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Review

Stable compounds containing heavier group 15 elements in the +1 oxidation state

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Abbreviations: 12-crown-4, 1,4,7,10-tetraoxacyclododecane; 15-crown-5, 1,4,7,10,13-pentaoxacyclopentadecane; 18-crown-6, 1,4,7,10,13,16-hexaoxacyclooctadecane; Ad, 1-adamantyl; ArCF$_3$, 2,4,6-tris(trifluoromethyl)phenyl; BAR$^{\mathrm{F}}$, tris(pentafluorophenyl)borane; BIAN, 1,2-bis(imino)acenaphthene; Cy, cyclohexyl; dcypb, 1,4-bis(dicyclohexylphosphino)butane; dcype, 1,2-bis(dicyclohexylphosphino)ethane; dcypm, bis(dicyclohexylphosphino)methane; depe, 1,2-bis(diethylphosphino)ethane; depp, 1,3-bis(diethylphosphino)propane; Dipp, 2,6-diisopropylphenyl; dis, bis(trimethylsilyl)methyl; DKA, diketoamido; dme, 1,2-dimethoxyethane; dmp, 2,6-bis(mesityl)phenyl; dmpe, 1,2-bis(dimethylphosphino)ethane; dmpm, bis(dimethylphosphino)methane; dppb, 1,4-bis-(diphenylphosphino)butane; dppben, 1,2-bis(diphenylphosphino)benzene; dppe, 1,2-bis(diphenylphosphino)ethane; dppE, *cis*-1,2-bis(diphenylphosphino)ethylene; dppmE, 1,1-bis(diphenylphosphinomethyl)ethylene; dppmm, tetrakis(diphenylphosphinomethyl)methane; dppNap, 1,8-bis(diphenylphosphino)naphthalene; dppox, α,α′-bis(diphenylphosphino)-*o*-xylene; dppp, 1,3-bis(diphenylphosphino)propane; Dtp, 2,6-bis(2,4,6-triisopropylphenyl)phenyl; Fl*, 2,7-di-*tert*-butylfluorenylidene; Mes, 2,4,6-trimethylphenyl; Mes*, 2,4,6-tri-*tert*-butylphenyl; Np, neopentyl; opbp, *o*-phenylenebis(phenylphosphide); OTf, triflate; Pmdeta, pentamethyldiethyleneytriamine; Py, pyridine; thf, tetrahydrofuran; tmeda, tetramethylethylenediamine; Tripp, 2,4,6-triisopropylphenyl

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Abstract

This review provides an oxidation state model that emphasizes the similarities in the structural features, bonding and reactivities of molecules containing main group elements in a particular oxidation state. Using this model, the syntheses, structural features and selected aspects of the chemistry of stable compounds containing group 15 elements (pnictogens) in the +1 oxidation state are examined. Molecular types that are considered include: triphosphenium salts, phosphamethine cyanine dyes, phosphide anions, certain pnictaalkenes, certain phosphinidenes and their heavier analogues, among others. Theoretical models are presented to rationalize the factors that render such molecules stable.

Keywords: Low oxidation state; Main group; Group 15; Pnictogen; Phosphorus; Arsenic; Antimony; Bismuth; Molecular structure; Bonding

1. Introduction

The concept of an atom existing in a particular oxidation state is one of the fundamental ideas that may be used to rationalize the structural features, bonding and reactivity of a molecule. The utility of the oxidation state model derives from the understanding that the oxidation state of a particular atom in a molecule provides insight into the number of electrons directly associated with, and hence the chemistry of, the atom in question. In this review, the synthesis, structural features and reactivity of organo-element compounds containing group 15 centers in certain relatively low oxidation states is outlined. Because the assignment of oxidation states is sometimes ambiguous or contentious, the criteria used in this work and some reasons for their choice are presented prior to the discussion of the experimental and theoretical observations regarding the chemistry of the compounds that we consider to meet the criteria.

Although several methods may be used to assign an oxidation state, perhaps the most common method employed for organic and p-block compounds is the use of counting rules based on the relative electronegativities of the atoms in a compound and a few assumptions (e.g. H is always in the +1 oxidation state, O is always in the −2 oxidation state). Using such rules, the group 15 elements (pnictogens, Pn) are assigned formal oxidation states ranging from −3 to +5 under normal conditions [1–3]. The idea of elements having formal oxidation states or oxidation numbers is certainly useful in the context of balancing reduction–oxidation (RedOx) reactions however the rules used to assign such formal oxidation states sometimes yield results that are not chemically intuitive. For example, whereas the formal oxidation state of the phosphorus center in PH_3 is −3, the formal oxidation state of the phosphorus center in PMe_3 may be either +3 or −3 (depending on the electronegativity scale that is used) and the formal oxidation state of the phosphorus center in $P(NMe_2)_3$ is +3 in spite of the similar chemical behaviors and electronic structures of the three Lewis bases. Likewise, the formal oxidation state of the nitrogen in NPh_3 is −3, while that of the Pn center in each of the heavier $PnPh_3$ analogues (Pn = As, Sb, Bi) is +3 despite the obvious chemical, electronic and structural relationships observed for the series. In a similar vein, whereas the metathesis reaction of PCl_3 with LiMe to form PMe_3 and LiCl could be considered a RedOx reaction ($P^{III} \rightarrow P^{-I}$ and $C^{-IV} \rightarrow C^{-II}$), the analogous reaction of PCl_3 with $LiNMe_2$ to form $P(NMe_2)_3$ and LiCl is never considered to involve oxidation or reduction. Somewhat more oddly, the counting rules used to assign formal oxidation numbers suggest that the oxidation states of the nitrogen atoms in Li_3N, NMe_3 and $NMe_4{}^+$ are the same despite the drastic differences in the structures and reactivities exhibited by the nitride, the amine and the ammonium cation. Also from the perspective of chemical reactivity, such counting rules suggest that while the coordination of the “lone pair” of electrons on a molecule such as PH_3 to H^+ does not change the oxidation state of the phosphorus center, the identical Lewis acid–base reaction between PH_3 and $CH_3{}^+$ might change the oxidation state of P, and the related reaction of PH_3 with an O atom will certainly change the oxidation state of the phosphorus center. Such conclusions are seemingly absurd in the context that each of the three reactions produces a tetrahedral-shaped molecule with no remaining “lone pair” of electrons on the phosphorus atom and each of the reactions involves the formation of a new bond between phosphorus and an isolobal fragment. Given the foregoing, it is necessary to remember that the formal oxidation states obtained from the use of such counting methods are simply models that are useful in many instances but they should not be overly interpreted.

An alternative model one can use to define the oxidation state of an atom in a molecule is based on the number of non-bonding electrons associated with that particular atom. Such an approach corresponds perhaps more closely with the less-commonly used concept of a “valence state” [4] and is also more compatible with the use of the isolobal analogy [5] to understanding chemical structure and reactivity. This model, illustrated in Fig. 1, is advantageous in that it more obviously emphasizes the similarities in the electronic structures, geometrical features and perhaps chemical behaviors of compounds containing elements in a given “oxidation state”. The implicit assumption in the model presented in Fig. 1 is that the Pn atom is less electronegative than all of the elements to which it may be bonded. While this assumption may be unrealistic when Pn = N, the model eliminates many of the ambiguities and oddities in the chemistry of compounds containing an element in a given oxidation state. For example, whereas the counting rules might suggest that the phosphorus atom in PMe_2H is +1, the phosphine has more structural and chemical similarities to $AsMe_2H$, containing As^{III}, than to a phosphinidene that contains P^I. Using the method outlined in Fig. 1, both $PnMe_2H$ compounds are considered to contain Pn^{III} and both are expected to have different structural properties and chemistry than the compound containing Pn^I.

There are a few notable generalizations that are apparent using the proposed oxidation state model. Firstly, organopnictogen compounds that contain pnictogen atoms in even oxidation states are anticipated to be paramagnetic and are rela-