Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2022, **32**, 582–584

Mendeleev Communications

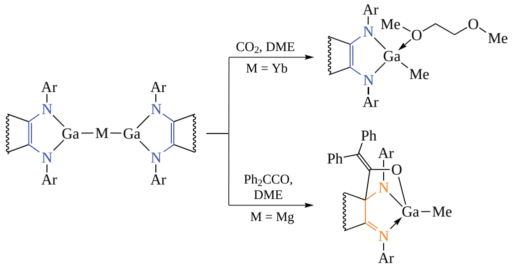
Reactions of ytterbium and magnesium gallylene complexes with carbon dioxide and diphenylketene

Vladimir A. Dodonov, Alexandra A. Skatova and Igor L. Fedushkin*

G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,
603137 Nizhny Novgorod, Russian Federation. E-mail: igorfed@iomc.ras.ru

DOI: 10.1016/j.mencom.2022.09.004

Reactivity of ytterbium and magnesium complexes of gallylenes against carbon dioxide and diphenylketene has been assessed. Ytterbium complex of redox-active gallylene [{(dpp-bian)Ga}$_2$Yb(DME)$_2$] (dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) on treatment with CO$_2$ gives complex [(dpp-bian)Ga(DME)Me], while the treatment of magnesium-stabilized gallylene [{(dpp-bian)Ga}$_2$Mg(DME)$_2$] with Ph$_2$CCO affords cycloadduct [(dpp-bian)(Ph$_2$CCO)GaMe].



Keywords: gallylenes, carbon dioxide, ketenes, non-innocent α-diimine ligands, cycloaddition, magnesium, ytterbium, X-ray diffraction.

Transition metal gallylene complexes[1] attract attention due to their peculiar reactivity. For instance, facile hydrogenation of CO$_2$ to formate was achieved by the application of rhodium gallylene complexes.[2] Gallylenes efficiently stabilize subvalent centers of ‘Co$^{1–}$’ that can bind dihydrogen[3] while ‘Ni$^{1–}$’ complexes supported with gallium ligands can promote disproportionation of CO$_2$ into carbonate and CO.[4] Gallium ligands may act as Lewis acids for transition metal atoms.[5] Complexes of transition metal atoms coordinated even to naked Ga$^+$ center were detected.[6]

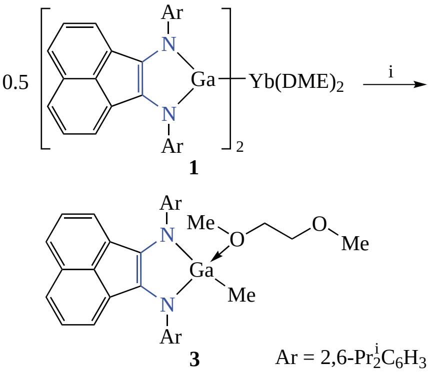
Gallylenes being the derivatives of low-valent gallium are quite reactive species. Their stabilization can be achieved by introduction of bulky ligands such as cyclopentadienyl,[7] β-diketoiminate,[8] silyl,[9] aryl,[10] pincer type ligands[11] or boryl[12] ligands. Our approach for stabilization of low-valent Na,[13] Mg,[14] Ga[15] or Al[16] metal centers is based on dpp-bian α-diimine ligand (dpp-bian is 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene). An astonishing feature of these reagents is that they react in a cooperative mode, that is, both the ligand and the coordination center participate in the reactions. Importantly, these derivatives may find practical application, for example, in the cyclic ester ring-opening polymerization.[17]

Despite a great progress in transition metal gallylene complexes, the data on the gallylene complexes of lanthanide and s-block metals is severely limited. By the time of this publication, there were only three documented ytterbium gallylene complexes such as [{(dpp-bian)Ga}$_2$Yb(DME)$_2$] **1**,[18] [Cp$^*_2$Yb(THF)GaCp*][19] and [(dpp-dad)GaYb(TMEDA)$_2$Ga(dpp-dad)][20] as well as only three magnesium gallylene complexes such as [{(dpp-bian)Ga}$_2$Mg(DME)$_2$] **2**,[21] [{(dpp-dad)Ga}$_2$Mg(THF)$_3$][22] and β-diketiminate complex [(Nacnac)Mg(TMEDA)Ga(dpp-dad)].[23] Their reactivity, not to mention, remains unknown.

In this communication, we have pioneered in studying the reactivity of complexes **1** and **2** towards some typical heteroalkene electrophiles. The starting compounds [{(dpp-bian)Ga}$_2$Yb(DME)$_2$] **1**[18] and [{(dpp-bian)Ga}$_2$Mg(DME)$_2$] **2**[21] were obtained by a rather straightforward procedure *via* refluxing digallane [(dpp-bian)Ga]$_2$ with excess of the appropriate metal in an ethereal solvent. In our experiments, complexes **1** and **2** readily reacted with CO$_2$, phenyl iso(thio)cyanate, diphenylketene and Bu^{t}NC under mild conditions; however, in the most cases inseparable mixtures were obtained. Meanwhile, in two of them the products were isolated, which may give an insight on the processes taking place in these reactions.

Treatment of complex **1** with two equivalents of CO$_2$ results in instant solution colour change to blue-green. The following work-up gives light blue crystals of product **3** in 26% yield (Scheme 1). Being stable in a crystalline state at –20 °C for at least a week, this compound is extremely sensitive to vacuum or treatment with solvents except for DME. That is also why no meaningful NMR spectra can be recorded (the longest half-life in C$_6$D$_6$ is ~0.5 min).

Notably, attempts to synthesize compounds of type [(dpp-bian)GaR] (R is organyl) by the salt metathesis of [(dpp-bian)Ga(I)]$_2$[15(a)] with alkylmagnesium or alkyllithium

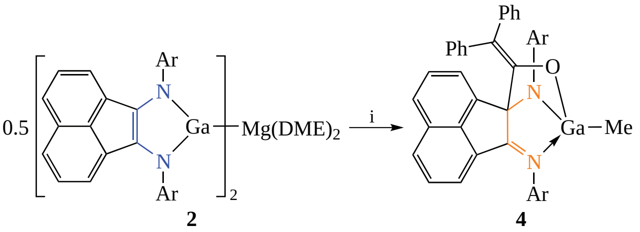


Scheme 1 *Reagents and conditions*: i, CO$_2$ (2 equiv.), DME, 25 °C.

reagents were unsuccessful. The solvent molecule coordinated to the gallium atom is expected to play a crucial role in the stabilization of such compounds because analogous complexes of pyridine [(dpp-bian)Ga(Py)PCO][24] are relatively stable.

In the crystal,† complex **3** is organized in individual molecules, and short-interatomic contacts are absent. Interatomic distances within the GaC_2N_2 metallacycle (see Online Supplementary Materials, Table S2) agree well with the other [dpp-bian^{2-}]Ga structures[15(*c*)] and complex **1**[18] (the difference is less than 0.07 Å), which accounts for the dianionic state of the dpp-bian ligand. The structure of compound **3** consists of a DME molecule coordinated to a gallium atom in an unusual monodentate manner (Figure 1). According to the Cambridge Structural Database, such coordination type of DME is an unprecedented example. Interatomic Ga–C distance fell into the range typical for gallium–carbon bonds.[25]

Treatment of the solution of compound **2** with diphenylketene (1 equiv.) results in a yellow-green solution. Complex **4** was isolated as light-yellow crystals in 25% yield (Scheme 2). Interestingly, compound **4** in comparison to **3** is quite thermally stable and gives well-resolved NMR spectra. Like previously reported dpp-bian gallium cycloadducts [(dpp-bian)(PhN=C–S)Ga]$_2$ and [(dpp-bian)(PhN–C=O)Ga]$_2$ [refs. 15(*b*),(*c*)], compound **4** reveals a characteristic ^{1}H NMR pattern of the cycloadduct of eight distinct doublets (3H) and four septets (1H).[15(*b*)] This is well compared with a simplified set of ^{1}H NMR signals of two doublets (12 H each) and one septet (4H), which are characteristic for [dpp-bian^{2-}]Ga derivatives with two symmetry planes.[15(*a*)] Signals δ_H 0.08 and δ_C –14.9 ppm correspond to the isolated Ga-attached methyl group. IR spectrum exhibits an intense band of 1624 cm^{-1} that corresponds to C=N stretching vibrations. There are no characteristic bands for the ketene (~2200 cm^{-1}) or carbonyl group (~1700 cm^{-1}).



Scheme 2 *Reagents and conditions*: i, Ph_2CCO, DME, 25 °C.

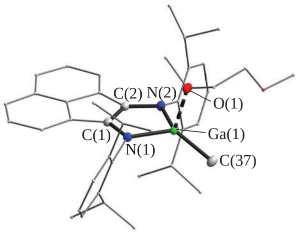


Figure 1 Molecular structure of complex **3** (thermal ellipsoids are drawn at 30% probability level, hydrogen atoms are omitted).

The XRD structure of compound **4** is very similar to gallium cycloadducts of iso(thio)cyanates to digallane [(dpp-bian)Ga]$_2$, [(dpp-bian)(RN=C–S)Ga]$_2$[15(*b*)] or [(dpp-bian)(RN–C=O)Ga]$_2$ (Figure 2).[15(*c*)] After cycloaddition, the conjugated system of dpp-bian is broken (Table S2), which results in one short double C=N and one long C–N single bond.[15(*c*)] The quaternary carbon atom makes the compounds chiral. However, the crystalline cell of the compound is centrosymmetric space group $P\bar{1}$ and it consists of both enantiomers.

Both reactions presented in Schemes 1 and 2 involve similar heterocumulene reagents and thus are proposed to proceed in a similar fashion. On the first step, CO_2 or Ph_2CCO molecules may coordinate to Mg/Yb atom and undergo single electron transfer from metallacenter. That may initiate homolytic dissociation of Ga–M bond with simultaneous attack of the generated species (dpp-bian)Ga* and (dpp-bian)GaM* to the coordinated DME molecule. Significantly more oxophilic Mg/Yb atoms attack oxygen atom of the solvent molecule while gallium atom attacks methyl group, the reaction results in formation of species **3**. Diphenylketene that is present in the reaction mixture may further undergo [4 + 2] cycloaddition reactions with species **3** like [(dpp-bian)(RN=C–S)Ga]$_2$ or [(dpp-bian)(RN–C=O)Ga]$_2$ [*cf.* refs. 15(*b*),(*c*)]. This is not the case for CO_2 that is much weaker dienophile than Ph_2CCO. The fact of attack to the solvent molecule is well supported by the earlier observation of the thulium analogue of **1**, [{(dpp-bian)Ga−Ga(dpp-bian)}(C_4H_8O)TmI(THF)$_5$],[18] that instead of expected bis-gallylene structure L–Tm–L, consists, in fact, of an opened ring of THF molecule.

In conclusion, gallylene complexes of ytterbium and magnesium in the reactions with CO_2 or Ph_2CCO have demonstrated their low-valent nature. Both isolated products **3**

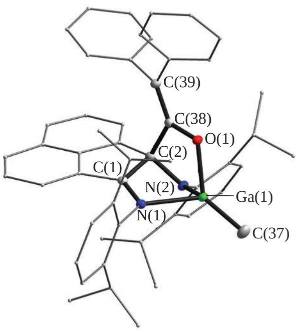


Figure 2 Molecular structure of complex **4** (thermal ellipsoids are drawn at 30% probability level, hydrogen atoms are omitted).

---

† *Crystal data for* **3**. $C_{43}H_{58}GaN_2O_3$ (M = 720.63), monoclinic, space group $P2(1)/c$, 150 K, a = 10.3594(2), b = 24.2428(4) and c = 15.8450(2) Å, β = 102.977(2)°, V = 3877.70(11) Å^3, Z = 4, d_{calc} = 1.234 g cm^{-3}, μ(CuKα) = 1.274 mm^{-1}, F(000) = 1540. Dark blue prism-shaped single crystal with dimensions 0.586 × 0.196 × 0.130 was selected and intensities of 15817 reflections were measured. 7615 independent reflections (R_{int} = 0.0202) were used for a structure solution and refinement. Final R factors: R_1 = 0.0366 [6759 reflections with $I > 2\sigma(I)$], wR_2 = 0.1016 (all reflections), and GOF = 1.085.

Crystal data for **4**. $C_{53}H_{58}GaN_2O_2$ (M = 824.73), triclinic, space group $P\bar{1}$, 150 K, a = 10.3097(3), b = 12.3361(4) and c = 19.5856(6) Å, α = 79.234(3)°, β = 85.282(3)°, γ = 65.649(3)°, V = 2229.34(13) Å^3, Z = 2, d_{calc} = 1.229 g cm^{-3}, μ(CuKα) = 1.161 mm^{-1}, F(000) = 874. Orange plate-shaped single crystal with dimensions 0.268 × 0.196 × 0.042 was selected and intensities of 15797 reflections were measured. 8706 independent reflections (R_{int} = 0.0277) were used for a structure solution and refinement. Final R factors: R_1 = 0.0381 [8033 reflections with $I > 2\sigma(I)$], wR_2 = 0.0995 (all reflections), and GOF = 1.092.

The X-ray diffraction data were collected on an Agilent SuperNova diffractometer (CuKα radiation, λ = 1.54184 Å). The data were integrated using the CrysAlisPro[26] software. The SCALE3 ABSPACK[27] was used for absorption corrections. The structures were solved by dual-space method using the SHELXT[28] software and refined on F^2_{hkl} with SHELXTL[29] and OLEX2[30] packages. Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and refined in the ‘riding model’ with $U_{iso}(H) = 1.2\,U_{eq}$ [$U_{iso}(H) = 1.5\,U_{eq}$ for the hydrogen atoms in CH_3 groups] of their parent atoms. Crystals contain solvate molecules DME (**3**, **4**), disposed either at the common or at the special positions, and part of them is disordered. Molecules of complex **4** contain disordered fragments.

CCDC 2158171 (**3**) and 2158172 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

and **4** contain a Ga–Me bond, that is supposed to be formed *via* the reduction of DME solvent molecules. Nevertheless, such high reactivity of gallylene complexes of lanthanides and s-block metals may be employed for the activation of stable molecules such as dihydrogen and dinitrogen.

The investigations were supported by the Russian Science Foundation (grant no. 20-13-00052). The work was carried out using the equipment of the center for collective use 'Analytical Center of the IOMC RAS' with the financial support of the grant 'Ensuring the development of the material and technical infrastructure of the centers for collective use of scientific equipment' (Unique identifier RF-2296.61321X0017, agreement no. 075-15-2021-670).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.09.004.

References

1 (*a*) S. González-Gallardo, T. Bollermann, R. A. Fischer and R. Murugavel, *Chem. Rev.*, 2012, **112**, 3136; (*b*) M. Asay, C. Jones and M. Driess, *Chem. Rev.*, 2011, **111**, 354; (*c*) C. Jones and A. Stasch, in *The Group 13 Metals Aluminium, Gallium, Indium and Thallium: Chemical Patterns and Peculiarities*, eds. S. Aldridge and A. J. Downs, Wiley, 2011, pp. 285–342.

2 S. P. Desai, J. Ye, J. Zheng, M. S. Ferrandon, T. E. Webber, A. E. Platero-Prats, J. Duan, P. Garcia-Holley, D. M. Camaioni, K. W. Chapman, M. Delferro, O. K. Farha, J. L. Fulton, L. Gagliardi, J. A. Lercher, R. L. Penn, A. Stein and C. C. Lu, *J. Am. Chem. Soc.*, 2018, **140**, 15309.

3 M. V. Vollmer, J. Xie and C. C. Lu, *J. Am. Chem. Soc.*, 2017, **139**, 6570.

4 M. V. Vollmer, R. C. Cammarota and C. C. Lu, *Eur. J. Inorg. Chem.*, 2019, 2140.

5 H. Braunschweig, R. D. Dewhurst, F. Hupp, C. Kaufmann, A. K. Phukan, C. Schneider and Q. Ye, *Chem. Sci*., 2014, **5**, 4099.

6 J. K. Schuster, J. H. Muessig, R. D. Dewhurst and H. Braunschweig, *Chem. – Eur. J.*, 2018, **24**, 9692.

7 (*a*) Y. Liu, J. Li, X. Ma, Z. Yang and H. W. Roesky, *Coord. Chem. Rev*., 2018, **374**, 387; (*b*) P. W. Roesky, *Dalton Trans*., 2009, 1887.

8 J. Turner, J. A. B. Abdalla, J. I. Bates, R. Tirfoin, M. J. Kelly, N. Phillips and S. Aldridge, *Chem. Sci.*, 2013, **4**, 4245.

9 G. Linti and W. Köstler, *Chem. – Eur. J.*, 1998, **4**, 942.

10 M. L. McCrea-Hendrick, C. A. Caputo, C. J. Roberts, J. C. Fettinger, H. M. Tuononen and P. P. Power, *Organometallics*, 2016, **35**, 579.

11 N. Saito, J. Takaya and N. Iwasawa, *Angew. Chem., Int. Ed*., 2019, **58**, 9998.

12 D. Dange, C. P. Sindlinger, S. Aldridge and C. Jones, *Chem. Commun.*, 2017, **53**, 149.

13 V. A. Dodonov, O. A. Kushnerova, R. V. Rumyantsev, A. S. Novikov, V. K. Osmanov and I. L. Fedushkin, *Dalton Trans.*, 2022, **51**, 4113.

14 V. A. Dodonov, A. A. Skatova and I. L. Fedushkin, *Russ. J. Coord. Chem.*, 2019, **45**, 301 (*Zh. Koord. Khim*., 2019, **45**, 249).

15 (*a*) I. L. Fedushkin, A. A. Skatova, V. A. Dodonov, V. A. Chudakova, N. L. Bazyakina, A. V. Piskunov, S. V. Demeshko and G. K. Fukin, *Inorg. Chem*., 2014, **53**, 5159; (*b*) W. Zhang, V. A. Dodonov, W. Chen, Y. Zhao, A. A. Skatova, I. L. Fedushkin, P. W. Roesky, B. Wu and X.-J. Yang, *Chem. – Eur. J*., 2018, **24**, 14994; (*c*) V. A. Dodonov, W. Chen, Y. Zhao, A. A. Skatova, P. W. Roesky, B. Wu, X. J. Yang and I. L. Fedushkin, *Chem. – Eur. J.*, 2019, **25**, 8259; (*d*) V. A. Dodonov, O. A. Kushnerova, E. V. Baranov, A. S. Novikov and I. L. Fedushkin, *Dalton Trans.*, 2021, **50**, 8899.

16 (*a*) W. Chen, V. A. Dodonov, V. G. Sokolov, L. Liu, E. V. Baranov, Y. Zhao, I. L. Fedushkin and X.-J. Yang, *Organometallics*, 2021, **40**, 490; (*b*) V. A. Dodonov, W. Chen, L. Liu, V. G. Sokolov, E. V. Baranov, A. A. Skatova, Y. Zhao, B. Wu, X.-J. Yang and I. L. Fedushkin, *Inorg. Chem*., 2021, **60**, 14602.

17 V. A. Dodonov, A. G. Morozov, R. V. Rumyantsev, G. K. Fukin, A. A. Skatova, P. W. Roesky and I. L. Fedushkin, *Inorg. Chem*., 2019, **58**, 16559.

18 T. Sanden, M. T. Gamer, A. A. Fagin, V. A. Chudakova, S. N. Konchenko, I. L. Fedushkin and P. W. Roesky, *Organometallics*, 2012, **31**, 4331.

19 M. Wiecko and P. W. Roesky, *Organometallics*, 2007, **26**, 4846.

20 C. Jones, A. Stasch and W. D. Woodul, *Chem. Commun*., 2009, 113.

21 I. L. Fedushkin, A. N. Lukoyanov, A. N. Tishkina, G. K. Fukin, K. A. Lyssenko and M. Hummert, *Chem. – Eur. J.*, 2010, **16**, 7563.

22 C. Jones, D. P. Mills, J. A. Platts and R. P. Rose, *Inorg. Chem.*, 2006, **45**, 3146.

23 O. Bonello, C. Jones, A. Stasch and W. D. Woodul, *Organometallics*, 2010, **29**, 4914.

24 D. W. N. Wilson, W. K. Myers and J. M. Goicoechea, *Dalton Trans.*, 2020, **49**, 15249.

25 A. Kassymbek, J. F. Britten, D. Spasyuk, B. Gabidullin and G. I. Nikonov, *Inorg. Chem*., 2019, **58**, 8665.

26 *Data Collection, Reduction and Correction Program, CrysAlisPro 1.171.40.67a – Software Package*, Rigaku OD, 2019.

27 *SCALE3 ABSPACK: Empirical absorption correction, CrysAlisPro 1.171.40.67a – Software Package*, Rigaku OD, 2019.

28 G. M. Sheldrick, *Acta Crystallogr.*, 2015, **A71**, 3.

29 G. M. Sheldrick, *SHELXTL, Version 6.14, Structure Determination Software Suite*, Bruker AXS, Madison, WI, 2003.

30 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.

Received: 20th April 2022; Com. 22/6872