Contents lists available at ScienceDirect

Inorganica Chimica Acta

X-ray structures and oxidative electrochemistry of phosphine sulfides and phosphine selenides ☆

Margaret A. Tiedemann [a], Chelsea L. Mandell [a,1], Benny C. Chan [b], Chip Nataro [a,*]

[a] Department of Chemistry, Lafayette College, Easton, PA 18042, United States
[b] Department of Chemistry, The College of New Jersey, Ewing, NJ 08628, United States

ABSTRACT

A variety of mono- and bisphosphine sulfides and selenides were synthesized and structurally characterized by NMR spectroscopy. In addition, the X-ray crystal structures were determined for eleven of these compounds. The percent buried volume was determined from the X-ray structures and the use of this measurement in estimating the steric bulk in phosphine sulfides and selenides was further developed. The oxidation of the mono- and bisphosphine chalcogenides was examined using cyclic voltammetry in methylene chloride and acetonitrile. The solvent had little effect on the observed trends in the potentials at which oxidation occurred. Both the mono- and bisphosphine chalcogenides display an irreversible oxidative wave. Many of the phosphine selenides also display a follow-up, irreversible reductive wave indicative of the formation of a Se–Se bond upon oxidation. However, the products for the oxidation of the phosphine selenides could not be isolated by chemical oxidation. The potential at which oxidation of the phosphine sulfides occurs is more positive than the analogous phosphine selenides.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The one electron, iron-centered oxidation of ferrocene has been known for almost as long as ferrocene itself [1]. While many derivatives of ferrocene undergo an iron-centered oxidation, the two electron oxidation of 1,1′-bis(di-tertbutylphosphine selenide)ferrocene (dtbpfSe$_2$) is selenium based and yields a dicationic species in which intramolecular Se–Se bond formation has occurred (Fig. 1) [2]. While the cyclic voltammograms of the oxidation of other 1,1′-bis(phosphine selenide)ferrocene compounds are similar to that of dtbpfSe$_2$, similar Se–Se bonded dications have not been isolated [3–6]. The oxidation of the monophosphine Se=PFc$_3$ also suggests the formation of a Se–Se bonded dimer, but the oxidation product has not been isolated [7]. Oxidation of the analogous phosphine sulfides has also been investigated, but the oxidation appears to be iron-based rather than occurring at the sulfur atoms [2–6].

There are a limited number of examples in the literature that suggest that the presence of the ferrocenyl backbone is not necessary for formation of an E–E bond (E = S or Se) upon oxidation of a phosphine selenide or phosphine sulfide. The oxidation of phosphine selenides that do not contain a ferrocenyl substituent has received surprisingly little attention as these compounds can serve as a model for peptides bridged by Se–Se bonds formed by oxidation [8–10]. Chemical oxidation of Se=P(NMe$_2$)$_3$ with excess BiCl$_3$ yields the Se–Se bonded dication, [(Me$_2$N)$_3$P–Se–Se–P(NMe$_2$)$_3$]$^{2+}$, which was structurally characterized [11]. The oxidation of the anionic phosphine selenides [N(^{i}Pr$_2$P=Se)$_2$]$^-$, [N(Ph$_2$P=Se)$_2$]$^-$, [(ring)P(=E)Se]$^-$ (E = O or S, ring = –OCH$_2$C(CH$_3$)$_2$CH$_2$O–), and [(PhO)$_2$P(=S)Se]$^-$ have also been shown to yield products in which Se–Se bond formation has occurred [12–14]. The formation of the chalcogen bridge was studied using cyclic voltammetry through the investigation of the oxidation of diphenyl diselenide, Ph–Se–Se–Ph. The selenium centered oxidation cleaves the Se–Se bond to form [PhSe]$^+$ and [PhSe]$^·$, and the follow-up reduction is proposed to reform the selenium bridge [15]. Conversely, chemical oxidation of the neutral phosphine selenides Se=PPh$_3$ and Se=PMePh^{n}Pr results in cleavage of the Se=P bond and the formation of elemental selenium as a product [16,17]. The phosphine selenides Se=P^{i}Pr$_3$ and Se=P^{t}Bu$_3$ were reacted with I$_2$, but instead of oxidation, a 1:1 adduct, I$_2$Se=PR$_3$ was proposed, although the products were not characterized [18].

---

* Corresponding author. Address: Department of Chemistry, Hugel Science Center, Lafayette College, Easton, PA, 18042, United States. Tel.: +1 (610) 330 5216.
E-mail address: nataroc@lafayette.edu (C. Nataro).
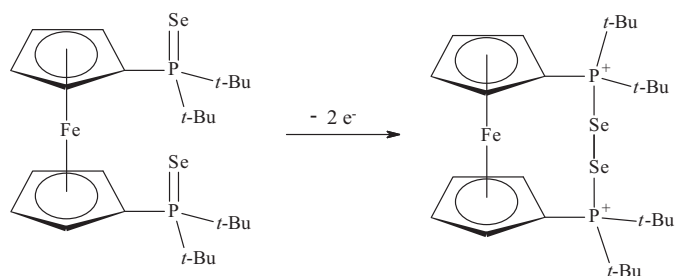1 Current address: Department of Chemistry, Texas A&M University, College Station, TX 77842, United States.

Fig. 1. Oxidation of dtbpfSe₂.

The oxidation of phosphine sulfides has received significantly more attention. The reaction of S=P(NR₂)₃ (R = Me or Et) with copper (II) or bromine yields the S–S bonded dications, [(R₂N)₃P–S–S–P(NR₂)₃]²⁺, which were spectroscopically characterized but not structurally characterized [19–21]. The reaction of copper (II) with the monophosphine sulfide, S=PMe₂Ph, and the bisphosphine sulfides, S=PMe₂-Me₂P=S and S=PPh₂CH₂Ph₂P=S, was examined [21]. A S–S bonded cation was not observed, leading the authors to conclude that the S–S bonded dication would only form if the phosphine had strongly donating dialkylamino-substituents. Similarly, the reaction of copper (II) with the monophosphine sulfide S=PMe₃ results in the reduction of the metal to copper (I) and no S–S bonded product [22]. In addition, the reaction of S=PPr₂–Pr₂P=S with BiCl₃ yielded a 1:1 adduct, BiCl₃·(S–PPr₂)₂, as opposed to giving oxidative S–S bond formation [11]. The reaction of the phosphine sulfides S=PR₃ (R = Me, Et, ⁱPr or Ph) with copper (II) was proposed to yield a dicationic species in which P–P bond formation was implied, but structural or spectroscopic characterization of the dications was not reported [23]. Further studies of this reaction report ¹H NMR data and suggested that the dication products contained a S–S bond, [R₃P–S–S–PR₃]²⁺, but the dications were not structurally characterized [24]. Oxidation of S=PPh₃, either chemically with [NO]⁺ or electrochemically, is reported to yield [Ph₃P–S–S–PPh₃]²⁺ which was characterized by ¹H NMR [25]. Additional electrochemical studies of phosphine sulfides have been performed, but have focused on the reduction of aryl phosphine sulfides [26,27].
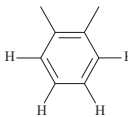
To further examine these systems, the oxidative electrochemistry of a variety of mono- and bisphosphine chalcogenides was examined. For the monophosphine chalcogenides, various alkyl and aryl substituted phosphines were investigated (Table 1).

The substituents were also varied for the bisphosphine chalcogenides, as were the groups linking the two phosphorus atoms (Table 2). The oxidative electrochemistry of all of the compounds was examined by cyclic voltammetry, which was performed in methylenechloride and acetonitrile. In the course of preparing the compounds of interest, crystals of eleven compounds suitable for X-ray diffraction were prepared and the structures obtained.

Table 1
Abbreviations for monophosphines (PR₃).

R group	Abbreviation	R group	Abbreviation
Methyl	PMe₃	ethyl	PEt₃
iso-propyl	PⁱPr₃	*tert*-butyl	PᵗBu₃
phenyl	PPh₃	*p*-C₆H₄F	P(C₆H₄F)₃
p-C₆H₄Cl	P(C₆H₄Cl)₃	1-naphthyl	P(1-Nap)₃
Cyclohexyl	PCy₃		
ⁱBuSB		MeSB	

Table 2
Abbreviations for bisphosphines (R₂P(bridge)PR₂).

R group	Bridge	Abbreviation
Ph	–CH₂–	dppm
Ph	–CH₂CH₂–	dppe
Me	–CH₂CH₂–	dmpe
Ph	(–CH₂–)₃	dppp
Ph	(–CH₂–)₄	dppb
Ph	(–CH₂–)₅	dpppent
Cy	–CH₂CH₂–	dcpe
1S,4S-PhCHCH₂CH₂CHPh	–CH₂CH₂–	ᴾʰple
Ph	–CHMe–CHMe–	2,3-dppb
Ph		dppbz

2. Experimental

2.1. General procedures

Standard Schlenk and glovebox techniques were employed and all reactions were performed under an atmosphere of argon. Hexanes, methylene chloride (CH₂Cl₂), and diethyl ether (Et₂O) were purified under Ar using a Solv-tek purification system [28]. Toluene, benzene and CDCl₃ were dried over molecular sieves and degassed prior to use. Acetontrile (MeCN) was distilled over CaH₂ prior to use. Ferrocene, decamethylferrocene, sulfur, selenium, nitrosonium hexafluorophosphate ([NO][PF₆]), nitrosonium tetrafluoroborate ([NO][BF₄]) and all phosphines were purchased from Strem Chemicals, Inc. The tris-4-(bromophenyl)ammoniumyl hexachloroantimonate ([N(*p*-C₆H₄Br][SbCl₆]) and tetrabutylammonium hexafluorophosphate ([NBu₄][PF₆]) were purchased from Aldrich; [NBu₄][PF₆] was dried *in vacuo* at 100 °C prior to use. Unless otherwise noted, the sulfides and selenides were prepared according to the literature procedures [29–48]. The synthesis of SP(1-Nap)₃ was a modification of the literature procedure [49]. While SeP(1-Nap)₃ has been reported, no experimental details were provided [50]. ¹H and ³¹P{¹H} NMR spectra were obtained using a JEOL Eclipse 400 FT-NMR spectrometer. The ¹H spectra were referenced to internal TMS while the ³¹P{¹H} spectra were referenced to an external sample of 85% H₃PO₄. Mass spectrometry data was collected on a Fisons Instruments Trio 1000 instrument with the solids probe and electron ionization. Elemental analyses were performed by Quantitative Technologies, Inc.

2.2. Synthesis

2.2.1. SP(1-Nap)₃

P(1-Nap)₃ (0.5124 g, 1.242 mmol) and sulfur (0.0560 g, 1.748 mmol) were heated at reflux in toluene (30 mL) for 60 h. Upon cooling, the colorless solution was filtered and the solvent was removed *in vacuo*. The resulting white solid was triturated with Et₂O (3 × 5 mL) to give white SP(1-Nap)₃ (0.2372 g, 43% yield). ³¹P{¹H} NMR (CDCl₃): δ(ppm) 42.3 (s). ¹H NMR (CDCl₃): δ(ppm) 8.78 (br s, 3H), 7.95 (dd, J₍H–H₎ = 19.6 Hz, J₍H–H₎ = 3.25 Hz, 9H), 7.48–7.32 (m, 9H). *Anal.* Calc. for C₃₀H₂₁PS: C, 81.06%; H, 4.76%. Found: C, 80.95%; H, 4.77%.

2.2.2. SeP(1-Nap)₃

P(1-Nap)₃ (0.5830 g, 1.413 mmol) and selenium (0.1216 g, 1.540 mmol) were heated at reflux in toluene (30 mL) for 48 h. Upon cooling, the colorless solution was filtered and the solvent was removed *in vacuo*. The resulting white solid was triturated with Et₂O (3 × 5 mL) to give white SeP(1-Nap)₃ (0.6539 g, 94%