(a) Kinetic investigations

The kinetics of the formation of the metallacyclic compound 10 from [Cp*Ti(N^XylN)(N-2,6-C_6H_3Me_2)] (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-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 Aexp(-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 \([\text{Cp}^*\text{Ti}(\text{N}^{\text{Xyl}}\text{N})(\text{N}-2,6-\text{C}_8\text{H}_3\text{Me}_2)]\) (5) (5 to 25 \(\mu\text{mol}\)) with an excess of phenylacetylene (20 molar equivalents) in toluene-\(d_8\) (0.6 ml) at 10 °C. The reaction was monitored by \(^1\text{H}\) 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 \(\text{versus}\) imido compound 5 concentration indicated a linear relationship (Figure S2).

![Figure S2](image)

The rate of cleavage of the metallacyclic compound \([\text{Cp}^*\text{Ti}(\text{N}^{\text{Xyl}}\text{N})\{\kappa^2\text{N}(2,6-\text{C}_8\text{H}_3\text{Me}_2)\text{CPh}=\text{CH}]\}\) (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 \(\mu\text{mol}\)) 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 \(^1\text{H}\) 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**

![Graph showing the relationship between initial rate and concentration of MC](graph.png)