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Review

Well-defined organo-gallium complexes as Lewis acids for molecular catalysis: Structure–stability–activity relationships

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ABSTRACT

While the coordination chemistry of gallium is very rich, only a few applications of organo-gallium compounds as catalysts for molecular transformations have been reported. Nevertheless, some studies containing both families of X-ray characterized species and their catalytic activity allow the establishment of a structure–activity and a structure–stability relationship. They show that coordination compounds of gallium enable reactions that encroach upon the territory of transition metals. The interest of using specific ligands in gallium catalysis is also becoming clear in classical Lewis acid chemistry. In this review, the physical properties of gallium complexes are analyzed and related to their ability to activate alkynes toward nucleophilic additions, peracetic acid toward olefin epoxidation, and aldehydes toward hetero Diels–Alder reactions.

1. Introduction

The replacement of precious metals by abundant and less toxic main group elements in catalytic processes has become a thriving area of research [1,2]. For instance, organocatalytic methods for constructing biaryls through haloarene coupling or aromatic C—H activation have been devised [3–6]. Other classical reactions that are the territory of late transition metal catalysis have been conquered by *s*- and *p*-block-based compounds. Among them, hydrogenation of alkenes is now possible using frustrated B/P Lewis pairs [7–13] or calcium complexes [14–16]. Gallium compounds also catalyze important transformations such as coupling reactions, radical reactions, reductions, oxidations, cycloadditions, cycloisomerizations, insertions, etc. While most of the reported methods use simple GaR_3 salts as catalysts (R = halide, alkoxide, amido, triflate, etc.) [17–23], well-defined species enjoy increasing applications in polymer and molecular chemistry. The use of discrete gallium complexes for ring-opening polymerization of cyclic ethers, esters, and carbonates has been reviewed recently [24]. Herein are presented organo-gallium compounds that can imitate transition metals in homogeneous molecular catalysis. Moreover, ways to enhance the Lewis acidity of gallium compounds by ligand design for classical applications (i.e. Lewis acid catalyzed hetero Diels–Alder reaction) is also presented.

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Nomenclature

$\%V_{bur}$	percent buried volume
bispicen	N^1,N^2-bis(pyridin-2-ylmethyl)ethane-1,2-diamine
CAAC	cyclic alkyl amino carbene
CDC	carbodicarbene
CDP	carbodiphosphorane
diMe-IMD	1,3-dimethylimidazol-2-ylidene
diMe-MDI	1,3-dimethyl-2-methylene-2,3-dihydro-1H-imidazole
dpp-Bian	1,2-bis[2,6-diisopropylphenyl)imino]acenaphthene
en	ethylenediamine
$IBioxMe_4$	3,3,7,7-tetramethyl-2,3,7,8-tetrahydrodioxazolo[3,2-c:3′,2′-e]imidazol-4-ylidene
IMes	1,3-dimesitylimidazol-2-ylidene
IPr	1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene
IR	infrared
NHC	N-heterocyclic carbene
NMR	nuclear magnetic resonance
NH_2-phen	1,10-phenanthrolin-5-amine
NO_2-phen	5-nitro-1,10-phenanthroline
PAA_R	peracetic acid of pH ~4
phen	1,10-phenanthroline
SIMes	1,3-dimesitylimidazolidin-2-ylidene
SIPr	1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene
THF	tetrahydrofuran
TFB	2,4,6-trifluorobenzonitrile
TMB	2,4,6-trimethoxybenzonitrile
trispicen	N^1,N^1,N^2-tris(pyridin-2-ylmethyl)ethane-1,2-diamine
tpen	N^1,N^1,N^2,N^2-tetrakis(pyridin-2-ylmethyl)ethane-1,2-diamine

Our purpose is to emphasize the advantages in terms of reactivity of using donor–acceptor species displaying judiciously chosen ligands instead of simple gallium salts. Therefore, we focused on studies offering the possibility to establish structure–activity and structure–stability relationships. For more general reviews on the structure and the reactivity of the complexes of heavier Group 13 elements, the reader can refer to the references provided herewith [25–27].

2. Activation of alkynes toward hydroamination and hydroarylation reactions

The issue of the activation of alkynes toward nucleophilic attack (π-acid catalysis) has been amply addressed with late carbophilic transition metal complexes of palladium, rhodium, iridium, ruthenium, platinum, and gold [28,29]. In this section, we will show that specific gallium complexes can emulate the ability of transition metals to coordinate alkynes and trigger hydroamination or hydroarylation reactions.

2.1. Digallane with a redox active bis-amido ligand

Whereas transition metals easily cycle between n and $n+2$ oxidation states (i.e. oxidative addition/reductive elimination), catalytic processes using redox catalysts based on main group elements remain exceedingly rare because of unfavorable potentials [30]. In theory, this pitfall could be circumvented by using ligands that store and release electrons during a catalytic process [31–34]. In that respect, redox active aluminum(III) complexes convert CO_2 into $MgCO_3$ or $CaCO_3$ in a synthetic cycle using Mg or Ca metal [35]. Regarding gallium, the dinuclear complex [(dpp-Bian)Ga—Ga(dpp-Bian)] (compound **1**, Scheme 1) [36] proved able to catalyze hydroamination of alkynes [37,38].

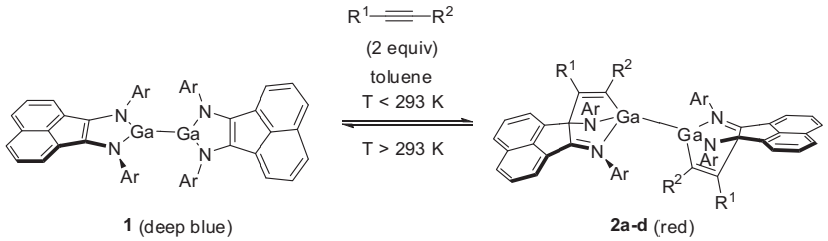
In contrast with (dpp-Bian)$Mg(THF)_3$ and [(dpp-Bian)Zn—Zn(dpp-Bian)] which follow acid–base and reduction paths with phenylacetylene respectively [39,40], the digallane **1** reacts at $T < 293$ K with alkynes in toluene to give [3+2] cycloadducts (Scheme 1). Interestingly, the digallane **1** proved inert toward alkenes, ketones, nitriles, and isonitriles.

The crystal structures of the adducts show that the alkynes add across the Ga—N—C fragments in each case, resulting in the formation of C—C and C—Ga bonds (see Fig. 1 for phenylacetylene). The amido-imino character of the N-chelating fragment is revealed by the difference in the Ga—N bond lengths.

The regioselectivity of the process agrees well with a concerted 1,3-dipolar addition (Scheme 2): with phenylacetylene, the phenyl group is orientated away from the metal, whereas with ethyl or methyl but-2-ynoate, the ester group points toward gallium.

Considering the clear change in hybridization of the alkyne carbons to sp^2, as well as the length of the newly formed C—C and C—Ga bonds, it would seem that the cycloaddition is not reversible. Unexpectedly, electron-absorption spectroscopy showed that the starting digallane is restored upon raising the temperature. Going back to 293 K renews the formation of the cycloadduct. The ability of **1** to reversibly coordinate alkynes and cycle between oxidation states is reminiscent of transition metal coordination chemistry. Besides, this complex proved able to imitate transition metal-based catalytic systems for hydroamination reactions [41]. Using 2 mol% of the digallane **1** in C_6D_6 at 90–110 °C, various anilines reacted with phenylacetylene to give imines regioselectively (Markovnikov hydroamination) (Table 1). While the reaction gives excellent yields in most cases, it is hampered by the steric demand (entry 7) and by the presence of a bromine atom (entry 3). In the latter case, cleavage of the C—Br and oxidation of the dpp-Bian dianion has been suggested. With 1-aminonaphthalene, a mixture of hydroamination and hydroarylation products has been obtained (entry 8). On the other hand, 1-aminoanthracene transformed exclusively into the hydroalkylation product (entry 9).

Of particular interest, the use of $GaCl_3$ instead of the digallane as catalyst gave rise to the hydroamination product exclusively with



Scheme 1. Reaction of alkynes with digallane **1** (Ar = 1,2-bis[2,6-diisopropylphenyl; **2a**: $R^1 = R^2 = H$; **2b**: R^1 = Ph, $R^2 = H$; **2c**: $R^1 = CH_3$, $R^2 = CO_2Me$; **2d**: $R^1 = CH_3$, $R^2 = CO_2Et$) [37].