Abstract The development of polydentate ligands based on ferrocene platform has driven progress in homogeneous catalysis. Catalyst longevity and ultra-low catalyst loadings have been used to reach high turnover numbers (TONs > 10,000). These performances were based on original multidentarity effects, which are now used to develop very efficient methods for palladium-catalysed C–C, C–N and C–O cross-couplings, thus direct C–H and O–H functionalization of demanding substrates including organic chlorides are feasible. The features of robust, air-stable polyphosphine auxiliaries and their performances in recent low loading palladium-catalyzed reactions in direct arylation and etherification reactions of heteroaromatics will be detailed. Mechanisms in oxidative addition and reductive elimination (electroanalysis, kinetics, DFT modeling) have revealed net differences with traditional monophosphine ligands that will be described.