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Dimerization of organocyanides ligated to aryldicyclopentadienylytitanium.

Boer, E.J.M. de; Teuben, J.H.

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Dimerization of organocyanides ligated to
aryldicyclopentadienyltitanium.

E.J.M. de Boer and J.H. Teuben.

Ninth Sheffield-Leeds International Symposium,
Sheffield, 1977.

Intermolecular formation of carbon-carbon bonds by
dimerization of dicyclopentadienylaryltitanium-
nitrile complexes.

The Ti(III) complexes $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{Ar}]$
(Ar=C₆H₅, CH₂C₆H₅, o-CH₃C₆H₄, m-CH₃C₆H₄, p-CH₃C₆H₄, C₆F₅, Cl)
react with nitriles RCN (R=CH₃, t-C₄H₉, C₆H₅, o-CH₃C₆H₄,
2,6-(CH₃)₂C₆H₃) to give simple adducts
[Ti(η⁵-C₅H₅)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.