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GALLIUM AND INDIUM COMPOUNDS IN HOMOGENEOUS CATALYSIS (EIBC2416).

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ABSTRACT. The present contribution highlights the most recent and representative developments on the use of Ga and In species in homogeneous catalysis. Recent studies of various ligand-supported Ga(III) and In(III) compounds in cyclic esters polymerization catalysis for the production of biodegradable polyester materials are also included. Various organic transformations may now be catalyzed using Ga(III) and In(III) Lewis acids allowing access to a wide range of valuable organic molecules through diverse reaction sequences. The recent use of stable and robust *N*-heterocyclic carbene Ga(III) and In(III) compounds as strong π -Lewis acid catalysts for various organic reactions is also discussed: such species are certainly promising for the future developments of Ga(III)- and In(III)-mediated reactions. Though Lewis-acid-assisted reactions certainly dominate the field in Ga(III) and In(III) chemistry, discrete low valent In(I) species, presently emerging in catalysis, clearly display a distinct reactivity allowing their exploitation both as soft Lewis acids and alkyl-/allyl-/aryl-ating agents.

KEYWORDS. Gallium – Indium — Homogeneous Catalysis – Organic Chemistry – Lewis Acidic Metals — Organometallic Species – Coordination Compounds – Polymerization – *N*-Heterocyclic Carbene Ligands – *N*-donor Ligands – *O*-donor Ligands.

GLOSSARY (ABBREVIATIONS)

ADPE, (1*S*,2*R*)-(+)-2-amino-1,2-diphenylethanol;

CHD, 1,4-cyclohexadiene;

CHO, Cyclohexene oxide;

DDP, Diphenyl phosphoric acid;

DCE, 1,2-dichloroethane;

DFT, Density Functional Theory;

Dipp-BIAN, 1,2-bis[2,6-di*isopropyl*phenyl]imino]acenaphthene;

DTBN, Di-*tert*-butylnitroxide;

EDG, Electron donating group;

Et₂O, Diethylether;
EWG, Electron withdrawing group;
IB, Isobutene;
IDipp, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene;
M.S., Molecular sieves;
MCR, Multi-component reaction;
Mes, 2,4,6-trimethylphenyl (2,4,6-Me₃C₆H₂);
NHC, *N*-heterocyclic carbene;
NMSM, *E-N*-methyl-1-(methylthio)-2-nitroethenamine;
NTf, Triflimidate;
phen, Phenanthroline;
py, Pyridine;
PAA_R, peracetic acid;
PDI, Polydispersity index (M_w/M_n);
PLA, Poly(lactic acid);
PMHS, Polymethylhydrosiloxane;
 P_m , Probability of mesomeric linkage;
 P_r , Probability of racemic linkage;
PS, Polystyrene;
rac-LA, *rac*-Lactide;
ROP, Ring-opening polymerization;
SET, Single electron transfer;
TFB, Trifluorobenzonitrile;
TFMK, Trifluoromethyl ketone;
Tf, Triflate;
THF, Tetrahydrofuran;
TMB, Trimethoxybenzonitrile;
TMDS, 1,1,3,3-tetramethyldisiloxane;
Ts, Tosyl;
XRD, X-ray-determined;

1. INTRODUCTION

The development of new methodologies for the construction of molecules of interest, such as molecular synthons for the synthesis of biological or pharmaceutical compounds, relay to the foreground homogeneous catalysis and metal-mediated reactions. In this regard, group 13 metal species are important reagents/catalysts in numerous catalytic transformations, typically acting as strong Lewis acids or/and alkylating/aryllating agents. Till recently, such processes overwhelmingly involved Al derivatives. Ga and In compounds have indeed long been considered less attractive species than their aluminium analogues due to their lower nucleophilicity and Lewis acidity. However, such derivatives have attracted much attention since the early 2000's and are now well-established catalysts for a number of organic transformations.^{1,2} When compared to their Al analogues, Ga and In derivatives exhibit several attractive features for use as catalysts: (i) they are much less sensitive to hydrolysis and may usually be easily handled, (ii) due to their lower heterophilicity (*vs.* Al) such reagents are tolerant to nitrogen- and oxygen-containing functional groups, (iii) the low first ionization potential of In metal (5.8 eV), comparable to that of alkali metals, allows its use in single-electron reduction reactions.

A recent book comprehensively covering all aspects of group 13 metal compounds detailed the use of Ga and In derivatives in homogeneous catalysis up to 2009, though the use of such compounds in polymerization catalysis was not addressed. The latter mainly included the use of aluminum derivatives and their extensive exploitation in Lewis-acid mediated reactions, though gallium and indium derivatives already emerged as efficient Lewis acids that may outperform Al analogues in several instances.^{2,3} This present EIBC contribution highlights the latest developments (primarily since 2009) on the use of Ga and In species in homogeneous catalysis (including as polymerization catalysts). It is structured according to the class of compounds while sub-parts follow the type of catalyzed reactions.

2. GALLIUM COMPLEXES

2.1 Gallium(III) halides, salts and alkyls/aryls without stabilizing ligands

A recent review provided a complete account on the broad applications of gallium in organic synthesis, with a special emphasis on the growing importance of gallium halides in this field.^{3,4} Noteworthy applications include allylation, alkenylation, ethynylation, coupling, cycloaddition or cycloisomerization reactions, taking advantage of the Lewis acidity and the well-known π -complexing ability of Ga(III) salts towards aromatics and alkynes.

2.1.1 Gallium(III) chloride

2.1.1.1 Cycloisomerization/Friedel-Crafts cascade reaction

The reaction between 1,6-arenynes and electron-rich arenes in the presence of GaCl₃ (10 mol%) afforded the corresponding 1-aryl-1,2,3,4-tetrahydronaphthalenes *via* cycloisomerization of the 1,6-enyne followed by bimolecular Friedel-Crafts addition (eq. 1).⁵ GaBr₃ is slightly less efficient for such a transformation, while the reaction does not proceed using AlCl₃ or Ga(OTf)₃. InCl₃ or other catalytic systems involving precious metals [AuCl(PPh₃)/AgSbF₆ (1:1), PtCl₄, or [RuCl₂(CO)₃]₂/AgOTf (1:2)] only promoted the cycloisomerization step, leading to 1,2-dihydronaphthalene derivatives. The possible occurrence of a GaCl₃-catalyzed intramolecular double to quadruple hydroarylation of alkynes was also mentioned.

When NTs-tethered arenynes (0.25 mmol) were reacted with an arene in the presence of GaCl₃ (10 mol%) the expected tetrahydroisoquinolines or tetrahydrobenzo[*h*]isoquinolines were isolated as major products (6-*exo*, eq. 2), along with 12-22% of dihydrobenzoazepine or dihydronaphthoazepine (7-*endo*, eq. 3).⁵ The latter could be selectively formed by reaction of the

corresponding 1,6-arenynes with a catalytic amount of GaCl₃ (10 mol%) (eq. 3), and high-yield access to the tetrahydroazepine derivatives was possible by further gallium-catalyzed hydroarylation (eq. 4).

The one-pot tandem cycloisomerization/Friedel-Crafts alkylation of indoles may be catalyzed by GaCl₃ (10 mol%) to form 2,5-disubstituted furans (eq. 5).⁶ The reaction proceeds *via* the activation of both the alkyne and the epoxide substrates by the Ga(III) Lewis acid center, followed by a nucleophilic attack on the epoxide and subsequent isomerization of the propargylic acetate to 2,5-disubstituted furans.

2.1.1.2 Catalyzed cycloisomerization of alkynyl indenenes

Following initial studies using platinum- and ruthenium-based catalysts, GaCl₃-catalyzed cycloisomerizations of various alkynyl indenenes were reported and provide access to the tricyclic

core of the icetexane family (natural product).^{7,8} More recently, the preparation of a key intermediate in the synthesis of hetidine and hetisine diterpenoid alkaloids was achieved using GaI₃ as catalyst (eq. 6).⁹

2.1.1.3 Dimerization of dimethyl 2-(naphthalene-1-yl)cyclopropane-1,1-dicarboxylate to [3+2], [3+3], [3+4] and spiroannulation products

The Lewis acidity of GaCl₃ was also exploited for the dimerization of dimethyl 2-(naphthalene-1-yl)cyclopropane-1,1-dicarboxylate using various reaction conditions. While the reaction between the cyclopropane derivative (0.70 mmol) and a catalytic amount of GaCl₃ (20 mol%) led to the *bis*-naphthylcyclopentane [3+2] annulation product (68%, only one diastereoisomer), a similar reaction with an equimolar amount of [GaCl₃•THF] afforded a mixture of [3+3] and [4+3] annulation products, which are derived from an electrophilic substitution at the aromatic ring (eqs. 7 and 8 respectively).¹⁰ The GaCl₃-mediated dimerization of donor-acceptor cyclopropanes (2-arylcyclopropane-1,1-dicarboxylates) proceeded in the presence of dimethyl 3,5-dimethyl-1-pyrazoline-3,5-dicarboxylate (20 mol%), *via* a dual Lewis acid/organo-catalytic process, to produce the corresponding polysubstituted 2-oxabicyclo[3.3.0]octane derivatives (eq. 9).¹¹

2.1.1.4 Ethynylation of cyclopentadienes and silylated 1,4-dienes

The acidic C-H proton of 1,2,3,4,5-pentamethylcyclopenta-1,3-diene may be activated by GaCl_3 to a presumed dienylgallium intermediate that further reacts with chloro-triisopropylsilylacetylene in the presence of *tert*-butyldiphenylsilanol and 2,6-di(*tert*-butyl)-4-methylpyridine to form 5-(triisopropylsilylethynyl)-1,2,3,4,5-pentamethylcyclopentadiene.¹² Various 1,4-diene derivatives may be accessed following a similar approach such as (*E*)-1-(triisopropylsilylethynyl)-1-[2-(*tert*-butyldimethylsilyl)ethenyl]-2-cyclohexene (eq. 10).

2.1.1.5 Coupling of naphtol, alkynes and aldehydes

The three-component coupling of naphtol with various alkynes and aldehydes catalyzed by GaCl_3 was reported to yield the corresponding 1,3-disubstituted-3*H*-benzo[*f*]chromenes (eq. 11).¹³

It was also shown that arylacetylenes and vinylarenes readily undergo hydroarylation with naphthols and phenols in the presence of GaCl_3 (10 mol%) as catalyst to produce the corresponding 2-vinylnaphthols and 2-vinylphenols in good yields with high regioselectivity.¹⁴

2.1.1.6 Insertion of isocyanides into C-S bonds

GaCl_3 (20 mol%) was shown to catalyze the insertion reaction of 2,6-dichlorophenylisocyanide into the C-S bond of various aliphatic and aromatic dithioacetals, leading to the corresponding thioimides (eq. 12).¹⁵

2.1.1.7 Bromocyanation and cyanation reactions

An efficient, high regio- and stereo-selective methodology to access (*Z*)- β -bromoacrylonitriles was developed by reaction of various alkynes with cyanogen bromide in the presence of GaCl_3 (10 mol%, eq. 13).¹⁶ Such an approach also allows the regioselective cyanation of aromatic or heteroaromatic substrates (eq. 14).¹⁷

2.1.1.8 Cyclopropylmethylation of alkyl chlorides

The cyclopropylmethylation reaction of benzylic and allylic chlorides with cyclopropylmethylstannane may be catalyzed by gallium and indium halides (best performed with GaCl₃ and InBr₃) to afford various cyclopropane derivatives along with the corresponding terminal alkene products (eq. 15).¹⁸ The X-ray determined (XRD) molecular structure of a butenylgallium dichloride species (see inset in eq. 15) comforted the proposed mechanism, thought to proceed *via* an initial transmetalation between the stannane species and GaCl₃ yielding a butenylgallium complex. The latter activates the alkyl chloride, possibly leading to the formation of a zwitterionic GaCl₃⁻/carbocation adduct. The final step consists in the cyclization and concomitant release of GaCl₃. A hydride shift occurring on the zwitterion would yield the alkene product.

2.1.1.9 Hydroamination reactions

GaCl₃ is a suitable catalyst for the hydroamination of alkynes with aromatic amines with the exclusive formation of Markovnikov products (eq. 16).¹⁹ DFT studies suggest the initial coordination of the alkyne to GaCl₃, followed by nucleophilic addition of the aniline derivative resulting into a zwitterionic GaCl₃⁻/NH₂Ar⁺ alkene intermediate. The latter can lead to the enamine/ketamine intermediate and regenerate GaCl₃ *via* an aniline-assisted proton transfer.

2.1.2 Gallium bromide

2.1.2.1 Carbogallation of alkynes

GaBr₃ (1 equiv) reacted with a mixture of a silyl ketene acetal derivatives and aromatic alkyne derivatives or 1-octyne to generate an alkenylgallium intermediate, which may further be quenched with I₂ to yield the corresponding iodoalkene product (eq. 17).²⁰ The mechanism was proposed to first involve the activation of the alkyne by the Lewis acidic Ga(III) center, followed by a nucleophilic *anti*-attack of the ketene silyl acetal to produce the corresponding monoalkenylgallium dibromide derivative along with elimination of Me₃SiBr. The resulting Ga(III) vinylic species may then activate a second alkyne and promote, *via* attack of a second ketene silyl acetal, the formation of a stable dialkenylgallium bromide complex. The XRD molecular structure of a pyridine adduct analogue (see inset in eq. 17) supports the proposed mechanism. It is noteworthy that such alkenylgalliums may be *in-situ* generated and used as reagents for sequential Pd-catalyzed cross-coupling reactions with various aryl iodides.

2.1.2.2 [4+3] cycloaddition of indoles, aldehydes/ketones and dienes to cyclohepta[*b*]indoles

The formation of cyclohepta[*b*]indole derivatives by a three-component [4+3] cycloaddition, using various indoles, aldehydes or ketones and dienes may be mediated by GaBr₃ (10 mol%, eq. 18).²¹ Interestingly, InBr₃ and Ga(OTf)₃ also proved to be efficient catalysts for this transformation, though GaCl₃ was found inactive. The solvent also strongly influences the reaction and coordinative solvents such as THF and Et₂O should be avoided.

2.1.2.3 Reduction of esters and lactones

GaBr₃ (1 mol%) was also demonstrated to catalyze the reduction of biomass-derived fatty esters, triglycerides and lactones with 1,1,3,3-tetramethyldisiloxane (TMDS) to afford the respective ethers in good yields (eq. 19).²² Interestingly, no alcohol formation is observed, and the reducing agent TMDS is polymerized to high-molecular-mass polydimethylsiloxane during the reaction, facilitating the separation and isolation of the ether product.

2.1.3 Gallium iodide

GaI₃ was very recently found to be an efficient (though stoichiometric) agent for the iodocyclization of 1,6-diynes to produce vinyl iodides under mild conditions (eq. 20).²³ Under acidic conditions, the iodocyclization products may undergo *in-situ* Friedel-Crafts cyclization. Alternatively, the isolated vinyl iodides may be used as substrates for cross-coupling reactions.

2.1.4 Gallium triflate

A recent review detailed the synthetic applications of Ga(OTf)₃ as a Lewis acid catalyst for numerous organic transformations along with its attractive features compared to other Lewis acids.²⁴

2.1.4.1 Direct substitution of alcohols with sulfur nucleophiles

The strong Lewis acid $\text{Ga}(\text{OTf})_3$ may efficiently catalyze the substitution of primary and secondary alcohols (including aromatic and heteroaromatic derivatives) with sulfur nucleophiles (eq. 21), leading to useful synthetic intermediates for the synthesis of sulfones.²⁵

2.1.4.2 Synthesis of quinoxaline and 1,5-benzodiazepine derivatives

Quinoxaline and 1,5-benzodiazepines are important structural motifs in the biological and pharmaceutical fields since they most notably constitute the core structure of various antibiotics, analgesics and anti-inflammatory drugs. Therefore, the high yield synthesis of quinoxalines and 1,5-benzodiazepines by condensation of 1,2-diaminoaryls with 1,2- and 1,3-diketones in the presence of a catalytic amount of $\text{Ga}(\text{OTf})_3$ (5 mol%) represents an important contribution (eq. 22).²⁶

$\text{Ga}(\text{OTf})_3$ (10 mol%) was also shown to readily catalyze [4+3] and [4+2+1] cycloaddition reactions of *o*-phenylenediamines with various functionalized ketones to access a large library of 2,3-, 2,4- and 2,5-disubstituted benzodiazepine derivatives.^{27,28}

2.1.4.3 Propargyl-allenyl isomerization/intramolecular [4+2] cycloaddition cascade reaction

A $\text{Ga}(\text{OTf})_3$ -promoted intramolecular [4+2] cycloaddition occurred under mild conditions from a vinylallene intermediate, derived from a propargyl-allenyl isomerization, to produce 1,3-dihydrobenzo[*c*]thiophene derivatives (eq. 23).²⁹

2.1.4.3 Hydroamination of aldehydes

The efficient synthesis of aryl benzyl amines bearing various functional groups was achieved *via* a one-pot, three-component (aldehyde, aryl amine, organosilane) reaction catalyzed by $\text{Ga}(\text{OTf})_3$ (5 mol%, eq. 24).³⁰ It was suggested that the reaction involves silane addition to a $\text{Ga}(\text{OTf})_3$ -activated aldimine intermediate.

2.1.4.4 Reduction of ketones

In a similar vein to the GaBr_3 -catalyzed reduction of esters, the reduction of alkyl and aryl ketones to the corresponding methylene products was performed using Me_2SiHCl and $\text{Ga}(\text{OTf})_3$ (5 mol%) as Lewis acidic catalysts.³¹

2.1.4.5 Domino arylation/oxycyclization of allenes with phenols

Access to dihydrobenzofuran-appended oxindoles, a common motif in a variety of natural products, may be realized through a $\text{Ga}(\text{OTf})_3$ -catalyzed reaction between allenols and phenols (eq. 25).³² The simultaneous interaction of $\text{Ga}(\text{OTf})_3$ with the allene and phenol moieties was proposed with the formation of a $\text{Ga}(\pi\text{-allene})$ phenolate species.

2.1.5 Tris(pentafluorophenyl)Gallium

The strong and robust Lewis acid organometallics $\text{Ga}(\text{C}_6\text{F}_5)_3$, readily accessible from GaCl_3 and $\text{Zn}(\text{C}_6\text{F}_5)_2$ (eq. 26), was recently used as olefin polymerization initiator. For instance, $\text{Ga}(\text{C}_6\text{F}_5)_3$ effectively polymerizes styrene for the production of medium-to-high molecular weight polystyrene (PS, $M_w = 26.05 \text{ kg}\cdot\text{mol}^{-1}$, $\text{PDI} = 2.4$) in aqueous solution. It is much less active in isobutene (IB) polymerization. These polymerizations are likely initiated by proton transfer from the $(\text{H}_2\text{O})\text{Ga}(\text{C}_6\text{F}_5)_3$ adduct to the monomer and subsequent chain growth would proceed through a cationic mechanism (eq. 27).³³

2.2 Gallium(III) coordination compounds in organic Synthesis

This section describes the use of discrete ligand-supported gallium complexes for the mediation of organic synthesis (polymerization catalysis will be discussed in the section 2.3). Two recent reviews detail the applications of well-defined gallium (pre)catalysts for various catalytic applications and associated structure/activity relationships.^{34,35}

2.2.1 *N,O,N*-diamino-ether tridentate ligand

2.2.1.1 [(*N,O,N*)Ga(NMe₂)]-catalyzed hydroamination of terminal alkynes

The tetracoordinate Ga complex [κ^3 -(*N,O,N*)-{(C₅H₉)N-C₆H₄O}₂Ga(NMe₂)] (eq. 28, inset), prepared by an amine elimination reaction between the diamino-ether ligand precursor and [Ga₂(NMe₂)₆], catalyzes the hydroamination of various terminal alkynes with aniline or butylamine to yield Markovnikov-type products (eq. 28).³⁶ Such complexes are much more effective than [Ga₂(NMe₂)₆], which was attributed to a ligand-imposed constrained geometry in (*N,O,N*)Ga amido species resulting into an enhanced Lewis acidity at Ga(III).³⁷ It is thought that the catalysis occurs *via* an initial reaction of the amine substrate by the Ga(III) precursor to generate an gallium amido species that would act as the actual catalyst. The XRD molecular structure of the dimeric amido species [(*N,O,N*)Ga(NHPh)]₂ supported such a proposal.

2.2.2 *O*₃-tris(*m*-arylbenzyl)arene cage-shaped ligands

2.2.2.1 [(*O*₃)Ga] tri- and tetra-coordinate complexes-catalyzed hetero Diels-Alder reaction

The hetero Diels-Alder reaction between Danishefsky's diene and benzaldehyde catalyzed by cage-shaped tetrahedral gallium(III) complexes of the type (*O,O',O''*)Ga(L) (10 mol%, L = pyridine) was reported.³⁸ The latter Ga(III) chelates were found much more efficient than the corresponding [(py)Ga(OPh)₃] analogue. Effect of the substituents on both the phenoxy rings and the connecting arene were studied and the best performances were observed for R = H and R' = Me, respectively (eq. 29 inset).

2.2.3 *N*-heterocyclic carbene (NHC) ligand

The coordination chemistry of NHCs to Ga(III) was recently investigated to access robust Ga(III) complexes of potential use in catalysis as alternatives to gold-based catalysts.³⁹ The exceptional σ -donating properties of NHC ligands were shown to be beneficial to the stability of the resulting NHC-based Ga(III) compounds.⁴⁰ Ga(III) cations of the type $[(\text{NHC})\text{GaX}_2]^+$ were readily synthesized from their corresponding neutral analogues $[(\text{NHC})\text{GaX}_3]$ (X = halogen) *via* chloride abstraction, a well-established methodology for the generation of group 13 cationic compounds.^{41,42}

2.2.3.1 Cationic NHC-Ga complexes for cycloisomerization/Friedel-Crafts cascade reaction

NHC-Ga(III) cations are effective catalysts for the cycloisomerization/Friedel-Crafts cascade reaction of 1,6-arenynes and anisoles and perform much better than simple gallium halides (Section 2.1.1.1). The salt $[(\text{IDipp})\text{GaCl}_2][\text{SbF}_6]$ (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) displayed the highest activity (eq. 30).^{42,43} However the latter is moisture sensitive and *in-situ* generation of the active cationic species is preferred. At best, a 1/2 $[(\text{IDipp})\text{GaCl}_3]/\text{AgSbF}_6$ catalytic mixture (1 mol% in Ga) led to the quantitative formation of the desired product. The nitrile-stabilized four-coordinate Ga cation $[(\text{IDipp})\text{Ga}(\text{Cl})_2(\text{TFB})]^+$ are also active in such a catalysis.

Both the salt [(IDipp)GaCl₂(TFB)][SbF₆] (5 mol%) and [(IDipp)GaCl₃]/AgSbF₆ (5:7 mol%, respectively) system efficiently catalyze the tandem cycloisomerization/Friedel-Crafts reaction of a bicycle substrate (eq. 31).

The cycloisomerization of an enyne and trapping with anisole may also be mediated (eq. 32).⁴³

2.2.3.2 (NHC)-Ga cationic complexes-catalyzed transfer hydrogenation

NHC-supported Ga(III) cations also efficiently catalyze under mild conditions the chemoselective reduction of various alkenes *via* transfer hydrogenation using 1,4-cyclohexadiene (CHD) as hydrogen source (eq. 33), a type of reaction only thus far mediated by noble-metal catalysts.⁴⁴ The one-pot catalytic hydrogenative cyclization of arenynes may also be mediated allowing the isolation of bi- and tri-cyclic products (eqs. 34 and 35).⁴⁴

2.2.4 *N*₂-, *N*₄-, *N*₅-, and *N*₆-polyamine ligands

2.2.4.1 [(*N*_{*x*})GaCl₂]Cl-catalyzed alkene epoxidation

Gallium-catalyzed alkene epoxidation was investigated using polyamine-supported [(*N*_{*x*})_{*y*}GaCl₂]Cl (*x* = 2; *y* = 2 and *x* = 4, 5, 6; *y* = 1) cationic complexes (eq. 36), readily accessible by reaction of the neutral polydentate amine ligands with GaCl₃, in the presence of peracetic acid (PAA_R). The use of phenanthroline (phen) ligands led to the highest catalytic activities with the selective formation of the epoxide product.^{45,46} Penta- and hexa-dentate polyamine ligands exhibited the lowest activity, suggesting the competition between the N-ligand and the coordination of PAA_R. Such trends were rationalized by means of DFT calculations.

N-ligands:

for $x = 2$; $y = 2$:

or $H_2N-CH_2-CH_2-NH_2$

for $x = 4-6$; $y = 1$:

2.3 Gallium(III) coordination compounds in polymerization catalysis

2.3.1 Ring-opening polymerization (ROP) of cyclic esters and carbonates

A recent review summarized the use of Ga(III) and In(III) compounds in the ROP of cyclic ethers, esters and carbonates up to 2013, a class of species much less explored than their Al(III) counterparts.⁴⁷ The present sub-section will highlight the most representative developments in the ROP of cyclic esters/carbonates, an area of topical interest due to the biodegradability of the derived polymers.^{48,49,50,51} The main challenges in metal-catalyzed ROP of cyclic esters and carbonates are the development of systems exhibiting high polymerization activity and control (including stereocontrol) for the production of well-defined and possibly stereoregular polymers. The possible stereochemical outcomes are depicted in eq. 37 for the ROP of *rac*-lactide (*rac*-LA).

The possible use of well-defined gallium complexes as ROP initiators of cyclic esters and carbonates was only recently investigated. Dimeric Ga(III) alkyl/alkoxide (alkoxide = (*S*)-lactate) complex (*S,S*)-[GaMe₂(μ-OCH(Me)CO₂Me)]₂ (**1**, Figure 1) was shown to polymerize *rac*-LA in a living and controlled manner to afford narrowly disperse atactic PLA.⁵² Interestingly, the addition of an external Lewis base, such as THF or moreover γ -picoline led to a stereoselective polymerization of *rac*-LA with the production of heterotactically enriched PLA ($P_r = 0.60$ - 0.78). The addition of organic super-bases, *i.e.* 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) led to the isoselective ROP of *rac*-LA ($P_m = 0.79$) and significantly improved ROP performances.^{53,54} NHC-supported Ga(III) species of the type (NHC)GaMe₂OR (**2**, Figure 1) displayed higher ROP activity, which was ascribed to the increased basicity of the Ga-OR moiety due to the coordination of the NHC.

The constrained trigonal-monopyramidal (*N,O,N*)-gallium(III) complex, κ^3 -*N,O,N*-{[(C₅H₉)NC₆H₄]₂O}Ga(NMe₂) (**3**, Figure 1) effectively mediates the controlled ROP of *rac*-LA to afford chain-length controlled and narrow disperse PLA ($M_{n(\text{theo})} = 14400$, $M_{n(\text{GPC})} = 12400$, PDI = 1.12). In addition, isotactically enriched PLA ($P_m = 0.70$) may also be produced.⁵⁵ Remarkably, the Ga(III) compound **3** exhibits better ROP activity and control than its Al(III) analogue, which clearly highlights the interest of Ga species in cyclic esters polymerization. Compound **3** also initiates the controlled ROP of ϵ -caprolactone (ϵ -CL) and trimethylene carbonate (TMC). Likewise, the *bis*-8-quinolinolato gallium(III) *tert*-butoxide species [Ga(O*t*Bu)(*N,O*)₂] (**4**, Figure

1), *in-situ* generated by reaction of the $[\text{GaCl}(\text{N},\text{O})_2]$ chloride derivative with 1 equiv. KOtBu , also efficiently mediates the controlled and isoselective polymerization of *rac*-LA for the production of well-defined PLA ($M_{\text{n(GPC)}} = 14600$, $\text{PDI} = 1.25$, $P_{\text{m}} = 0.70$) and was found to be nearly 3 times faster than its Al analogue $[\text{Al}(\text{OtBu})(\text{N},\text{O})_2]$.⁵⁶

Recently, the potential of chiral salen-supported Ga(III) complexes in ROP was also investigated: a series of bimetallic Ga(III) dialkyl complexes (**5**, Figure 1) were reported to polymerize *rac*-lactide, albeit with a poor ROP control.⁵⁷

Figure 1. Gallium(III) compounds synthesized for application in ring-opening polymerization (ROP) of cyclic esters and carbonates.

2.4 Gallium(II) complexes of *N,N*-BIAN ligands

2.4.1 $[(\text{Dipp-BIAN})\text{Ga-Ga}(\text{Dipp-BIAN})]$ -catalyzed hydroamination of alkynes

The digallane Ga(II)-Ga(II) species **6** (Scheme 1), which bears a redox-active BIAN-type ligand, was shown to catalyze the hydroamination of alkynes (using various anilines) to afford the corresponding Markovnikov imine products with a low catalyst loading (2 mol%). The catalysis

proceeds *via* the formation of unusual [3+2] cycloadducts such as **7** (Scheme 1).^{58,59} The regioselectivity of the hydroamination products agrees well with a concerted 1,3-dipolar addition with, in the case of the phenylacetylene cycloaddition product, a Ph group pointing away from the Ga(II) center. Amine nucleophilic attack on species **7** occurs and subsequent proton transfer produces the imine final product and regenerates digallane **6**.

Scheme 1. Proposed mechanism for hydroamination of alkynes catalyzed by digallane **6**. The addition adduct **7** was also isolated.

2.5 Gallium(I) salts

2.5.1 $[\text{Ga}(\text{Arene})_2]^+[\text{Al}(\text{OR}^F)_4]^-$ salts in olefin polymerization

The synthesis of a series of Ga(I) cations (as $[\text{Al}\{\text{OC}(\text{CF}_3)_4\}]$ salts) (inset, eq. 38), which are stabilized by *ansa*-type *bis*-arenes was recently developed.^{60,61} The latter complexes are highly active initiators for isobutene (IB) polymerization (with a catalyst loading down to 0.007 mol%) to afford highly reactive polyisobutylene (α -content > 60%, $M_n < 2300 \text{ g}\cdot\text{mol}^{-1}$) in good yields (eq. 38). The nature of the arene ligands and the reaction temperature strongly affect the activity/control of the polymerization. All experimental and computational data agree with a coordinative polymerization mechanism.

3. INDIUM COMPLEXES

Over the past few years, a growing number of reports has been published on indium catalysis, recognizing that In(I) and In(III) complexes exhibit highly desirable properties to build efficient and ecofriendly catalytic systems.^{62,63} Up to a few years ago, indium catalysis was mainly being developed for Barbier type-, cross coupling-, transesterification-, Mukaiyama-, cyanation-, esters or aziridine ring opening-reactions. The ring opening polymerization (ROP) of polar cyclic monomers mediated by indium species remained in its infancy.⁴⁷ Since 2009, a rich diversity of indium mediated reactions⁶⁴ has been developed including the first use of well-defined and isolated In(I) species in homogeneous catalysis.

3.1 Indium(III) halides and salts

3.1.1 Indium chloride (InCl_3)

3.1.1.1 Cyclization of α -azido chalcones with dicarbonyls: Synthesis of substituted pyrroles

The reaction of α -azido chalcones with 1,3-diketones in the presence of InCl_3 (20 mol%) produces tetrasubstituted pyrroles (eq. 39).⁶⁵ The reaction proceeds by denitrogenative decomposition of the α -azido chalcone to form a highly strained 2H-aziridine which undergoes a nucleophilic attack from the diketone. The role of indium is likely to promote the formation of a more nucleophilic indium-enolate intermediate from diketone tautomerization.⁶⁶ Surveying other Lewis acids based on Zn(II), Fe(III), Ag(I), Sc(III) and BF_3 results in lower reaction yields.

3.1.1.3 Heck coupling: Synthesis of internal alkenes

The reaction of terminal alkenes with aryl iodides in the presence of 5 mol% of InCl_3 and sodium acetate produces stereoselectively internal *E*-aryl alkenes (eq. 40).⁶⁷ Compared to classical

palladium Heck coupling (Pd(II)/Pd(0) cycles), a different mechanism was proposed involving alkene insertion into the In(III)-C_{aryl} bond of an aryliindium^{III} dichloride intermediate and subsequent β -H elimination. The presence of electron donating groups (EDGs) on terminal aryl alkenes led to high yields above 90% whereas the presence of electron withdrawing groups (EWGs) lowers the yields to 70 - 80%. Aliphatic- or ester-functionalized terminal alkenes are also suitable coupling partners. Aryl iodides with EDGs or EWGs, 1-iodonaphthalene, 2-iodopyridine, and even 2-iodothiophene provide reaction yields above 80%.

3.1.1.4 One pot coupling of *E*-*N*-methyl-1-(methylthio)-2-nitroethenamine (NMSM), aromatic aldehydes and 3-cyanoacetyl indoles: Synthesis of indolylpyrans

The multi-component reaction (MCR) of NMSM, 3-cyanoacetyl indole and functionalized benzaldehydes in the presence of 20 mol% of InCl₃ produces chemo- and regio-selectively highly functionalized 3-pyranyl indoles (eq. 41).⁶⁸ This reaction takes advantage of the versatility of NMSM which contains four reactive sites (nitro-, amine-, thio, olefin- groups). This robust protocol may be used with various aldehydes and substituted 3-cyano-acetyl indoles. Other Lewis acids or Lewis bases such as piperidine, triethylamine, FeCl₃, Cu(OTf)₂ catalyze this reaction less efficiently than InCl₃.

3.1.1.5 Direct benzylic addition of trifluoromethyl ketones (TFMKs) to 2-methylazaarenes: Synthesis of 2-trifluoromethyl-alkoxy-azaarenes

The reaction of 2-methylazaarenes with TFMKs in the presence of InCl₃ (5 mol%) affords 2-trifluoromethyl-alkoxy-azaarenes (eq. 42).⁶⁹ In this C(sp³)-H functionalization of 2-

methylazaarenes, the Lewis acidic In(III) center activates both substrates. Coordination of TFMKs to In(III) enhances the electrophilicity of the carbonyl fragment while the N-coordination of 2-methylazaarenes to In(III) promotes the formation of nucleophilic tautomer In-enamide complexes. Lewis acids based on Yb(III), Fe(III), Co(II), Cu(II), Mn(II), Ni(II) and Pd(II) metals results in lower reaction yields. Ester-, heterocycle-, aliphatic-, and EWG-aryl-TFMKs are suitable substrates unlike EDG- or *o*-substituted aryl TFMKs.

3.1.1.6 Dehydrative thiolation of allenols: Synthesis of 1,3-dien-2-yl-sulfanes

The InCl_3 -catalyzed dehydrative addition of thiols to allenols was reported to produce stereoselectively (*E,E*)-1,3-dien-2-yl-sulfanes (eq. 43).⁷⁰ Depending on thiol acidity, two reaction mechanisms were proposed, involving a thiol nucleophilic attack at either a π -allenylindium complex or at an In(III) alkoxide intermediate. Alkyl-, heterocycle-, EDG-aryl-, and slightly EWG-aryl- allenols are suitable substrates. Interestingly, the reaction remains stereoselective with alkyne- or alkene-allenols yielding ynediene- and triene-type scaffolds. Thiophenols with EWGs are also excellent substrates.

3.1.1.7 ROP of lactide: Synthesis of PLA

InCl_3 may readily initiate the controlled ROP of lactide (up to 800 equiv of lactide) in the presence of 1 equiv of *n*BuOH and 2 equiv of triethylamine to produce narrow disperse PLA with controlled molecular weights (M_n) and $\text{PDI} < 1.10$ and end-capped with a *n*BnO-group (eq. 44).⁷¹ Experimental data suggest a coordination-insertion mechanism with an *in situ* generated dinuclear

InCl₃ 0.125 - 2 mol%
 NEt₃, BuOH
 neat, 25 °C,
 5 - 24 h

7 examples (conversions > 97%)

(44)

3.1.2.1 Cross-Claisen condensation between carboxylic acids and ketene silyl acetals: Synthesis of β -keto esters

(45)

29

The one pot reaction of carboxylic acids with alcohols in the presence of InBr_3 (5 mol%) and excess polymethylhydrosiloxane (PHMS) afforded the corresponding ether derivatives (eq. 46).⁷⁴ Such a In(III) -catalyzed reduction reaction proceeds *via* the initial formation of the ester derivatives and a subsequent reduction by PHMS to form the ether product along with reticulated polymethylsiloxane. Other hydrosilanes such as triethylsilane, phenylsilane, or TMDS were less effective. Aliphatic-, and EWG-aryl- carboxylic acids are suitable substrates. With thioether functionalized carboxylic acids, the reaction stops at the ester formation, suggesting competition between the softer sulfur atom and the carbonyl group for coordination to In(III) .

3.1.2.3 Prins cyclization and homobromination of dienyl alcohols with aldehydes: Synthesis of 4-(2-bromoethylidene)tetrahydropyrans

The synthesis of 4-(2-bromoethylidene)tetrahydropyran derivatives may be achieved via an InBr_3 -catalyzed process involving the reaction of aldehyde substrates with dienyl alcohols in the presence of trimethylsilylbromide (eq. 47).⁷⁵ The reaction is highly stereoselective toward the formation of *cis*-tetrahydropyranyl rings with exocyclic *E*-alkenes that may be converted (*via* allylic substitution) to more stable 2-(tetrahydropyran-4-ylidene)ethyl 3,5-dinitrobenzoate esters. The reaction mechanism involves the formation of an oxacarbenium intermediate responsible for the *exo*-alkene configuration. InCl_3 , InI_3 and In(OTf)_3 are less efficient catalysts. *E*-selectivity decreases with sterically bulky alkylaldehydes, benzaldehydes bearing EDGs and dienyl alcohols. Interestingly, a reversal of selectivity is observed with dienyl alcohols bearing two methyl substituents at the 2-position, with the quantitative formation of the *Z*-alkene products.

3.1.2.4 Coupling between silyl enolates and alkyl chlorides or alkyl ethers: Synthesis of α -alkyl carbonyl compounds

α -Alkyl-esters/ketones/aldehydes may be accessed *via* an InBr_3 -catalyzed reaction of alkyl chlorides and ketene silyl acetals, silyl ketone enolates and silyl aldehydes enolates, respectively, eq. 48).⁷⁶ The key step of the reaction mechanism involves a nucleophilic attack from the silyl enolate on a carbocation generated *via* Br^- abstraction (at R-Br) by InBr_3 . Coordinative solvents quench the reaction while essentially no reaction was observed with common metal-based Lewis acids or other In(III) salts. Benzyl chlorides and tertiary alkyl chlorides, with or without *O*-groups, are good substrates. Primary-, and secondary-alkyl chlorides are unreactive, in line with a reaction occurring through the formation of a carbocation intermediate. It is also noteworthy that dialkyl-, monoalkyl-ketene silyl acetals, dialkyl ketone silyl enolates, and dialkyl aldehyde silyl enolates also efficiently react with primary and secondary methyl ethers in the presence of InBr_3 (eq. 49).

3.1.2.5 Reductive bromination/iodination of carboxylic acids: Synthesis of alkyl bromides/iodides

The reduction of carboxylic acids may be mediated by InBr_3 (5 mol%) in the presence of trimethylsilylbromide and excess TMDS to yield alkyl bromides (eq. 50).⁷⁷ Experimental data on the mechanism unveils three steps promoted by In(III). First, the carboxylic acid reacts with TMDS to generate a silyl ester that is then converted to the corresponding silyl ether *via* double hydrosilylation with TMDS. A bromide substitution by trimethylsilylbromide at the formed silyl

ether then yields the alkyl bromide and siloxane. Other common bromine sources such as Br₂, PBr₃, *N*-bromosuccinimide, LiBr or [N(*n*Bu)₄]Br were unsuccessful for the present reaction. Aliphatic carboxylic acids including those with halogen-, hydroxyl-, ester-, alkene-, thio- groups, and benzoic acids with EDGs and EWGs are suitable substrates.

Likewise, the InBr₃-catalyzed reductive iodination of carboxylic acids to afford the corresponding alkyl iodides was also described using I₂ as an iodine source (eq. 51).⁷⁸

3.1.2.7 One pot hydroamination/hydrosilylation of terminal alkynes with anilines: Synthesis of aromatic secondary and tertiary amines

A hydroamination/hydrosilylation sequence catalysis was recently reported using InBr₃ (3 mol%) to afford secondary and tertiary aromatic amines starting from alkyne and amine reagents (eq. 52).⁷⁹ With unsymmetrical alkynes, the hydroamination step is highly regioselective with the formation of Markovnikov-type enamines. Experimental data support a reaction mechanism involving an aniline nucleophilic attack at a In(III) π -alkyne complex to yield an enamine/imine product. In(III) activation of the imine moiety promotes hydrosilylation to afford, after hydrolysis, the amine product. Other Lewis acids based on Al(III), Ga(III), Zn(II) or silanes such as TMDS and PMHS are less efficient. Also, the reaction does not proceed with primary aliphatic amine substrates.

3.1.2.8 Addition of carbon dioxide to epoxide: Synthesis of cyclic carbonates

The preparation of cyclic ethylene carbonates from CO₂ and epoxides may be realized through the use of a InBr₃/PPh₃ catalytic mixture (eq. 53), a reaction not occurring when using InCl₃ instead of InBr₃.⁸⁰ It seems likely that a bis- or mono-phosphine In(III) tribromide complex initially forms *in situ*, enhancing the nucleophilicity of the In–Br bonds. Coordination of the epoxide to the In(III) center and subsequent ring-opening by an In–Br moiety yields an In(III) 2-bromoethan-1-olate dibromide that further reacts/cyclizes with carbon dioxide to yield the final ethylene carbonate. Such reaction may be carried out efficiently with epoxides bearing aliphatic-, aromatic-, vinyl-, halide-, ether- and ester- groups.

3.1.3 Indium iodide (InI₃)

3.1.3.1. Cascade polycyclization of polyenyl propargylic silyl ethers: Synthesis of chiral (terpenoid) polycycles

Tricyclic-, tetracyclic-, or pentacyclic-incorporating organics may be prepared with In(III) catalysis through Lewis-acid-assisted cascade polycyclization. The reaction of 6-enyl-9-aryl-, 6,10-dienyl-13-aryl-, or 6,10,14-trienyl-17-aryl- propargylic silyl ethers in the presence of InI₃ (20 mol%) afforded the corresponding tricyclic-, tetracyclic-, or pentacyclic-allylic silyl ethers (eq. 54).⁸¹ The use of InBr₃ and other metal-based Lewis acids led to lower catalytic activity. This cascade reaction likely starts with the formation of a highly electrophilic In(III) π -alkynyl complex acting as a masked carbocation. The presence of phenolic-, hydroxyl-, ester-groups is tolerated, which renders this polyannulation strategy appealing for the total synthesis of terpenoids and sterols.

3.1.3.2 Direct use of esters in the Mukaiyama aldol reaction: Synthesis of β -alkoxy esters

The InI_3 -catalyzed reaction of esters with ketene silyl acetals in the presence of dimethylphenylsilane afforded β -alkoxy esters (eq. 55).⁸² Other In(III) salts, including the more Lewis acidic InBr_3 , InCl_3 , In(OH)_3 , In(OTf)_3 analogues led, at best, to low yields in β -alkoxy esters. The reaction likely occurs with an initial In(III) -ester adduct that is then hydrosilylated to afford a silyl acetal species. In(III) activation of the latter may promote the elimination of the alkoxide group to afford either a silyl oxonium intermediate and an In(III) alkoxide, or an In(III) -aldehyde adduct complex and a silyl ether. The nucleophilic attack of the ketene silyl acetal on the oxonium- or aldehyde- intermediates would yield a β -siloxycarbonyl species, following the Felkin-Anh rules for stereoselectivity. Upon reaction quenching, hydrolysis of the β -siloxycarbonyl compound yields the final β -alkoxy ester. Dialkyl-, and unsubstituted-ketone silyl enolates afforded β -alkoxy ketones, albeit in moderate yields.

3.1.3.3 Reductive sulfidation of aromatic carboxylic acids or aldehydes: Synthesis of aromatic thioethers

The combination of benzoic acid and benzaldehyde with elemental sulfur (S_8) in the presence of InI_3 (5 mol%) and excess of TMDS allowed access to symmetrical dibenzyl thioethers (eq. 56).⁸³

Based on experimental data, a disilathiane derived from the reaction In(III)-activated S₈ with TMDS is probably the sulfur source for this multistep reaction.

3.1.3.4 Intramolecular hydroarylation of aryl propargylic esters: Synthesis of 2H-chromenes

Aryl propargylic ethers may undergo an intermolecular cyclization catalyzed by InI₃ (5 mol%) to produce 2H-chromenes (eq. 57).⁸⁴ In contrast to Au(I) catalysis, the In(III)-mediated process occurs with high regioselectivity with the formation of 6-*endo*-products. This suggests that the product is formed by an aromatic electrophilic addition at a preformed In(III) π -alkynyldichloride complex to yield a cationic bicyclic In(III) alkenyl intermediate. A subsequent aromatization and protolysis affords the 2H-chromene product. Here again, going from InI₃ to InBr₃, InCl₃ or In(OTf)₃ as catalysts resulted in lower conversions or extensive decomposition. Overall, in term of efficiency and regioselectivity, InI₃ outperforms other well-established systems based on Ru(II), Ga(III), Au(I) and Pt(II).

3.1.4 Indium triflate (In(OTf)₃)

3.1.4.1 Nazarov reaction of aryl vinyl ketones: Synthesis of indanones

The strong Lewis acid $\text{In}(\text{OTf})_3$ may catalyze the formation of indanones from aryl vinyl keto-esters in the presence of diphenyl phosphoric acid (DDP, 2 mol%, eq. 58).⁸⁵ The bulkiness of the α -ester *O*-groups does not impact ketone reactivity. Finally, the presence of *meta*-methoxyl group (EDG) on the α -ketone aryl substituents led to a faster reaction, suggesting a mechanism involving an electrophilic aromatic substitution.

3.1.4.2 Head-to-tail heterodimerization of vinylarenes and 1,1-diarylethenes:

Synthesis of trisubstituted triarylalkenes

The coupling of vinylarenes with 1,1-diarylethenes in the presence of $\text{In}(\text{OTf})_3$ (10 mol%) produces triarylalkenes (eq. 59). The presence of $\text{In}(\text{III})$ appears crucial to ensure chemo- and regio-selective head-to-tail heterodimerization, presumably thanks to the stabilization of carbocationic species formed during the reaction.⁸⁶ It seems probable that coordination of $\text{In}(\text{III})$ to styrene yields the benzylic carbocation that reacts with 1,1-diarylethene to generate a diaryl-stabilized tertiary carbocation. Proton migration and regeneration of $\text{In}(\text{OTf})_3$ affords the triarylalkene product. Homodimerization of styrene is minimized due to the preferred generation of a diaryl tertiary carbocation. Besides, the reversible coordination of 1,1-diarylethene to $\text{In}(\text{III})$ ensures a kinetic protection by the aryl groups preventing the formation of undesired hetero- or homo- dimerization products. Other Lewis acids based on $\text{Fe}(\text{III})$, $\text{Cr}(\text{III})$, $\text{Zn}(\text{II})$, $\text{Cu}(\text{II})$, $\text{Yb}(\text{III})$ resulted in lower yields.

3.1.4.3 Nucleophilic aromatic substitution on thiophenes using indoles: Synthesis of heteroaryl-heterocycles compounds

Lewis acid catalysis using $\text{In}(\text{OTf})_3$ was exploited to generate heteroaryl/heterocycle compounds upon combining methoxythiophenes and indoles (eq. 60).⁸⁷ Deuterium-labeling experiments support a reaction mechanism based on aromatic nucleophilic substitution ($\text{S}_{\text{N}}\text{Ar}$). Other $\text{In}(\text{III})$ salts were less efficient catalytic systems. Indoles with EDGs and moderate EWGs are also suitable nucleophiles. Thiophenes with EWGs are unreactive, presumably reflecting their inability to form reactive $\text{In}(\text{III})$ π -complexes. Other heterocycles such as 1-methyl-pyrroles or 3-(carboxylate)-indoles also undergo efficient $\text{In}(\text{OTf})_3$ -catalyzed $\text{S}_{\text{N}}\text{Ar}$ with various indoles.

3.1.5 Indium triflimidate ($\text{In}(\text{NTf}_2)_3$)

3.1.5.1 Reductive alkylation of indoles with alkynes: Synthesis of 2-functionalized indoles

Though less studied, $\text{In}(\text{NTf}_2)_3$ also lies among the efficient and readily available $\text{In}(\text{III})$ -based Lewis acids suitable for catalysis. Thus, alkynes and indoles readily react in the presence of $\text{In}(\text{NTf}_2)_3$ (15 to 30 mol%) and excess methyldiphenylsilane to afford 2- or 3- alkylindoles (eq. 61).⁸⁸ A mechanistic proposal included the formation of an $\text{In}(\text{III})$ π -(3-indolyl)alkenyl species and a silane-water adduct as key intermediates for the reaction to occur. Various indoles and alkynes were successfully reacted, highlighting the broad applicability of this indium-based Lewis acid catalysis.

3.1.5.2 Conia-ene type cyclization of α -(ω' -alkynyl)- β -ketoesters and ω -alkynyl- β -ketoesters: Synthesis of five to fifteen membered rings

The intramolecular cyclization of α -(ω' -alkynyl)- β -ketoesters and ω -alkynyl- β -ketoesters may be efficiently mediated by $\text{In}(\text{NTf}_2)_3$ (1 to 5 mol%) to produce five-, six-, and more interestingly, up to fifteen-membered rings (eq. 62).⁸⁹ Contrary to transition metals which promote thermal Conia-ene-type cyclization *via* enol-, alkyne-, or enyne- activation, indium displays a specific enol/alkyne double activation. Thus, an $\text{In}(\text{III})$ enolate species forms and activates the alkyne moiety. This push-pull activation of the substrates by a single metal site circumvents the entropic and enthalpic drawbacks inherent to the formation of medium- and large-sized rings. α -(ω' -alkynyl)- β -ketoesters yield exclusively to 5-6- or 7- membered rings while ω -alkynyl- β -ketoesters provide access to larger cycles containing up to 15 carbons. For instance, this methodology allowed a two-step synthesis of ($\pm$)-muscone from methyl 3-oxoheptadec-16-ynoate.

3.1.6 Indium nonafluorobutanesulfonate ($\text{In}(\text{ONf})_3$)

3.1.6.1 Annulation of arylindoles with propargylic ethers: Synthesis of (hetero) aryl-*c*-carbazoles

The annulation of arylindoles with propargylic ethers may be carried out in the presence of the Lewis acid $\text{In}(\text{ONf})_3$ (20 or 30 mol%) to afford the corresponding aryl-*c*-carbazoles in a stereoselective manner (eq. 63).⁹⁰ A possible mechanism may involve an indole nucleophilic attack at an $\text{In}(\text{III})$ π -alkynyl complex to form an $\text{In}(\text{III})$ π -indolylalkynyl species. The latter may undergo an annulation reaction *via* nucleophilic attack of the pyrrole moiety to afford, after aromatization, the final product and ROH release. Such a reaction proceeds with various *N*-aryl-, *N*-alkyl- indoles, indoles bearing EDGs or EWGs. 3-thienyl-, 3-benzothiophenyl- or 3-indolyl- indoles, and α -substituted alkylpropargylic ethers are also suitable reagents.

3.2 Catalysis mediated by discrete In(III) coordination compounds

3.2.1 *N,N,N*-ligands: Chiral indene-oxazoline-pyridine (indapybox)

3.2.1.1 Asymmetric addition of pyrroles to isatins: Synthesis of 3-pyrrolyloxindoles

2,6-bis-[(3*aS*,8*aR*)-3*a*,8*a*-dihydro-8*H*-indeno[1,2-*d*]oxazolin-2-yl]pyridine In(III) *tris*-triflate, (indapybox)In(OTf)₃, was reported to catalyze the highly enantioselective formation of 3-pyrrolyloxindoles from isatin and pyrrole substrates (eq. 64).⁹¹ Interestingly, such an In(III) chelate outperforms its indapybox Sc^{III} and Y^{III} analogues regarding regio- and/or enantioselectivity. Importantly, the reaction stops after the addition of one pyrrole moiety, and 3,3-dipyrrolyloxindoles are not detected. *N*-substituted pyrroles and *N*-substituted isatins with EWGs and EDGs are suitable substrates.

3.2.2 *N*-Heterocyclic Carbenes (NHCs)

3.2.2.1 In(III) dibromocations as π -Lewis acids

The air-stable *N,N'*-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene indium tribromide adduct [(IDipp)InBr₃] may be readily ionized by [Ag][SbF₆] to produce the well-defined salt species [(IDipp)InBr₂⁺][SbF₆⁻]. Likewise, the reaction of InBr₃ with [Ag][SbF₆] affords [InBr₂⁺][AgBr][SbF₆⁻].⁹² Interestingly, [(IDipp)InBr₂⁺][SbF₆⁻] displays a superior catalytic activity

compared to cation $[\text{InBr}_2^+]$ for the dihydroarylation of arenynes, and transfer hydrogenation of cyclohexenybenzene (eqs. 65 and 66). Thus, such air-stable NHC-In(III) Lewis acids may well complement/replace hygroscopic In(III) inorganic salts for a number of catalytic applications.

3.2.3 *N,N,O,O*-ligands: Chiral salicylidene (*salen*)

3.2.3.1 Polymerization of lactide (LA): Synthesis of stereoregular polylactide (PLA)

Discrete In(III) species supported by various multidentate ligand platforms have recently been demonstrated to be effective ROP initiators of cyclic esters such as lactide. For instance, *(R,R)*-bis- $[(N,N'$ -bis-(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine-In(III)- μ -ethoxy) $]$ ₂, *salenIn* (inset in eq. 67), efficiently polymerizes up to 1000 equiv of *rac*-lactide to quantitatively produce PLA with controlled molecular weights and PDIs ranging from 1.3 to 1.6 (eq. 67).⁹³ The In(III) complex polymerizes preferentially the *L*-LA enantiomer with a constant rate five times superior to that of *D*-LA enantiomer, which allows the formation of stereoblock isotactic polymers of the type PLLA-*b*-PDLA. The dinuclear In(III) species $[(\text{dap})\text{InCl}]_2\text{-}\mu\text{-Cl,}\mu\text{-OEt}$ also polymerizes (*rac*)-LA with good control and activity (inset in eq. 68).⁹⁴

3.2.4 *N,N,O*-ligands: Chiral diaminophenoxide (*dap*)

3.2.4.1 Polymerization of β -butyrolactone (BBL): Synthesis of polyhydroxybutyrates (PHB)

Bis-(2,4-di-*tert*-butyl-6-((((1*R*,2*R*)-2-(dimethylamino)cyclohexyl)amino)methyl)phenoxy In(III) chloride)- μ -chloro,- μ -ethoxy complex [(*dap*)InCl]₂- μ -Cl, μ -OEt] may polymerize up to 5000 equiv of *rac*-BBL under mild conditions to quantitatively afford PHBs with controlled molecular weights and PDIs below 1.07 (eq. 68).⁹⁵ Kinetic studies suggest a coordination-insertion mechanism with a chain growth through successive insertions into the In-OR bond. Addition of ethanol or polyethylene glycol (PEG), acting as chain transfer agents, results in a highly controlled and immortal polymerization.

3.2.5 *N,O*-ligands: Phenoxy-imines (*poxi*)

3.2.5.1 Polymerization of lactide: Synthesis of polylactide

Phenoxy-imino In(III) dicarbonyl derivatives of the type [(*poxi*)In(CH₂SiMe₃)₂] mediate the ROP of *rac*-LA (up to 1000 equiv) in the presence of isopropyl alcohol (acting as CTA) to afford atactic PLA, albeit with a moderate level of control (eq. 69).⁹⁶

3.3 Catalysis mediated by In(I) species

3.3.1 Indium chloride (InCl)

3.3.1.1 Asymmetric borono variant of Hosomi-Sakurai reaction with hemiaminals: Synthesis of chiral homoallyl amides

The high enantioselective formation of chiral homoallylamides was achieved *via* an In(I)-catalyzed reaction of (*rac*)-*N*-benzoyl,*O*-hemiaminals with allylboronic acid pinacol ester in the presence of Ag(I) (*R*)-4,8-bis-(4-methoxyphenyl)binol phosphate (AgBINOP, eq. 70) and through a dynamic kinetic resolution process.⁹⁷ Control experiments support the *in situ* formation of a chiral In(I) species as the active catalyst. The reaction is thought to follow a S_N1 pathway *via* a nucleophilic attack of the allyl boronate on an iminium intermediate. Aliphatic-, aromatic-, heteroaromatic-hemiaminals are excellent substrates. As a comparison, classical Hosomi-Sakurai allylation with allylsilyl ethers barely proceeds using InCl as catalyst.

3.3.2 Indium triflate (In(OTf))

3.3.2.1 Borono variant of Hosomi-Sakurai reaction with acetals or ketals: Synthesis of homoallyl ethers

The In(OTf)-catalyzed reaction of acetals or ketals with allylboronic acid pinacol esters allows access to various homoallyl ethers (eq. 71).⁹⁸ Deuterium-labeling experiments support a transmetalative S_N1 mechanism involving the reaction of an In(I)-allyl species with an oxonium triflate intermediate as a key step for product formation. Other In(I) and In(III) salts, as well as Lewis acids based on Ga(III), Cu(I), Cu(II), Sc(III), and Ag(I) yielded very low conversions. Aliphatic-, aromatic-, heteroaromatic- acetals or ketals are suitable substrates.

R¹ = alkyl, aryl, heteroaryl

R² = H, alkyl, aryl

18 examples (yields: 57-95%)

3.3.2.2. Alkyl-allyl cross coupling between ethers and 9-borabicyclo[3.3.1]nonane derived allylborane: Synthesis of functionalized terminal alkenes

Terminal alkenes may be functionalized by reaction of ethers with (1s,5s)-9-allyl-9-borabicyclo[3.3.1]nonane in the presence of In(OTf) (1 to 5 mol%) to afford terminal alkenes (eq. 72).⁹⁹ The reaction proceeds through a transmetalative S_N1 and first involves an In(I)-mediated C–O bond cleavage of the ether moiety to form a carbocation and InOMe. Transmetalation with allylborane may afford the corresponding In(I) allyl species that may then react the formed carbocation to yield the final product. Other common metal-based Lewis acids and conventional allyl reagents such as borates, silanes, stannanes, or Grignard species all resulted in much lower conversions.

R¹ = alkyl, aryl, benzyl...

20 examples (yields: 25-98%)

3.4 Catalysis mediated by discrete In(I) coordination compounds

3.4.1 *N,N* ligands: Chiral bis-oxazolines (biox)

3.4.1.1 Asymmetric allylation, crotylation of hydrazones: Synthesis of substituted *N'*-(but-3-en-1-yl)benzohydrazides

The enantioselective reaction of substituted *N'*-(methylene)benzohydrazides and allylboronic acid pinacol ester may be catalyzed by a 1/1 mixture of InI (5 mol%) and an enantiopure bidentate bis-oxazoline *N,N*-ligand to afford chiral substituted (*R*)-*N'*-(but-3-en-1-yl)benzohydrazides with high

ees (eq. 73).¹⁰⁰ Investigations on the reaction mechanism support the *in situ* formation of a monobiox In(I) species stable against disproportionation. The hydrazone initially acts as a Lewis base to activate the allylboronate toward transmetalation to form a (biox)In(allyl) species. A nucleophilic attack of the latter on the hydrazone substrate produces the final substituted (*R*)-*N'*-(but-3-en-1-yl)benzohydrazide. Heterocycle functionalized-, aromatic- *N'*-(methylene)benzohydrazides are excellent substrates. However, the presence of aliphatic substituents led to lower ees, as often observed in asymmetric catalysis.

Replacing allylboronic acid pinacol ester by (*rac*)- α -methylallylboronic acid pinacol ester provided an efficient tool for the highly regioselective and diastereoselective crotylation of hydrazones with good ees, with the formation of substituted *anti*-(*Z*)-*N'*-2-methylbut-3-en-1-ylidene)benzohydrazides (α -methyl selectivity, eq. 74). Contrary to other Lewis or Brønsted acids favoring exclusively γ -methyl selectivity, the regioisomers *N'*-((1*E*,3*E*/*Z*)-1-cyclohexylpent-3-en-1-ylidene)benzohydrazides are not detected with In(I) catalysis.

3.5 Catalysis mediated by In⁰ species

3.5.1 Metal powder

3.5.1.1 Radical aromatic *ipso*-substitution of arylstannanes with aroyl chlorides: Synthesis of diarylketones

The use of In(0) metal for the production of diarylketones from trialkylphenylstannanes and aroyl chlorides was reported (eq. 75).¹⁰¹ Addition of di-*tert*-butylnitroxide (DTBN) as radical scavenger inhibits drastically the reaction, thus suggesting a radical pathway as expected with In(0). Thus, SET from In⁰ to the aroylchloride substrate initially generates an acyl radical (and InCl) that reacts with the arylstannane specifically at the *ipso* position to afford the final diarylketone and a triaryltin radical. The latter generates a new acyl radical and trialkyltin chloride. No or very low conversions to the desired products are observed with highly electrophilic *o,o*-difluorobenzoyl-, and 3-methylthiophene-2-carbonyl-chlorides. This methodology may be extended to the synthesis of arylalkyl ketones from aryl stannanes and acyl chlorides.¹⁰²

3.5.1.2 *N*-Formylation of amines: Synthesis of amides

Amides synthesis may be catalyzed by In(0) from amines and excess formic acid to produce the corresponding acetamides (eq. 76).¹⁰³ The catalytic active Lewis acid is likely In(III) formate, derived from the oxidation of In(0) with formic acid. Primary- and secondary- aliphatic amines, or anilines with EDGs and EWGs are suitable substrates. Since alcohols are inactive towards the present In(0)-mediated formylation, this methodology is well suited for the selective *N*-formylation of amino alcohols.

3.5.1.3 Asymmetric Barbier-type propargylation with aldehydes: Synthesis of chiral propargylic alcohols

Barbier-type asymmetric reactions were recently developed to access chiral enantiopure propargylic alcohols. Thus, various (*S*)-propargylic alcohols may be efficiently prepared via

reaction of aldehyde and propargylic bromide substrates in the presence of In(0), pyridine and (1*S*,2*R*)-(+)-2-amino-1,2-diphenylethanol (ADPE) as a chiral auxiliary (eq. 77).¹⁰⁴ The best ees are observed with α -substituted aliphatic aldehydes. The formation of tertiary propargylic alcohols from ketones remains restricted to highly electrophilic substrates such as trifluoroacetophenone, despite the addition of various metal-based Lewis acids to enhance ketones reactivity.

6. RELATED ARTICLES

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