Dimerization of organocyanides ligated to aryldicyclopentadienyltitanium.

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Dimerization of organocyanides ligated to aryldicyclopentadienyltitanium.

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Intermolecular formation of carbon-carbon bonds by dimerization of dicyclopentadienylaryltitanium-nitrile complexes.
The Ti(III) complexes $[Ti(\eta^5\text{-}C_5H_5)_2Ar]$ (Ar=C_6H_5,$CH_2C_6H_5$,o-$CH_3C_6H_4$, m-$CH_3C_6H_4$, p-$CH_3C_6H_4$,C_6F_5,Cl) react with nitriles RCN(R=CH_3,t-C_4H_9,C_6H_5,o-$CH_3C_6H_4$, 2,6-$(CH_3)_2C_6H_3$) to give simple adducts $[Ti(\eta^5\text{-}C_5H_5)_2Ar(RCN)]$. At higher temperatures dimerization occurs by linkage via the nitrilic carbons with formation of a carbon-carbon bond. There is concomitant oxidation of the metal from (Ti(III) → Ti(IV).
The dimerization reaction is shown to be strongly dependent on the nature of Ar and R; both electronic and steric factors are shown to be important. Possible mechanisms for the intermolecular formation of the carbon-carbon bond are discussed.