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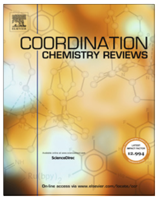

Review

Coordination chemistry of neutral mono-oxide, sulfide and selenide bis(diphenylphosphino)amine (DPPA)-based ligands and their *N*-substituted/functionalized derivatives ☆

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Dedicated to our friend and colleague, Pierre Braunstein, on the occasion of his 70th birthday, with our most sincere congratulations and best wishes.

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ABSTRACT

This review provides a summary, including spectroscopic and structural data, of the metal complexes accessible with mono-oxide, sulfide and selenide bis(diphenylphosphino)amine (DPPA)-based ligands and their *N*-substituted/functionalized derivatives. The nature of the E (O, S, Se) donor in these mixed *P*,P=*E* donor ligands strongly influences the nature of the resulting metal complexes, which can incorporate the DPPA-type ligand(s) as *P*-monodentate or *P*,*E*-chelate. When available, a comparison between the reactivity of the mixed *P*,P=*E* and parent *P*,*P* systems is given. The catalytic applications of *P*,*E*-supported metal complexes are also discussed.

Contents

Abbreviations: allyl, η^3-CH_2CHCH_2; av, average; COD, 1,5-cyclooctadiene; Cp, η^5-C_5H_5; Cp*, η^5-C_5Me_5; DME, 1,2-dimethoxyethane; DPPA, bis(diphenylphosphino)amine; DPPM, bis(diphenylphosphino)methane; eq, equivalent; FT-IR, Fourier transform infrared spectroscopy; methallyl, η^3-$CH_2C(CH_3)CH_2$; *p*-Cym, η^5-*p*-(Me)$C_6H_4(^iPr)$; Pip, $C_5H_{11}N$ (Piperidine); RT, room temperature; XRD, X-ray diffraction.

☆ Unless otherwise specified, ^{31}P and ^{13}C refer to decoupled ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR experiments.

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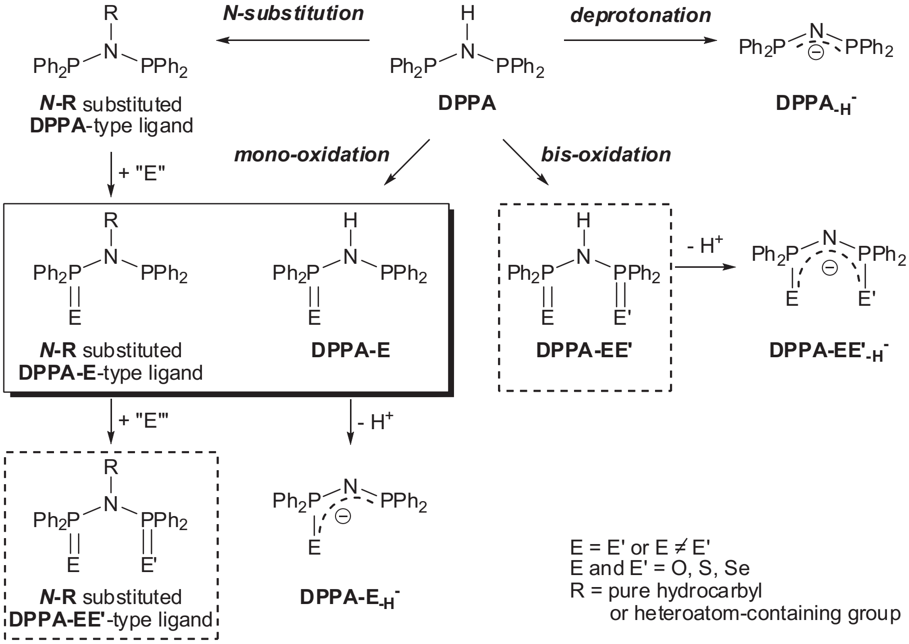
1. Introduction

Coordination/organometallic complexes hold a leading position in many areas of Chemistry, including for example homogeneous and heterogeneous catalysis, the development of high-tech materials or therapeutic molecules and photophysical chemistry. However, the development of suitable candidates for these applications is, in most cases, related to an appropriate design of the supporting ligand(s). In this context, short-bite ligands, such as bis(diphenylphosphino)amine (**DPPA**, Scheme 1) [1–3] or bis(diphenylphosphino)methane (**DPPM**), have attracted much attention for their ability to bring in close proximity two identical or different metal centers, allowing metal–metal interactions [4–14] or cooperative effects [15]. Derivatization of these ligands by mono- or bis-oxidation affects the bite-angle of the resulting chelating ligands, from 4- to 5- or 6-membered metallocycles, respectively. In addition, the presence of different chemical functions, which might be a combination of hard and soft donors, in such heterotopic/hybrid ligands within the same molecule may generate hemilabile systems [16–19]. Consequently, the weak chelation may facilitate the generation of (re)active and/or coordinatively unsaturated species and lower the activation energy of metal-mediated transformations [20–22].

The (coordination) chemistry of **DPPA** and related ligands, such as **DPPM** or other aminophosphines (P—N bond containing molecules), was the subject of several reviews [1–3,23]. A certain interest in the mono-anionic **DPPA$_{-H}^{-}$** ligand (Scheme 1), resulting from the deprotonation of the N—*H* group of **DPPA**, and analogous ligands (varying the P-substituents) is evidenced by a few review articles [24–26]. A comprehensive review dedicated to the synthesis, coordination chemistry and applications of **DPPA**-type ligands, functionalized on the N atom by an additional chemical function (*e.g.* amine, (thio)ether, phosphine, Scheme 1) was recently provided by Fliedel, Ghisolfi and Braunstein [27].

We were interested in providing a survey of the coordination chemistry of neutral mono- (**DPPA-E**) and homo- and hetero-bis-oxide (P═O), sulfide (P═S) and selenide (P═Se) (**DPPA-EE′**) bis(diphenylphosphino)amine-based ligands and their *N*-substituted/functionalized derivatives (Scheme 1, insets). The present review has been restricted to mono-oxidized systems (Scheme 1, solid inset), while a separate report will be dedicated to recent work on bis-oxidized systems (Scheme 1, dashed inset) [28]. The influence of (1) the nature of the P═*E* donor, and (2) the substitution of the N—*H* group by a hydrocarbyl or heteroatom-containing group will be highlighted, based (especially) on NMR and structural data. The reactivity and applications of the resulting complexes is also discussed. However, coordination compounds in which the ligand(s) is(are) deprotonated (**DPPA-E$_{-H}^{-}$** in Scheme 1) are outside the scope of this review, which will focus on metal complexes supported by neutral **DPPA-E** ligands and their *N*-substituted derivatives. Our objective is to provide the researchers studying the coordination chemistry of such **DPPA-E**-type ligands a rapid and comprehensive access to the characteristic spectroscopic and structural data available for all complexes reported to date.

The coordination chemistry of bis-oxidized **DPPA-EE′** (E, E′ = O, S, Se) [26], and derivatives in which the P*Ph* was replaced by other aryl, alkyl, or OR groups, has been overviewed in 1998 [29] and 2001 [30], but mostly concerns metal complexes in which the ligands are deprotonated. As mentioned above, we will shortly provide an update on the coordination chemistry of neutral bis-oxidized **DPPA-EE′** (E, E′ = O, S, Se) ligands and their *N*-substituted



Scheme 1. Bis(diphenylphosphino)amine (DPPA) ligand and its derivatives. The solid inset highlights the ligands topic of this review, and the dashed inset marks the subject of our complement report [28].