

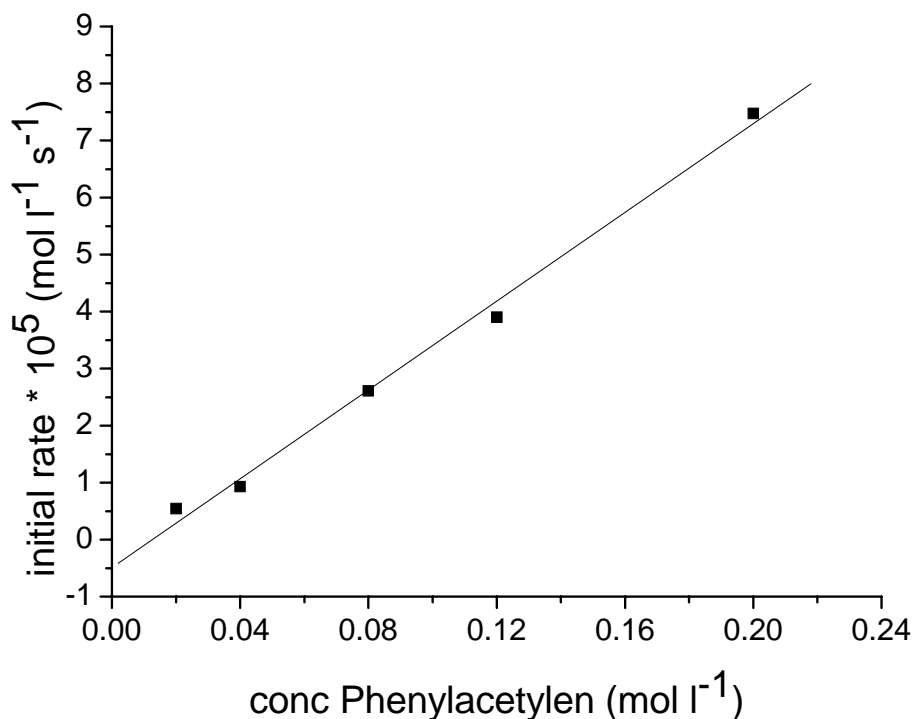
Supporting Information for
**Titanium Hydroamination Catalysts Bearing a 2-Aminopyrrolinato Spectator Ligand:
Monitoring the Individual Reaction Steps**

Katharina Weitershaus, Benjamin D. Ward, Raphael Kubiak, Carsten Müller,
Hubert Wadepohl, Sven Doye,* and Lutz H. Gade*

(a) Kinetic investigations

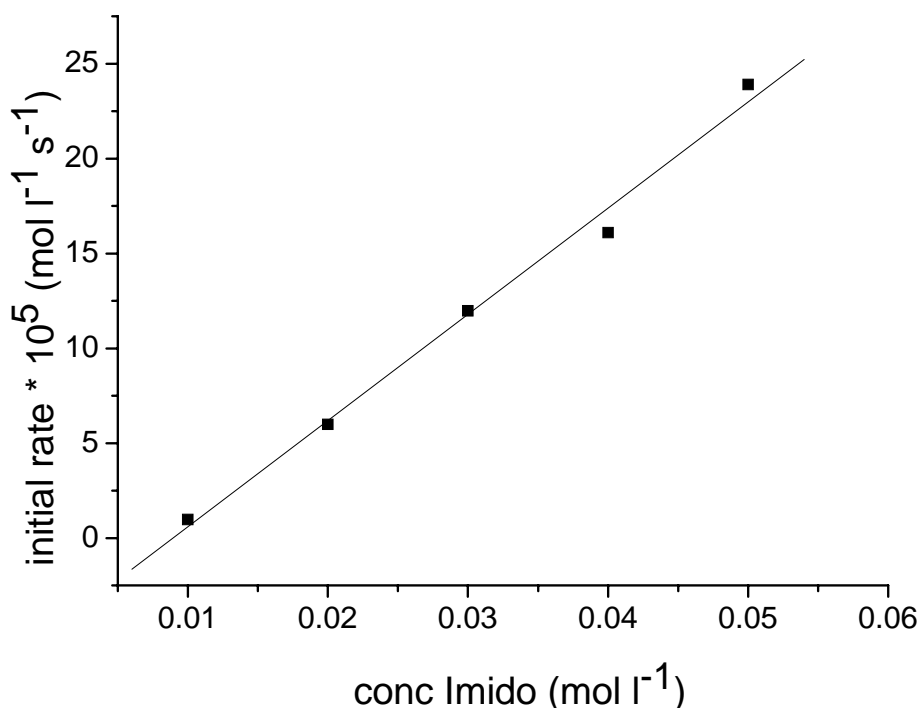
The kinetics of the formation of the metallacyclic compound **10** from [Cp*Ti(N^{Xyl}N)(N-2,6-C₆H₃Me₂)] (**5**) and phenylacetylene were investigated by the method of initial rates, which indicated a first order dependence on the concentration of phenylacetylene. Therefore the imido complex **5** (20 μmol) was reacted with 0.5, 1, 2, 3 and 5 molar equivalents of phenylacetylene in toluene-d₈ (0.6 ml) at 10 °C. The reaction was monitored by ¹H NMR spectroscopy and the concentration of the metallacyclic compound **10** was plotted against time. The conversion curve was line-fitted to a first order exponential decay $A\exp(-x/b)$; the initial rate was estimated from $-A/b$, derived from differentiation of the fitted line for $x = 0$. A plot of the initial rate *versus* alkyne concentration indicated a linear relationship (Figure S1).

Figure S1



A similar analysis was carried out by reacting varying amounts of $[\text{Cp}^*\text{Ti}(\text{N}^{\text{Xyl}}\text{N})(\text{N}-2,6\text{-C}_6\text{H}_3\text{Me}_2)]$ (**5**) (5 to 25 μmol) with an excess of phenylacetylene (20 molar equivalents) in toluene- d_8 (0.6 ml) at 10 °C. The reaction was monitored by ^1H NMR spectroscopy and the concentration of the metallacyclic compound (**10**) was plotted against time. The conversion curve was line-fitted to a first order exponential decay $A\exp(-x/b)$; the initial rate was estimated from $-A/b$, derived from differentiation of the fitted line for $x = 0$. A plot of the initial rate *versus* imido compound **5** concentration indicated a linear relationship (Figure S2).

Figure S2



The rate of cleavage of the metallacyclic compound $[\text{Cp}^*\text{Ti}(\text{N}^{\text{Xyl}}\text{N})\{\kappa^2\text{N}(2,6\text{-C}_6\text{H}_3\text{Me}_2)\text{CPh}=\text{CH}\}]$ (**10**) by an arylamine was determined using the method of initial rates, indicating a first order dependence on the concentration of **10** itself. Complex **10** (5 to 50 μmol) was reacted with 20 molar equivalents of 2,6-dimethylaniline in benzene- d_6 (0.6 ml) at 20 °C. The reaction was monitored by ^1H NMR spectroscopy and the concentration of **10** was plotted against time, and the conversion curve was line-fitted to a first order exponential decay $A\exp(-x/b)$. The initial rate was estimated from $-A/b$, derived from differentiation of

the fitted line for $x = 0$. A plot of the initial rate *versus* the concentration of **10** indicated a linear relationship (Figure S3).

Figure S3

