

## Introduction

Studies of the synthesis and reactivity of transition metal hydrazides, (L)M=NNR<sub>2</sub>, have been of sustained interest due to their relevance to the biological and synthetic fixation of N<sub>2</sub> to ammonia.<sup>1,2</sup> For this reason, much of the early work was based around Group 6 systems.<sup>3</sup> Although initial reactivity reports of Group 4 hydrazides appeared some time ago,<sup>4</sup> there has recently been a surge in activity and output in this area,<sup>5-7</sup> and a number of new reactions of the M=NNR<sub>2</sub> functional group have been discovered.

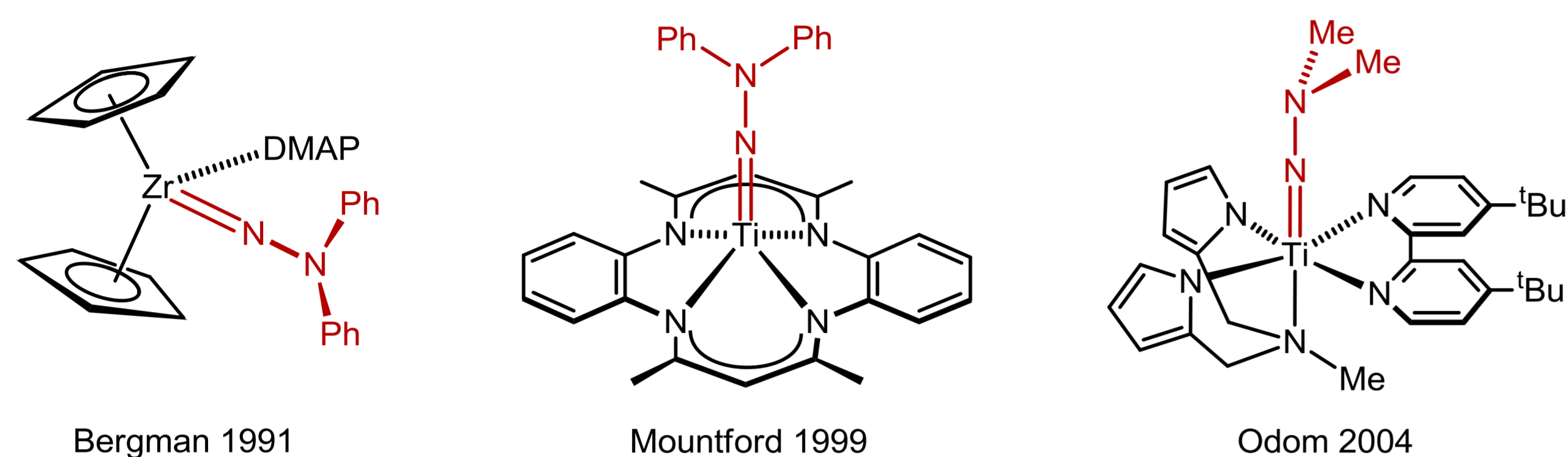


Fig. 1. Examples of Group 4 terminal hydrazide complexes.<sup>4,5</sup>

Some of the new reactions discovered recently include the cycloaddition of alkynes (as in I, Fig. 2) and heteroalkynes to the M=N<sub>α</sub> multiple bond, and N<sub>α</sub>-N<sub>β</sub> bond insertion reactions with substrates including alkynes and isocyanides (forming II and III, Fig. 2).<sup>7</sup>

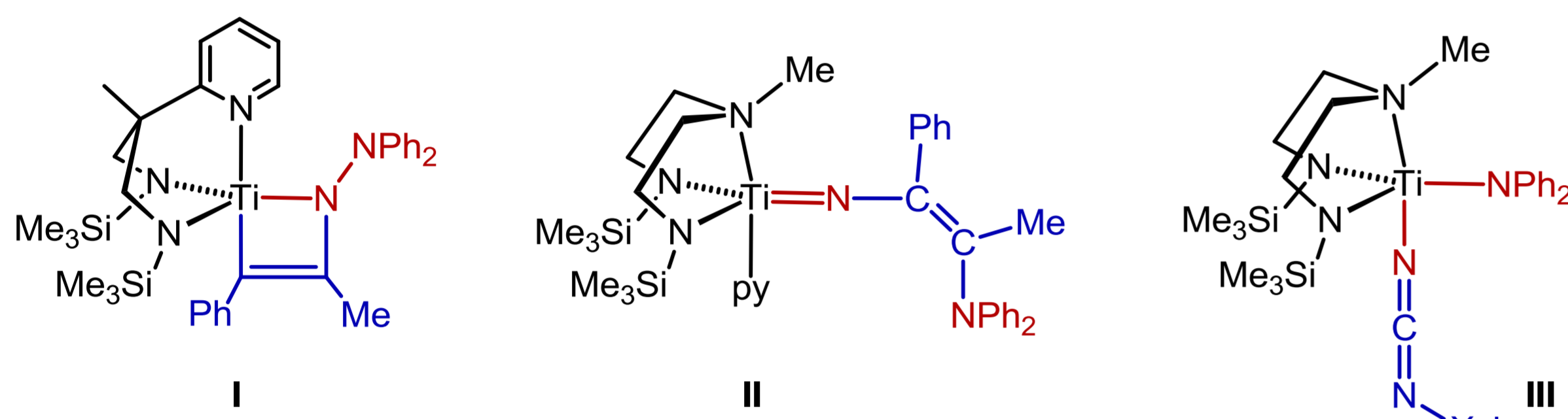
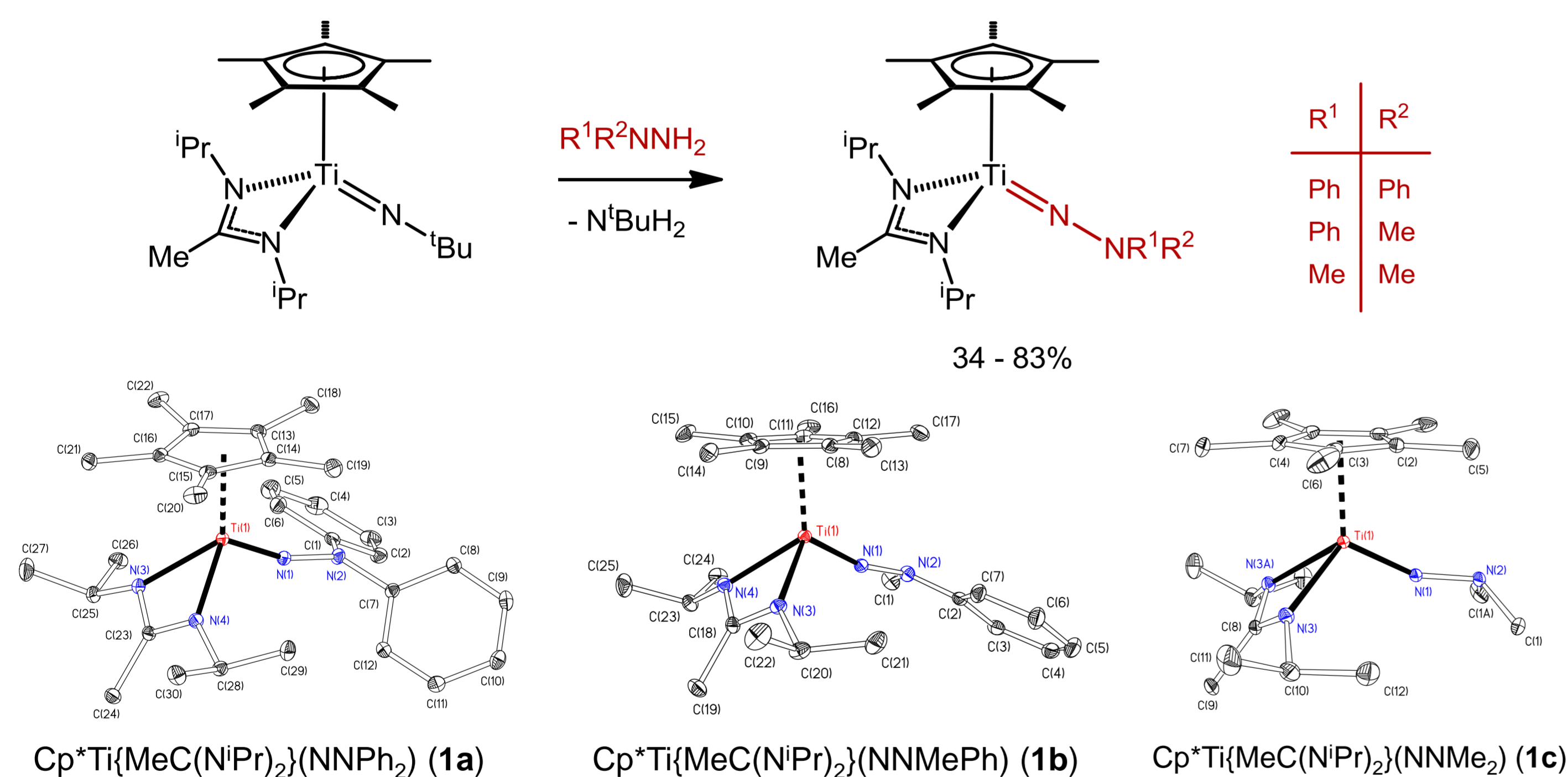


Fig. 2. Reaction products of Ti=NNPh<sub>2</sub> bonds with alkynes (I, II) and XyINC (III): M=N<sub>α</sub> cycloaddition and N<sub>α</sub>-N<sub>β</sub> bond cleavage.<sup>7</sup>

## Synthesis

A family of Cp\*-amidinate supported titanium hydrazides was synthesised by a *tert*-butyl imido/hydrazine exchange methodology,<sup>7</sup> and structurally characterised. The geometry at N<sub>β</sub> is strongly dependant on hydrazide substituents.



	1a	1b	1c	1a	1b	1c	
Ti(1)-Cp <sub>cent</sub>	2.097	2.067	2.063	Ti(1)-N(1)-N(2)	163.9(1)	166.3(2)	159.5(1)
Ti(1)-N(1)	1.734(2)	1.734(2)	1.723(2)	N(1)-N(2)-C(1)	118.9(2)	115.3(2)	110.7(1)
Ti(1)-N(3)	2.115(2)	2.110(2)	2.101(1)	N(1)-N(2)-C(7)	116.7(2)	118.2(2)	-
Ti(1)-N(4)	2.099(2)	2.090(2)	-	N(1)-N(2)-C(1A)	-	-	110.7(1)
N(1)-N(2)	1.369(2)	1.371(3)	1.386(2)	C(1)-N(2)-C(7)	121.5(2)	120.8(2)	-
N(2)-C(1)	1.409(3)	1.460(4)	1.461(2)	C(1)-N(2)-C(1A)	-	-	112.9(2)
N(2)-C(7)	1.425(3)	1.396(4)	-				

## Acknowledgements

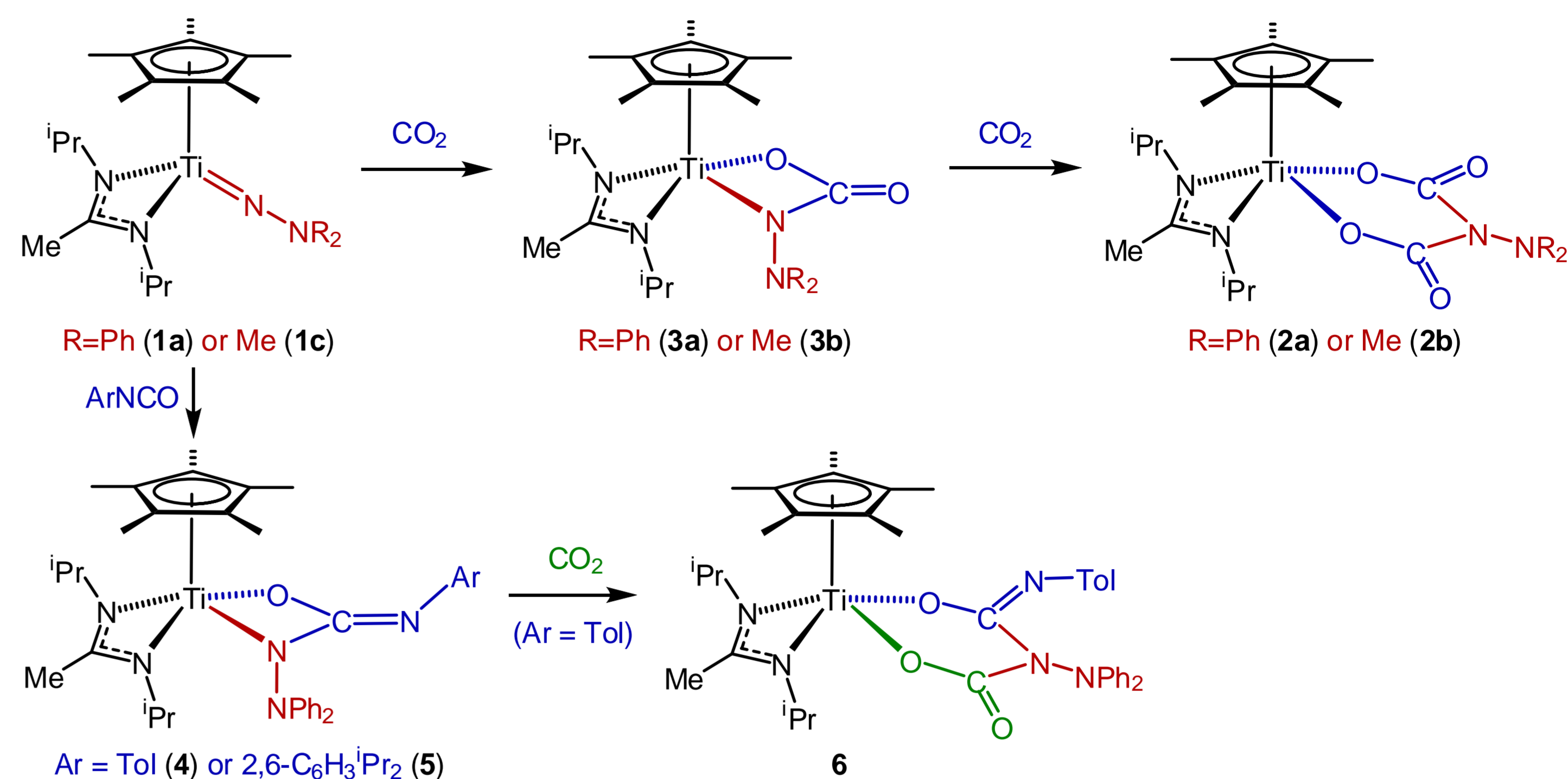
We thank Dr. A. D. Schwarz and A. D. Schofield for X-ray structure determinations, and the EPSRC, Linacre College, Oxford, and the Ministry of Higher Education, Malaysia for financial support.

## References

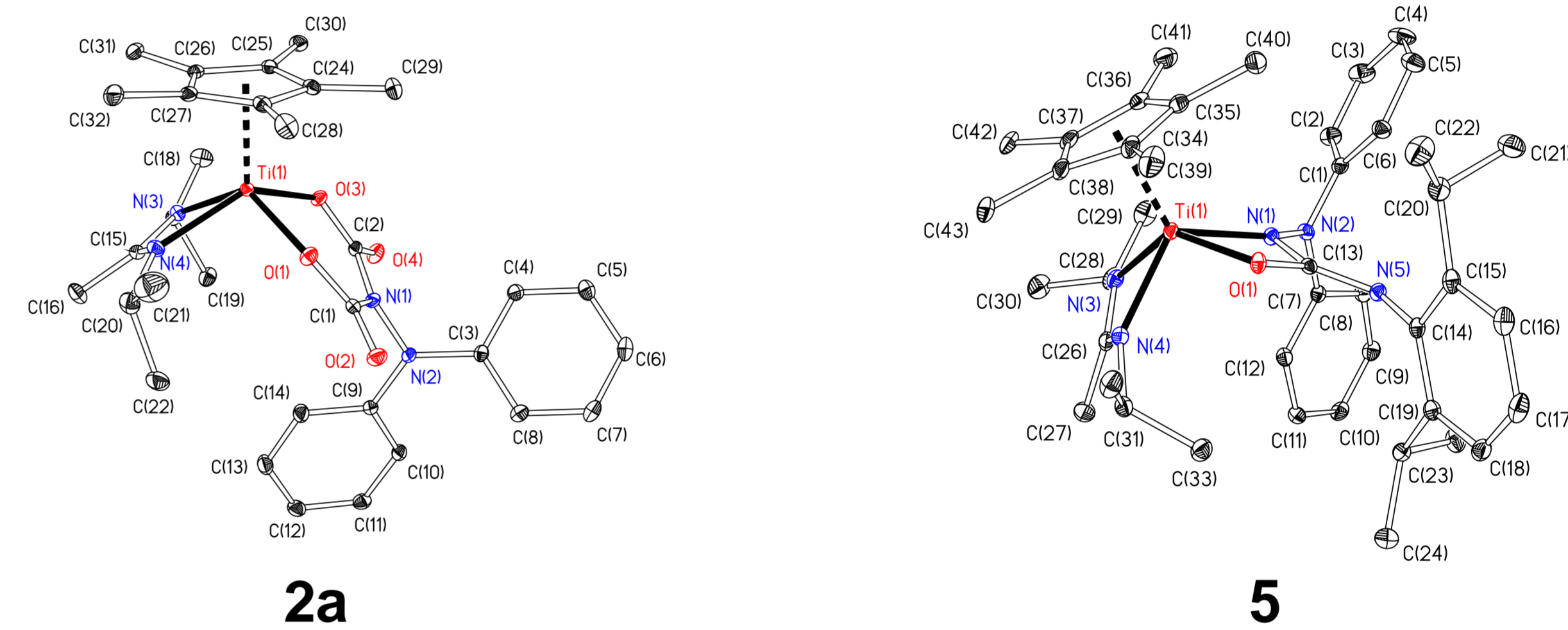
[1] Schrock, R. R. *Angew. Chem., Int. Ed.*, **2008**, *47*, 5512-5522. [2] Fryzuk, M. D. *Chem. Rec.*, **2003**, *3*, 2-11. [3] Hidai, M. *Coord. Chem. Rev.*, **1999**, *185-186*, 99-108. [4] Bergman, R. G. *et al*, *J. Am. Chem. Soc.*, **1991**, *113*, 6343-6345; Mountford, P. *et al*, *J. Chem. Soc., Dalton Trans.*, **1999**, 379-392. [5] Odom, A. L. *et al*, *J. Am. Chem. Soc.*, **2004**, *126*, 1794-1803; *Organometallics*, **2006**, *25*, 3099-3101; *Inorg. Chem.*, **2007**, *46*, 6373-6381. [6] Gade, L. H. *et al*, *Angew. Chem., Int. Ed.*, **2007**, *46*, 8426-8430; *Chem.-Eur. J.*, **2008**, *14*, 8131-8146; *Organometallics*, **2009**, *28*, 4747-4757; *Dalton Trans.*, **2009**, 4586-4602; *Organometallics*, **2009**, *28*, 3381-3389. *Angew. Chem., Int. Ed.*, **2009**, *48*, 2152-2156. [7] Mountford, P. *et al*, *Inorg. Chem.*, **2005**, *44*, 8442-8458; *Chem. Commun.*, **2007**, 4937-4939; *Chem. Comm.*, **2008**, 5101-5103; *Inorg. Chem.*, **2008**, *47*, 12049-12062; *Organometallics*, **2008**, *27*, 6479-6494; *Chem. Comm.*, **2010**, *46*, 85-87; unpublished results.

## Reactions with CO<sub>2</sub> and ArNCO

Reaction of Cp\*Ti{MeC(NiPr)<sub>2</sub>}(NNR<sub>2</sub>) (R = Ph (1a) or Me (1c)) with an excess of CO<sub>2</sub> gave Cp\*Ti{MeC(NiPr)<sub>2</sub>}{OC(O)N(NR<sub>2</sub>)C(O)O} (R = Ph (2a) or Me (2b)) through the formation of an intermediate cycloaddition product 3a and 3b.



Reaction of 1a with ArNCO (Ar = Tol or 2,6-C<sub>6</sub>H<sub>3</sub>iPr<sub>2</sub>) underwent 2+2 cycloaddition to give 4 and 5. Subsequent addition of CO<sub>2</sub> to 4 gave the mixed double insertion product 6.



## Reactions with silanes

Reaction of 1c with phenyl silanes PhSiHRR' gave different products, depending upon R and R'. For R = R' = H, Si-H activation occurs forming 7 which exists in equilibrium with 1c and free silane. For R = H, R' = Cl, Si-Cl bond activation is preferred giving 8 as the product. When R = R' = Cl, amidinate ligand transfer occurs to form the dichloride complex 10 via sequential Si-Cl bond cleavage steps.

