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Transition Metal Catalysts in the Synthesis of Functionalized Substituted Phosphonates

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Synthesis of new functionalized phosphonates was achieved by two ways, using either nucleophilic or electrophilic modification of organophosphorus compounds by transition metal catalytic reactions. The first way employs the transformation of carbonyl group in α -, β -, and γ -ketophosphonates by nucleophilic addition (silacyanation, hydrosilylation, etc.).

In the presence of chiral catalyst derived from titanium salt of S-binaphtylphosphoric acid enantioselective synthesis of α - and γ -phosphorus substituted cyanhydrines has been achieved with ee 56 and 72%. The second route utilizes the arylation (or hetarylation) of α -phosphoryl stabilized carbanions by Pd-catalyzed cross-coupling reaction and may become a promising way to functionalized arylphosphonates.

$$X_2P(O)CH_2Z$$

$$\frac{1.BuLiCul \text{ or NaH } 2.Ar(Het)l}{Pd-cat}$$
 $X_2P(O)CHArZ$

$$X = Et_2N, EtO; Z = H, COOR, P(O)(OEt)_2.$$

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