Coordination Chemistry Reviews 297–298 (2015) 91–126

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Molecular complexes of group 13 element trihalides, pentafluorophenyl derivatives and Lewis superacids

E.I. Davydova, T.N. Sevastianova, A.Y. Timoshkin*

Institute of Chemistry, St. Petersburg State University, University pr. 26, Old Peterhof, 198504 St. Petersburg, Russia

Contents

ARTICLE INFO

Article history:
Received 12 December 2014
Received in revised form 25 February 2015
Accepted 26 February 2015
Available online 6 March 2015

ABSTRACT

In the present review recent advances in the chemistry of group 13 Lewis acids, such as intermolecular complexes with donor–acceptor metal–metal bonds, bifunctional Lewis acids and complexes of Lewis superacids, as well as selected examples of their application in different areas of chemistry are presented. Structural properties of molecular donor–acceptor complexes formed by strong group 13 element Lewis

Abbreviations: acac, $C_5H_7O_2$; Ad, 1-adamantyl; ^{Ar}acnac, ArNC(Ph)CHC(Ph)O, Ar = 3,5-$^tBu_2C_6H_3$; bipy, bipyridine; DA, donor–acceptor; dbm, dibenzoylmethanoate; dfepe, $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$; Dipp, 2,6-$^iPr_2C_6H_3$; DME, 1,2-dimethoxyethane; DMP, 2,6-dimethylpiperidine; dmpz, 3,5-dimethylpyrazolyl; dtc, diethyldithiocarbamate; FcNH, dimethylaminomethylferrocen; FLP, Frustrated Lewis Pairs; HKS, Himmel, Krossing, and Schnepf; Ime, N,N′-bis(methyl)imidazol-2ylidene; IMes, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene; IP, iminopyridine; IPr, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; Mes, 2,4,6-$Me_3C_6H_2$; nacnac, $[ArNC(^tBu)]_2$, Ar = 2,6-$^iPr_2C_6H_3$; NCabH, *closo*-1-[(dimethylamino)methyl]-*o*-carborane; NHC, N-heterocyclic carbenes; Nmp, *N*-methyl-piperidin; NPN, $(PhNSiMe_2CH_2)_2PPh$; Py, pyridine; pyz, pyrazine; SIMe, (N,N′-bis(methyl)imidazolylidene); TA, thianthrene; TCNE, tetracyanoethylene; TCNQ, 7,7,8,8-tetracyano-*p*-quinodimethane; TEMPO, 2,2,6,6-tetramethylpiperidine-N-oxyl; THF, tetrahydrofuran; TM, transition metal; TMEDA, tetramethylethylenediamine; tmp, tetramethylpiperidin; Tm^R, tris(2-mercapto-1-R-imidazolyl)hydroborato ligand; Tp^{R2}, tris(3,5-(R_2)pyrazolyl)hydroborato ligand; Trip, 2,4,6-$^iPr_3C_6H_2$.

* Corresponding author. Tel.: +7 812 428 4071; fax: +7 812 428 6939.
E-mail address: a.y.timoshkin@spbu.ru (A.Y. Timoshkin).

http://dx.doi.org/10.1016/j.ccr.2015.02.019

Keywords:
Group 13 elements
Lewis superacids
Group 13 element trihalides
Donor–acceptor complexes
Metal–metal bond
Structure

acids EX_3 (E = B, Al, Ga; X = Cl, C_6F_5) with M,C,N,P,O,S-donor-ligands (M – main group or transition metal) are presented and changes in the geometry of the acceptor moiety upon complex formation are analyzed.

1. Introduction

Acid–base interactions are widespread in modern chemistry. Group 13 element derivatives in oxidation state +3 serve as strong Lewis acids, capable to form complexes of different structural types [1–4]. BF_3, along with $SbCl_5$, has become important compound for constructing Lewis acidity scale due to large number of known complexes. BF_3 acidity scale is considered [5] superior as compared to $SbCl_5$ acidity scale, due to cleaner complexation reactions and much simpler electronic structure of BF_3, as well as due to affordable titration calorimetry experiments.

The simplest donor acceptor complex is ammonia borane BH_3NH_3, reviewed in [6,7] and more recently in [8]. The covalent bond between boron and nitrogen is formed by so called donor–acceptor mechanism, where the lone pair of the donor molecule interacts with the vacant orbital of the acceptor molecule. Depending on the nature of participating HOMO and LUMO, classification of the DA complexes has been proposed [1]. In 1989, in excellent review Haaland [9] described three characteristic features of such bond: it is relatively weak, it has a longer distance than typical single bond, and it has a small degree of charge transfer. Chapter 16 of his recent book on bonding models is devoted to donor–acceptor interactions [10]. Dative bonds are distinguished from covalent bonds by heterolytic bond breaking in the first case and homolytic in the second (Fig. 1).

Historically, donor–acceptor (DA) bond has been denoted by several ways: using middle dot $BH_3{\cdot}NH_3$ to indicate that molecular complex (or adduct) is formed reversibly, using colon $BH_3{:}NH_3$ to indicate the shared electron pair, and using arrow $BH_3 \leftarrow NH_3$ to indicate the direction of transferred charge from the donor to the acceptor molecule. All these notations happily coexisted in the literature. However, quite recently, the discussion about the usefulness of the indication of the DA bond with arrows in main group element compounds has been provoked by an essay by Himmel, Krossing, and Schnepf (HKS) [11]. They advocate that “dative bond arrows should be avoided, when one single conventional representation is entirely sufficient” [11]. In response, Frenking [12] stress the importance of the modern methods of bonding analysis to gain quantitative support for the donor–acceptor bonding model representation. He also pointed out that definitions of the donor–acceptor bond by Haaland were formulated on weak classical 13–15 complexes known in 1989 and that donor–acceptor bonds can be very strong and short and associated with very significant charge transfer. Arguments are going back and forth, as in new paper HKS state “Put calculations and analyses aside!” and that the “concept should be insightful even with quick notation on a napkin” [13].

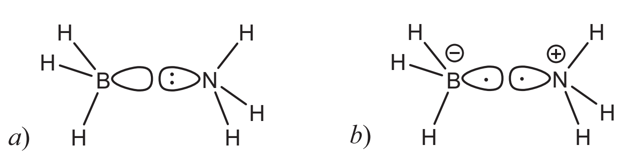

Fig. 1. Representation of heterolytic (a) and homolytic (b) donor–acceptor bond breaking in ammonia borane.

In the present review, we concentrate on intermolecular complexes and will denote such complexes with a middle dot separating acceptor and donor molecules. In using this notation, we emphasize the reversibility of the complex formation and existence of the donor and acceptor components as individual substances. In contrast to HKS, who “do not consider reversibility as neither sufficient nor necessary” [11], in our opinion, this is a very important feature for the molecular complexes, or adducts, to which the present review is devoted. However, when discussing the donor–acceptor bond, we will use the arrow notation to indicate the donor and the acceptor atoms. This will help to avoid a confusion in the case of metal–metal DA complexes (for example, group 13 donors with group 13 acceptors).

In the present review we will not discuss Frustrated Lewis Pairs (FLP) – complete coverage of recent advances in this exciting area can be found in excellent reviews [14–16] and two recent books [17,18]. We will also not consider compounds with intramolecular donor–acceptor bond, where Lewis acidic and basic centers are existed in the same molecule, separated by one or several bridges. Recent advances in this area are highlighted in reviews by Bourissou [19] on B–P systems, Braunschwieg [20,21] and Owen [22] on B-TM systems, and works of Uhl [23,24] on Al–N systems.

The present review is focused on intermolecular complexes of strong Lewis acids: group 13 halides and group 13 perfluorinated aryl derivatives. Structural features and thermodynamics of molecular complexes formed by halide derivatives of group 4,13,14 Lewis acids with classical N,P,O-donor ligands were considered in our 2010 review [4]. With the exception of the complex $AlCl_3{\cdot}$Quin, for which new structural data appeared [25], complexes considered in [4] are excluded from the present review. Herein we will focus on complexes with metal atoms (both main group and transition metals) acting as donors toward group 13 Lewis acids. Structural properties of molecular donor–acceptor complexes formed by strong group 13 element Lewis acids BF_3 and EX_3 (E = B, Al, Ga; X = Cl, C_6F_5) with O,S,N,P,C-donors are summarized. Complexes of group 13 Lewis superacids $B(CF_3)_3$ and $Al(C_6F_5)_3$ have been also considered, as well as bifunctional Lewis acids. On the basis of structural data in the solid state, changes in the geometry of the acceptor moiety upon complex formation are discussed. Finally, selected applications of complexes of group 13 Lewis acids are presented. Literature covered mostly for the past 15 years, in several cases results of earlier studies are also discussed.

2. Complexes with intermolecular group 13 element-metal DA bond

In recent years, chemistry involving direct metal–metal donor–acceptor bonds has attracted considerable attention. Interestingly, both main group metals and transition metals can serve as Lewis bases toward group 13 element Lewis acids. In the present review, we will briefly discuss these examples with the emphasis on the role of group 13 element derivatives.