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Activation of Unsaturated Molecules by Dicyclopentadienyltitanium Compounds

Teuben, J.H.; Weij, F.W. van der; Boer, E.J.M. de; Klei, E.; Zeinstra, J.

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146. Activation of Unsaturated Molecules by Dicyclopentadienyltitanium Compounds
J.H. Teuben, F.W. van der Weij, E.J.M. de Boer, E. Klei, J. Zeinstra.
 Inorganic Chemistry Department, Rijksuniversiteit, Nijenborgh 16, 9747 AG Groningen,
 The Netherlands.

The 15-electron complexes $CpTiR$ (R =alkyl, aryl) display, depending on the nature of R , an interesting variety in properties like thermal stability and reactivity towards unsaturated molecules. The vacant and reactive metal orbital is essential in thermal decomposition and stabilization is effected by blocking this site either sterically (bulky R) or by coordination (solvent, N_2 , nitriles, isonitriles etc.). On the other hand the ligands are sometimes activated and show unexpected reactions. In $(Cp_2TiR)_2N_2$ the dinitrogen ligand ($N-N$ distance 116 pm) can be reduced to NH_3 and N_2H_4 precursors. Coordinated nitriles tend to dimerize with formation of the $Ti(IV)$ complexes $(Cp_2TiR)N=C(R^1)-(R^2)C=N-(Cp_2TiR)$; isonitriles insert after complexation into the $Ti-R$ bond giving $Cp_2TiC(R)=NR^1$. Similar insertions are observed for small molecules like CO , CS_2 , $CH=CH$. Cp_2TiCH_3 (prepared in situ) shows interesting activating properties towards (substituted) pyridines. After initial coordination, metallation takes place at the 2-position of the ligand with formation of CH_4 . The product formed contains an η^2 -pyridyl ligand:

