

Review

Metal promoted charge and hapticities of phosphines: The uniqueness of carboranylphosphines



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ABSTRACT

The accurate selection of a ligand for a metal-catalyzed homogeneous reaction can be as decisive as the selection of the metal. Incorporating a carborane cage as a backbone to produce new phosphines often leads to remarkable properties, which are not accessible employing conventional organic entities. The synergy effects between the *o*-carborane cluster and the P atom in these *closo*- and

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nido-carboranylphosphines is observed from two points of view: the cluster and the P atom. The P atoms in the *closo*-carboranylmonophosphines grant to the cluster a unique plasticity on the $C_{\text{cluster}}-C_{\text{cluster}}$ distance. The cooperation between the carboranyl moiety and the P atom may result in mono-, di- and tridendicity according to the necessities of the metal, not an ever-available property for organic phosphines.

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1. Introduction

The 1,2-dicarba-*closo*-dodecaborane or trivially *o*-carborane, $1,2-C_2B_{10}H_{12}$, was the first carborane discovered and characterized, although it was not the first carborane reported in the literature. Nowadays, a half of century ago after its discovery, is the most widely used member of its genre. In a recent monograph on carboranes, the number of derivatives of this compound is set to thousands and their applications are extended over a wide range from supramolecular chemistry of polymers and dendrimers, to catalysis, medicine, molecular imaging and radiotherapy, ionic liquids, liquid crystals, NLO materials, electroactive systems, and other [1]. Our group and others were interested in the exploration of the properties of organometallic complexes derivatives of *o*-carboranes. In this scope a plethora of organometallic compounds were synthesized having on the *o*-carborane platform different homo or hetero coordination centers as: P-,P- [2]; P-,S- [3]; P-,N- [4]; P-,C- [5]; S-,S- [6]; S-,N- [7]; S-,C- [8] and N-,C- [9]. Part of these compounds was recently reviewed [10].

Phosphines are notorious ligands in coordination chemistry, and can be tailored “on demand” by changing the groups bonded to the phosphorus atom, altering in this way their steric and electronic properties in a systematic and predictable manner. The accurate selection of a ligand for a metal-catalyzed homogeneous reaction can be as decisive as the selection of the metal. Incorporating a carborane cage as a backbone to produce new phosphines often leads to remarkable properties, which are not accessible employing conventional organic entities. As occurs with organic phosphines, carboranylphosphines present special interest in catalysis [11]. This is why a large number of metal complexes with carboranylphosphines were studied for their potential use as catalysts for different reactions. Derivatized phosphorus bonded at the C_{cluster} atoms of carboranes were found useful ligands for metal complexes that catalyze 12 different synthetic processes as: hydrogenation, hydroformylation, hydrosilylation, carbonylation, amination, alkylation and sulfonylation, Kharasch reaction, polymerization, ring-opening metathesis polymerization, cyclopropanation, cross-coupling with

Grignard reagents, and finally, Sonogashira coupling with hydride transfer [11c]. The *closo*- and *nido*-structures and the wide range of possibilities of coordination of the metals to the carborane cluster offers a broad spectrum of customization of the ligands and permit the synthesis of “on demand” tailored metal complexes. Further, photoluminescence properties of *nido*-carboranylphosphine ligands when bound within trigonal-planar Au complexes have been observed [12].

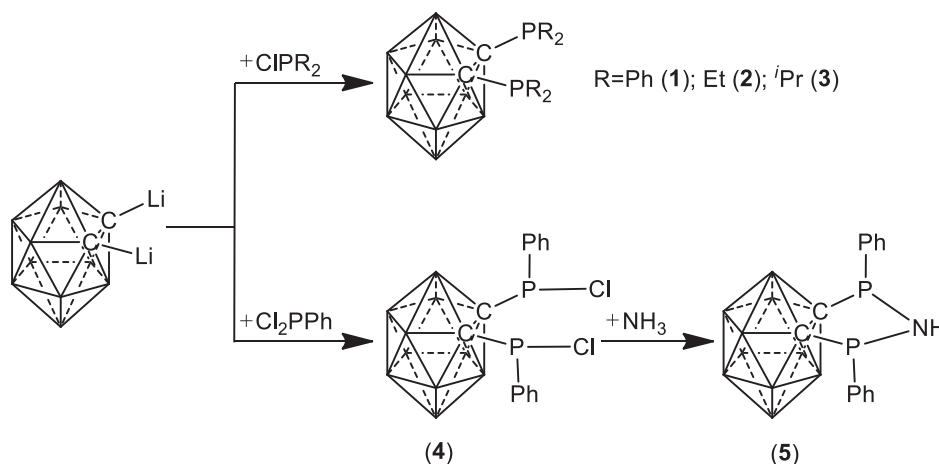
This review is aimed to present the *o*-carboranylphosphines and their metal complexes, as well as the four- and five-coordinated *o*-carboranylphosphine derivatives, from a synthetic point of view, starting from the synthesis of the first *o*-carboranylphosphine. The synergy effects between the *o*-carborane cluster and the P atom in these *closo*- and *nido*-carboranylphosphines is considered from two points of view: the cluster and the P atom. The P atoms in the carboranylmonophosphines and carboranyldiphosphines grant to the cluster a unique plasticity on the $C_{\text{cluster}}-C_{\text{cluster}}$ distance. The influence of the carboranyl moiety in the P atom is shown by ^{31}P NMR spectroscopy.

2. Synthesis of P(III) derivatives of *o*-carboranylphosphines

2.1. Synthesis of *closo*-carboranyldiphosphines

Interest in carboranylphosphine compounds started almost half a century ago, when $1,2-(\text{PPh}_2)_2-1,2\text{-}closo-C_2B_{10}H_{10}$, **1**, was synthesized [2a], by a simple reaction between dilithio-carborane and diphenylchlorophosphine (Scheme 1). When a dichlorophenylphosphine was used, the corresponding bis-chloro compound, $1,2-(\text{PClPh})_2-1,2\text{-}closo-C_2B_{10}H_{10}$, **4**, was obtained. This compound was subsequently used in an ammonolysis reaction to generate the bridging nitrogen carborane $\text{NH}(\text{PPh})_2-1,2\text{-}closo-C_2B_{10}H_{10}$, **5**.

Bis(dimethylamino)-*o*-carboranyldiphosphine, **6**, was also synthesized upon reaction of 1,2-dilithium-*o*-carborane with $\text{CIP}(\text{NMe}_2)_2$ (Scheme 2). Compound **6** can be transformed almost quantitatively into *o*-carboranylbis(dichlorophosphine), **7**, upon



Scheme 1. Reaction of 1,2-dilithium-*o*-carborane with chlorophosphines [2].

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