Coordination Chemistry Reviews 257 (2013) 1011–1025

Contents lists available at SciVerse ScienceDirect

Coordination Chemistry Reviews

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

Review

Recent developments in the chemistry of homoleptic azido complexes of the main group elements

Peter Portius*, Martin Davis

University of Sheffield, Department of Chemistry, Western Bank S3 7HF, UK

Contents

ARTICLE INFO

Article history:
Received 31 July 2012
Accepted 22 September 2012
Available online 3 October 2012

Keywords:
Azides
Pseudohalogens
Nitrogen-rich compounds
Vibrational spectroscopy
Hyper-coordinate complexes
Main group coordination chemistry

ABSTRACT

The chemistry of covalent azides of main group elements has developed rapidly during the last decade. Interest in this area of pseudohalogen chemistry arises from both fundamental questions of bonding in unusual, highly nitrogen-rich molecules as well as potential practical applications. Especially binary azides and homoleptic azido complexes were at the forefront of new developments which tested the limits of preparative inorganic and computational chemistry. This paper reviews and discusses the syntheses, structures and spectroscopic properties (^{14}N NMR, Raman and IR) of the homoleptic azido complexes with an emphasis on Groups 13–16.

Abbreviations: *A*, anion; Bpy, 2,2′-bipyridine; 4,4′-bpyH_2, 4,4′-bipyridinium; *C*, cation; DFT, density functional theory; dmso, dimethylsulfoxide; E, element of group 13, 14, 15, 16 or 17; lp, nonbonding electron pair (lone pair); mes, 2,4,6-trimethylphenyl; PPN, bis(triphenylphosphine)iminium(1+); py, pyridine; thf, tetrahydrofuran; tmp, 2,2′,6,6′-tetramethylpiperidino; tren, triethylenetetramine; VSEPR, valence shell electron pair repulsion.

* Corresponding author. Tel.: +44 0114 22 29385; fax: +44 0114 22 29346.
E-mail addresses: p.portius@sheffield.ac.uk (P. Portius), martindavis120@gmail.com (M. Davis).

0010-8545/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ccr.2012.09.019

1. Introduction

The chemistry of azides has been explored for more than a century since the first reported synthesis of azido benzene [1,2]. One of the major driving forces for this research is the fact that the azido group is regarded as an explosophoric group. The introduction of an azido group into an *organic* compound increases its energy by ~355 kJ mol^{-1} [3]. The azido group consists of three homonuclear atoms with identical electronegativity bearing different partial charges [4]. Due to the N–N multiple bonds there is a prospect of high-pressure induced polymerization and ultimately metallic material.

Compounds containing many azido groups may have a high nitrogen content and constitute one class of compounds used in high energy density materials in which nitrogen is incorporated mostly via N—N single and N═N double bonds. The high energy content (high endothermicity) of these compounds arises from the difference of the covalent bond enthalpies of N—N, N═N and N≡N bonds, which are ~163, ~409 and 945 kJ mol^{-1} at 298 K, respectively [5]. The difference in covalent single, double and triple bond enthalpies is unusually large for the element nitrogen. Therefore, the formation of dinitrogen in the thermal decomposition is accompanied by a large enthalpy change and release of heat. Usually, organic azides have poor thermal stability and relatively high sensitivity to mechanical stimuli. Inorganic azides have wide applications as precursors in the preparative chemistry of nitrogen compounds such as nitrides, as a source of chemically pure nitrogen, as explosives reagent in initiators and many others. Inorganic azides exhibit a broad range of stabilities with respect to explosive decomposition [4]; lead azide, a prime example, has found wide use as the initiating charge in detonators [6]. Azides of sufficiently simple constitution can be used to verify theoretical models of molecular bonding, crystalline structure, and chemical reaction dynamics.

With the increasing availability of a whole set of powerful techniques for the routine analysis of molecular structures such as X-ray diffraction, multinuclear NMR, infrared and Raman spectroscopy, inorganic azides especially have received increased attention with major breakthroughs in the recent decade. As a result, kinetically stable azides of most elements are known with the exception of the noble gases. Some azides are extremely short-lived, such as $O(N_3)_2$ [7]. Progress in the physics, chemistry and technology of inorganic azides has been comprehensively reviewed in 1977 [8], followed later by specialised accounts regarding preparation and synthetic uses of organic azides (1988) [9]. More recent reports appeared in 1997 [10], 2002 [11], 2005 [12], and 2010 [13], concentrating on syntheses and applications of covalent azides [14]. Inorganic azides have received less attention [14]. In the last decade the chemistry of main group element polyazides has made considerable progress, in particular in the areas of nitrogen-rich energetic salts and liquids [15] and azide-containing high energy materials [16].

Among polyazido and other nitrogen-rich complexes, homoleptic azido complexes are particularly interesting since they consist only of nitrogen and a second element. Investigation into these types of complexes addresses the fundamental search for molecules, charged or neutral, which support a maximum of reactive nitrogen while retaining some degree of kinetic stability. This concept has been taken to the extreme in the challenging search for polymeric nitrogen (N_∞) [17] and the synthesis of the all-nitrogen species N_5^+ [18].

There are advantages in viewing the azido group in these compounds as a pseudohalogen (Y) covalently bound to a main group element (E) [11]. The azido group is a prominent pseudohalogen [19], modern aspects of which have been discussed recently [20,21]. In a number of cases, one or several related pseudohalogen analogs of azido compounds are known, which incorporate typically Y = CN, NCO, NCS, NCSe, NCTe. Often the synthesis of these non-energetic pseudohalogen complexes preceded the synthesis of the related polyazido complex, for instance in the case of $(AsPh_4)_3[In(NCS)_6]$ [22]/$(PPh_4)_3[In(N_3)_6]$ [23] and $[Si(NCS)_6]^{2-}$ [24], $[Si(NCSe)_6]^{2-}$ [25]/$[Si(N_3)_6]^{2-}$ [26]. Pseudohalogen analogs can be used to study synthetic procedures targeting azides in the absence of the high-energy content; see for a guidance the reviews on (i) pseudohalides of group 13 and 14 elements [27], (ii) NCS complexes and their IR spectra [28] and (iii) the coordination chemistry of the cyanate, thiocyanate, and selenocyanate ions in transition metal complexes [29].

This review concerns experimental reports to date on covalent main group polyazides. Reports on many exciting theoretical investigations have appeared, such as the studies on the binary covalent azides $E(N_3)_3$ and $E(N_3)_4$ of groups 13 and 14 [30], and on the polynitrogen species $[N(N_3)_3]^{2+}$ and $[N(N_3)_4]^+$ [31] in which density functional theory calculations were employed. Computational studies accompanied most of the more recently published experimental investigations in the area (vide infra). Current research in the area of polyazido complexes is concerned with the following key questions and tasks:

- Identification of highly endothermic yet kinetically stable polyazido complexes.
- Identifying and testing preparative routes to such complexes.
- Elucidating the factors which lead to kinetic stabilisation.
- Refinement of ab initio quantum chemical methods to predict structure and reactivity.

The homoleptic azido complexes and covalent azides $[E(N_3)_n]^q$ can be subdivided into the following classes: $E(N_3)$, $E(N_3)_2$, $[E(N_3)_2]^-$, $[E(N_3)_3]^+$, $E(N_3)_3$, $[E(N_3)_4]^+$, $[E(N_3)_4]$, $[E(N_3)_4]^-$, $[E(N_3)_5]$, $[E(N_3)_5]^-$, $[E(N_3)_5]^{2-}$, $[E(N_3)_6]^-$, $[E(N_3)_6]^{2-}$ and $[E(N_3)_6]^{3-}$.

Table 1 accounts for the experimentally known, characterised covalent azides of groups 13–17. It is interesting to note that a number of potentially viable covalent azides have not been reported yet. Intriguingly, despite the existence of PCl_5 ($[PCl_4]^+[PCl_6]^-$), the pseudohalogen analog "$P(N_3)_5$" is unknown. The "simple" azides, such as $Ge(N_3)_2$, $Sn(N_3)_4$ and $Pb(N_3)_4$, have not been reported on, either. Furthermore, some azides such as $Ge(N_3)_4$ are known; however, they have not yet been obtained in a pure state. There are no reports on binary azides and homoleptic azido complexes of group 18.

2. Synthesis

There are approximately eleven synthetic approaches to homoleptic main group element azides (Scheme 1). The majority of reactions leading to homoleptic azido complexes are based on the transfer of azido groups or the coordination of azido anions in which hydrazoic acid (HN_3), sodium azide (NaN_3) and trimethylsilyl azide (SiN_3Me_3) are used as azide transfer reagents. While methods **1** and **5** have been used for a long time in the synthesis of binary azides [27], more sophisticated methods have been developed more recently in order to access charged homoleptic azido complexes in particular.

(1) The type 1 approach utilises Broensted acid-base reactions between hydrazoic acid (HN_3) and a hydrido complexes, which in Eq. (1a) leads to tetraazidoborate. The reaction is accompanied by the elimination of dihydrogen.

$$Li[BH_4] + 4HN_3 \rightarrow Li[B(N_3)_4] + 2H_2\ [32] \qquad (1a)$$

(2) Type 2 also uses HN_3 as azide transfer reagent, which also transfers protons to the amido ligand 2,2,6,6-tetramethylpiperid-1-yl (tmp) of an amidoborane, $B(tmp)Cl_2$, and leads to the formation