. *Tetrahedron Lett.* **2011**, *52*, 4996. (aa) Chagarovskiy, A. O.; Ivanova, O. A.; Budynina, E. M.; Trushkov, I. V.; Melnikov, M. Ya. *Tetrahedron Lett.* **2011**, *52*, 4421. (ab) Ivanova, O. A.; Budynina, E. M.; Chagarovskiy, A. O.; Trushkov, I. V.; Melnikov, M. Ya. *J. Org. Chem.* **2011**, *76*, 8852. (ac) Ivanova, O. A.; Budynina, E. M.; Chagarovskiy, A. O.; Rakhmankulov, E. R.; Trushkov, I. V.; Semeykin, A. V.; Shimanovskii, N. L.; Melnikov, M. Ya. *Chem. Eur. J.* **2011**, *17*, 11738. (ad) Novikov, R. A.; Timofeev, V. P.; Tomilov, Yu. V. *J. Org. Chem.* **2012**, *77*, 5993. (ae) Novikov, R. A.; Tomilov, Yu. V.; Nefedov, O. M. *Mendeleev Commun.* **2012**, *22*, 181.

(3) For some examples of the enantioselective reactions of donor−acceptor cyclopropanes, see: (a) Parsons, A. T.; Johnson, J. S. *J. Am. Chem. Soc.* **2009**, *131*, 3122. (b) Yu, M.; Pagenkopf, B. L. *J. Am. Chem. Soc.* **2003**, *125*, 8122. (c) Kang, Y. B.; Sun, X. L.; Tang, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 3918. (d) Sibi, M. P.; Ma, Z.; Jasperse, C. P. *J. Am. Chem. Soc.* **2005**, *127*, 5764. (e) Parsons, A. T.; Smith, A. G.; Neel, A. J.; Johnson, J. S. *J. Am. Chem. Soc.* **2010**, *132*, 9688. (f) Zhou, Y.-Y.; Wang, L.-J.; Li, J.; Sun, X.-L.; Tang, Y. *J. Am. Chem. Soc.* **2012**, *134*, 9066.

(4) For some examples of the synthesis of natural compounds using donor−acceptor cyclopropanes, see: (a) Snider, B. B.; Ahn, Y.; O'Hare, S. M. *Org. Lett.* **2001**, *3*, 4217. (b) Fuerst, D. E.; Stoltz, B. M.; Wood, J. L. *Org. Lett.* **2000**, *2*, 3521. (c) Fischer, C.; Meyers, C.; Carreira, E. M. *Helv. Chim. Acta* **2000**, *83*, 1175. (d) Leduc, A. B.; Kerr, M. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 7945. (e) Carson, C. A.; Kerr, M. A. *Org. Lett.* **2009**, *11*, 777. (f) Morales, C. L.; Pagenkopf, B. L. *Org. Lett.* **2008**, *10*, 157. (g) Carson, C. A.; Kerr, M. A. *Angew. Chem., Int. Ed.* **2006**, *45*, 6560. (h) Young, I. S.; Williams, J. L.; Kerr, M. A. *Org. Lett.* **2005**, *7*, 953. (i) Young, I. S.; Kerr, M. A. *J. Am. Chem. Soc.* **2007**, *129*, 1465.

(5) Meester, M. A. M.; Schenk, H.; McGillavry, C. H. *Acta Crystallogr., Sect. B* **1971**, *27*, 630.

(6) Jameson, C. J.; Mason, J. The Chemical Shift. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1989; pp 51−89. Akitt, J. W. Hydrogen and Its Isotopes: Hydrogen, Deuterium, and Tritium. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1989; pp 171−181. Mann, B. E. Carbon. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1989; pp 293−305.

(7) Novikov, R. A.; Korolev, V. A.; Timofeev, V. P.; Tomilov, Yu. V. *Tetrahedron Lett.* **2011**, *52*, 4996.

(8) Korotkov, V. S.; Larionov, O. V.; Hofmeister, A.; Magull, J.; de Meijere, A. *J. Org. Chem.* **2007**, *72*, 7504.

(9) For some reviews of ^{71}Ga NMR spectra, see: (a) Hinton, J. F.; Briggs, R. W. Group III-Aluminum, Gallium, Indium, and Thallium. In *NMR and the Periodic Table*; Mann, B. E., Harris, R. K., Eds.; Academic Press: New York, 1978; pp 279−308. (b) Akitt, J. W.; Greenwood, N. N.; Storr, A. *J. Chem. Soc.* **1965**, *8*, 4410. (c) Bock, S.; Noth, H.; Wietelman, A. *Z. Naturforsch.* **1990**, *45B* (7), 979.

(10) (a) Feeney, J.; Sutcliffe, L. H. *Progress of Nuclear Magnetic Resonance Spectroscopy*; Emsley, J. W., Ed.; Pergamon: Oxford, U.K., 1997; Vol. *11*, pp 115−118. (b) Hani, R.; Geanangel, G. A. Tin-119 NMR in Coordination Chemistry. *Coord. Chem. Rev.* **1982**, *44* (2), 229−246.

(11) (a) *Chemistry of Aluminium, Gallium, Indium and Thallium*; Downs, A. J., Ed.; Chapman & Hall: New York, 1993. (b) Lustig, C.; Mitzel, N. W. *Z. Naturforsch., B: Chem. Sci.* **2004**, *59*, 140. (c) Schaefer, H.; Becker-Kaiser, R. *Z. Anorg. Allg. Chem.* **1985**, *526*, 177. (d) Baxter, P. L.; Downs, A. J.; Goode, M. J.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Dalton Trans.* **1990**, 2873. (e) Helliwell, B. N.; Taylor, M. J. *Aust. J. Chem.* **1983**, *36*, 385.

(12) (a) Johnson, C. S., Jr. *Prog. Nucl. Magn. Reson. Spectrosc.* **1999**, *34*, 203. (b) Weingartner, H.; Holz, M. *Annu. Rep. Prog. Chem., Sect. C* **2002**, *98*, 121. (c) Pregosin, P. S.; Kumar, P. G. A.; Fernandez, I. *Chem. Rev.* **2005**, *105*, 2977. (d) Pregosin, P. S. *Prog. Nucl. Magn. Reson. Spectrosc.* **2006**, *49*, 261. (e) Macchioni, A.; Ciancaleoni, G.; Zuccaccia, C.; Zuccaccia, D. *Chem. Soc. Rev.* **2008**, *37*, 479. (f) Cohen, Y.; Avram, L.; Frish, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 520.

(13) Wu, D.; Chen, A.; Johnson, C. S., Jr. *J. Magn. Reson. A* **1995**, *115*, 260.

(14) Li, W.; Kagan, G.; Hopson, R.; Williard, P. G. *ARKIVOC* **2011**, 180.

(15) Nilsson, M. *J. Magn. Reson.* **2009**, *200*, 296.

(16) (a) Olah, G. A.; Porter, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 6877. (b) Olah, G. A.; Liang, G.; Westerman, P. *J. Am. Chem. Soc.* **1973**, *95*, 3698.

(17) *APEX2 and SAINT*; Bruker AXS, Madison, WI, 2005.

(18) (a) Shimada, S.; Hashimoto, Y.; Sudo, A.; Hasegawa, M.; Saigo, K. *J. Org. Chem.* **1992**, *57*, 7126. (b) Mume, E.; Munslow., I. J.; Kaellstroem, K.; Andersson, P. G. *Collect. Czech. Chem. Commun.* **2007**, *72*, 1005.