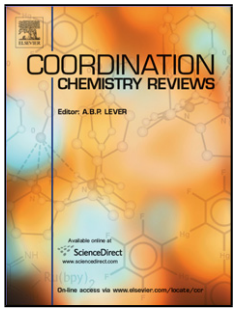


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# Beyond Triphos – New Hinges for a Classical Chelating Ligand

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## Abstract

Branched triphosphine ligands have been less widely studied than mono- and bi-dentate analogues. The most studied ligand of this type is Triphos$^{Ph}$ ($CH_3C(CH_2PPh_2)_3$). Substitution of the apical C–$CH_3$ moiety with boron, silicon, tin, nitrogen or phosphorus fragments has generated a new family of ligands, in some cases displaying varying coordination chemistry and reactivity to the parent carbon-based system. This review includes the synthetic strategies implemented to afford these ligands, as well as derivatives by way of varying the phosphine substituents. Although not exhaustive, relevant *types* of reported complexes featuring these ligands are discussed, as well as their reactivity and catalytic applications. Through critical analysis, common themes and chemical trends across this family of apical heteroatomic, branched triphosphines can be identified, leading to improvements in current chemical applications, as well as new areas that remain underdeveloped.

## Keywords

Triphos, Coordination Chemistry, Reactivity, Catalysis, Small Molecule Activation



## 1. Introduction

Triphosphine based ligands continue to attract much attention for both coordination chemistry and applications in catalysis [1-5]. Unlike the better known and more kinetically labile mono- and di-phosphine ligand systems, tridentate ligands can generally provide greater kinetic and thermal stability due to greater chelation, in addition to giving very well-defined coordination modes to transition metal centers [6].

*Abbreviations: In general structures with general formula R'E(CH2PR2)3 are abbreviated as $R'EP_3^R$; AACVD, aerosol-assisted chemical vapour deposition; acac, acetylacetone; ATRA, atom-transfer radical additions; ATRP, atom-transfer radical polymerization; cod, 1,5-cyclooctadiene; $Cp^-$, cyclopentadienyl; Cy, cyclohexyl; Cyp, cyclopentyl; DMAP, 4(dimethylamino)pyridine; DMO, dimethyl oxalate; DMP, 2,5-dimethylphospholane; DMSO, dimethyl sulfoxide; DPP, 2,5-diphenylphospholane; ED, ethane-1,2-diol; EDA, ethyl diazoacetate; Hdbabh, 2,3:5,6-dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene; Mes, 2,4,6-$Me_3C_6H_2$; MG, methyl glycolate; MT, (R)-PMe$^t$Bu; OBz, benzoate; $OTf^-$, triflate; PDIs, polydispersity indicies; THF, tetrahydrofuran; TMEDA, tetramethyl ethane diamine; tmm, trimethylenemethane; $Tp^-$, trispyrazolylborate; $Tp^{Me2}$, hydridotris(3,5-dimethylpyrazolyl)borate.*