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## Dimerization of organocyanides ligated to aryldicyclopentadienylyltitanium.

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=C<sub>6</sub>H<sub>5</sub>, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, m-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>F<sub>5</sub>, Cl)  
react with nitriles RCN (R=CH<sub>3</sub>, t-C<sub>4</sub>H<sub>9</sub>, C<sub>6</sub>H<sub>5</sub>, o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>,  
2,6-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) to give simple adducts  
[Ti(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ar(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.