



# Tetrakis-1,2,4,5-(bis(3,5-dimethylphenyl)phosphino)benzene (Me<sub>16</sub>tpbz): A soluble and spectroscopically simple variant of the 1,2,4,5-tetraphosphinobenzene ligand platform



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Dedicated to the memory of Professor Dietmar Seyferth, who gave me my first opportunity to do research

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## ABSTRACT

A preparation of 1,2,4,5-tetrakis(bis(3,5-dimethylphenyl)phosphino)benzene (Me<sub>16</sub>tpbz) has been devised as a two-step synthesis beginning with bis(3,5-dimethylphenyl)chlorophosphine and 1,2,4,5-tetrafluorobenzene, albeit in low overall yield of 10%. The crystal structure of Me<sub>16</sub>tpbz reveals slight pushing of the phosphorus atoms above and below the central arene ring, suggesting the effect of slight steric pressure, as compared to the fully planar C<sub>6</sub>P<sub>4</sub> core found in 1,2,4,5-tetrakis(diphenylphosphino)benzene (tpbz). Upon exposure to air, solution samples of Me<sub>16</sub>tpbz degrade to (3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>PP(O) (C<sub>6</sub>H<sub>3</sub>-3,5-Me<sub>2</sub>)<sub>2</sub>, identified by X-ray crystallography, which suggests P–C bond scission is a decomposition pathway. The dinickel compound [(mnt)Ni(Me<sub>16</sub>tpbz)Ni(mnt)] (mnt(2–) = [(NC)<sub>2</sub>C<sub>2</sub>S<sub>2</sub>]<sup>2–</sup>) has been structurally characterized by X-ray crystallography and reveals a chair-like conformation defined by a 32.3° angle between the NiP<sub>2</sub> planes with respect to the central C<sub>6</sub>P<sub>4</sub> mean plane. Compared to the analogous [(mnt)Ni(tpbz)Ni(mnt)], slightly weaker binding of Me<sub>16</sub>tpbz to Ni is implied by its modestly longer Ni–P bond lengths. The cyclic voltammogram of [(mnt)Ni(Me<sub>16</sub>tpbz)Ni(mnt)] in CH<sub>2</sub>Cl<sub>2</sub> shows reversible reductions at ~–1.01 V and –1.21 V, corresponding to sequential Ni<sup>2+</sup> + e<sup>–</sup> → Ni<sup>1+</sup> processes, while in DMF, under conditions where [(mnt)Ni(tpbz)Ni(mnt)] shows multiple, reversible reduction processes, its behavior is irreversible and more complex.

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## 1. Introduction

First described in 1988 by McFarlane and coworkers [1], 1,2,4,5-tetrakis(diphenylphosphino)benzene (tpbz) is a remarkably robust ligand that is easily accessible in gram quantities from inexpensive, commercial precursors in a single step. We have found this molecule to be useful as a rigid, bridging ligand between redox-active metallodithiolene end-groups. Such molecules support oxidation of the dithiolene ligands from fully reduced ene-1,2-dithiolates to radical monoanions that experience only very weak dipolar coupling, as gauged by computation and by EPR spectroscopy [2,3]. Such weak coupling of spatially well-defined, chemically stable spins provides a basis for the creation of coherent quantum states for quantum computing applications [4].

A decidedly useful property of the tpbz ligand is its capacity to chelate metal ions in a controlled, stepwise fashion, possibly

because of a slight, deactivating effect upon the second chelate after the first has been metallated. This ability to control binding of metal ions enables the assembly, in a deliberate, modular way, of hetero multimetallic complexes wherein differing metal ions can support different functions. By such a general methodology, Fox and coworkers, for example, have constructed an [(bipy)<sub>2</sub>Os(tpbz)Ni(tpbz)Pd(dppb)]<sup>6+</sup> complex (dppb = 1,2-bis(diphenylphosphino)benzene) and demonstrated its ability to act as a photoactivated electron switch [5].

One drawback of the tpbz ligand is that its surfeit of phenyl groups provides limited solubility when it is incorporated into a charge-neutral molecule with inversion symmetry. In such cases, growing of crystals well-suited for X-ray diffraction can be challenging. While spectroscopic characterization by <sup>31</sup>P NMR spectroscopy can be clear in showing chelation to a transition metal, <sup>1</sup>H NMR spectroscopy is relatively uninformative for distinguishing ligand from complex or one metal complex from another. Apart from tpbz itself, only 1,2,4,5-tetrakis(dimethylphosphino)benzene has been reported by Fox and coworkers [6], but its inherent air-sensitivity and more difficult synthesis position it disadvantageously as a ligand for broad implementation on a large scale.

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