This paper is published as part of a Dalton Transactions themed issue on:

The Synergy between Theory and Experiment

Guest Editor John McGrady University of Glasgow, UK

Published in issue 30, 2009 of Dalton Transactions



Image reproduced with permission of Christophe Coperet

Papers published in this issue include:

<u>A combined picture from theory and experiments on water oxidation, oxygen reduction and proton</u> <u>pumping</u> Per E. M. Siegbahn and Margareta R. A. Blomberg, *Dalton Trans.*, 2009,

DOI: 10.1039/b903007g

<u>Mechanisms of C–H bond activation: rich synergy between computation and experiment</u> Youcef Boutadla, David L. Davies, Stuart A. Macgregor and Amalia I. Poblador-Bahamonde, *Dalton Trans.*, 2009, DOI: 10.1039/b904967c

Are tetrathiooxalate and diborinate bridged compounds related to oxalate bridged quadruply bonded compounds of molybdenum? Malcolm H. Chisholm and Namrata Singh, *Dalton Trans.*, 2009 DOI: <u>10.1039/b901734h</u>

<u>Molecular recognition in Mn-catalyzed C–H oxidation. Reaction mechanism and origin of selectivity</u> <u>from a DFT perspective</u> David Balcells, Pamela Moles, James D. Blakemore, Christophe Raynaud, Gary W. Brudvig, Robert H. Crabtree and Odile Eisenstein, *Dalton Trans.*, 2009 DOI: 10.1039/b905317d

Visit the *Dalton Transactions* website for more cutting-edge inorganic and organometallic research <u>www.rsc.org/dalton</u>

Reactions of cyclopentadienyl-amidinate titanium imido compounds with CO₂: cycloaddition-extrusion *vs.* cycloaddition-insertion[†]

Aldo E. Guiducci,^a Catherine L. Boyd,^a Eric Clot*^b and Philip Mountford*^a

Received 27th January 2009, Accepted 24th March 2009 First published as an Advance Article on the web 27th April 2009 DOI: 10.1039/b901774g

A combined experimental and DFT study of the reactions of cyclopentadienyl-amidinate titanium imido complexes with CO₂ is reported. Cycloaddition reactions of the aryl imido compounds $Ti(\eta-C_5R_4Me)(NAr)\{R^2C(NR^1)_2\}$ (R = H or Me; R¹, R² = SiMe₃, Ph or ⁱPr, Me) with CO₂ gave the corresponding N,O-bound carbamate complexes $Ti(\eta-C_3R_4Me)\{N(Ar)C(O)O\}\{R^2C(NR^1)_2\}$. These reacted further with CO₂ by insertion into the Ti-N(Ar) bond to afford the new dicarboxylates $Ti(\eta-C_5R_4Me){OC(O)N(Ar)C(O)O}{R^2C(NR^1)_2}$ in which the original Ti=NAr bond has been completely cleaved. The X-ray structures of two of these have been determined. The CO₂ insertion reactions of the *para*-substituted phenyl carbamate complexes $Ti(\eta-C_5Me_5)$ {N(-4-C₆H₄X)-C(O)O {MeC(NⁱPr)₂} (X = Me, CF₃ or NMe₂) were first order with respect to both carbamate complex and CO₂ and the pseudo first order rate constants were effectively independent of the para substituent. The corresponding *tert*-butyl imido compounds $Ti(\eta-C_3R_4Me)(N'Bu)\{R^2C(NR^1)_2\}$ also reacted with CO₂ to form N,O-bound carbamate complexes, $Ti(\eta-C_3R_4Me){N('Bu)C(O)O}$ - $\{R^2C(NR^1)_2\}$. However, these did not insert a further molecule of CO₂ and instead extruded 'BuNCO' to form the crystallographically characterized oxo-bridged dimers $[Ti(\eta-C_5R_4Me)(\mu-O)\{R^2C(NR^1)_2\}]_2$. These reactions proceeded via transient terminal oxo intermediates, one of which was trapped by the addition of TolNCO (Tol = *p*-tolyl). DFT (B3PW91) calculations on $Ti(\eta-C_5H_5)(NR)\{MeC(NMe)_2\}$ $(R = Me, Ph, 4-C_6H_4Me, 4-C_6H_4NMe_2, 4-C_6H_4CF_3)$ reacting with CO₂ showed that the second CO₂ insertion is thermodynamically favoured over isocyanate extrusion, and that the rates of the two processes are similar. Calculations on $Ti(\eta - C_5 R_5)(N'Bu) \{MeC(N'Pr)_2\}$ (R = H or Me) showed that increasing the steric bulk increases the thermodynamic favourability of the isocyanate extrusion process and significantly raises the activation barrier for the second CO_2 insertion, making the latter process impossible.

Introduction

Since being established at the start of the 1990s,¹⁻⁴ the chemistry of terminal titanium imido compounds has been advanced enormously. In addition to aspects of their molecular and supramolecular^{5,6} structures and bonding,⁷⁻¹³ applications in olefin polymerisation¹⁴⁻²¹ and uses in materials chemistry,²²⁻²⁷ the main focus of the chemistry of titanium imido compounds has concerned transformations involving the polar and reactive Ti=NR bond itself. Some of this progress has been charted in a series of reviews,^{17,28-32} and the unsaturated substrates stoichiometrically or/and catalytically transformed by titanium imido compounds include: alkenes,³³ allenes,³⁴ alkynes,³⁴⁻³⁹ nitriles,⁴⁰ isonitriles,^{41,42} phospha-alkynes^{40,43-46} and heterocumulenes.⁴⁷⁻⁵⁷

We have been developing the chemistry of the half-sandwich cyclopentadienyl-amidinate compounds shown in Chart 1.^{56,58,59}





The straightforward and modular synthesis of these compounds allows for facile variation of the cyclopentadienyl-amidinate supporting ligand set and also the imido N-substituents. In this contribution, we focus on the reactions of these compounds with CO₂. Although the reaction chemistry of CO₂ in general continues to be of considerable interest,⁶⁰⁻⁶⁶ comparatively little has been reported for transition metal imido compounds⁶⁷⁻⁶⁹ and for group 4 in particular.^{47,48,51,53,54} The first structurally authenticated product for any metal was Cp*Ir{N('Bu)C(O)O}⁶⁸ and the first from group 4 was Ti{N(Tol)C(O)O}(Me₄taa).⁴⁷ A number of reports of reactions of group 4 imido compounds with CO₂ have since appeared.^{47,48,51,53,54} Both the *tert*-butyl and aryl imido-derived cycloaddition products typically undergo thermally promoted isocyanate extrusion,^{48,51,53,54} although in at least one

^aChemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford, U.K. OX1 3TA. E-mail: philip.mountford@chem.ox.ac.uk.

^bUniversité Montpellier 2, Institut Charles Gerhardt, CNRS 5253, Case Courrier 1501, Place Eugène Bataillon, 34095 Montpellier, France. E-mail: eric.clot@univ-montp2.fr

[†] Electronic supplementary information (ESI) available: Graphs used for determination of kinetic parameters. CCDC reference numbers 718337– 718339. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b901774g

case the reaction is promoted by ambient light.⁴⁷ In some cases, the reaction is very fast and an intermediate carbamate cannot be observed. With the exception of Me₄taa-supported⁴⁷ and related⁵¹ systems, the metal oxo by-products self-trap by dimerization.^{48,53,54} It has also been shown for a cationic tantalum system that the extruded *tert*-butyl isocyanate could undergo a C–H bond activation reaction at the newly formed metal–oxygen bond.⁶⁷

We have recently reported experimental and DFT computational results on pendant arm functionalised amidinate systems of the type $Ti(\eta - C_5 R_4 Me)(N'Bu) \{Me_3 SiNC(Ph)NCH_2 CH_2 R'\} (R' =$ NMe₂ (1a,b) or Me (2) in Chart 1)). These specifically probed for anchimeric effects of pendant donors on the Ti=N'Bu/CO₂ cycloaddition/extrusion reaction.53 We also recently reported complementary reactions of some cyclopentadienyl-amidinate titanium imides with other substrates, including isocyanates, CS₂, COS, PhNO, ketones and aldehydes, and organic primary amides.⁵⁶ In our present contribution, we describe a detailed experimental and computational study of the reactions of a range of cyclopentadienyl-amidinate titanium imido complexes with CO₂. In particular, we focus on how the rates of the cvcloaddition/extrusion or cvcloaddition/insertion reactions are critically dependent on the imido and other ligand substituents. Part of this work has been communicated.70

Results and discussion

Synthesis of new cyclopentadienyl-amidinate aryl imido compounds

As shown in Chart 1, a number of cyclopentadienyl-*tert*-butyl (1–6) and aryl imido (7, 8) have been reported previously.^{56,58,59} However, our preliminary work with CO_2^{70} and complementary studies with other heterocumulenes⁵⁶ found that the reactions of the *tert*-butyl and aryl imido systems differ considerably. We therefore decided to extend the range of aryl imido systems available so as to probe the effects of both steric and electronic factors on their reactions with CO_2 . The syntheses of the new compounds are summarized in Scheme 1 and eqn (1).



Reaction of the pentamethylcyclopentadienyl compound Ti(η -C₅Me₅)(N'Bu){MeC(N'Pr)₂} (4) with two *para*-substituted anilines at room temperature afforded the compounds Ti(η -C₅Me₅)(N-4-C₆H₄X){MeC(N'Pr)₂} (X = CF₃ (9) or NMe₂ (10)) in 87% yield (Scheme 1). These compounds complement compounds 7 and (especially) 8 (Chart 1) prepared previously by the same general route.⁵⁶ The less sterically protected monomethylcyclopentadienyl compound Ti(η -C₃H₄Me)(N-2,6-C₆H₃Me₂){MeC(N'Pr)₂} (11) was also formed cleanly (71% yield as a green oil after high vacuum distillation). The methylcyclopentadienyl-benzamidinate analogue Ti(η -C₅H₄Me)(N-2,6-C₆H₃Me₂){PhC(NSiMe₃)₂} (12) was also made by room temperature imido ligand exchange starting from the *tert*-butyl imido compound 5 (58% yield). In contrast, the pentamethylcyclopentadienyl-benzamidinate com-



Scheme 1

pound Ti(η -C₅Me₅)(N'Bu){PhC(NSiMe₃)₂} (**3**) does not undergo imide exchange reactions with anilines even after several days at 80 °C (benzene-d₆). This suggests that the PhC(NSiMe₃)₂ ligand is significantly more sterically demanding than the acetamidinate analogue MeC(NⁱPr)₂ since compound **4** easily undergoes this reaction (to form **7**). Fortunately, an alternative starting compound Ti(η -C₅Me₅)(N-2,6-C₆H₃Me₂)Cl(py) (**13**) was available.⁷¹ Reaction of **13** with Li[PhC(NSiMe₃)₂] (eqn (1)) afforded the target compound Ti(η -C₅Me₅)(N-2,6-C₆H₃Me₂){PhC(NSiMe₃)₂} (**14**) as a green powder in 36% yield and the X-ray structure has been determined (see Fig. 1).



Fig. 1 Displacement ellipsoid plot (25% probability) of $Ti(\eta-C_5Me_5)-(N-2,6-C_6H_3Me_2)$ {PhC(NSiMe_3)₂}(14). H atoms omitted for clarity.

Compound 14 is monomeric with a three-legged piano stool geometry, which is consistent with the solution NMR data.

Bond lengths/Å			
Ti(1)–N(1) Ti(1)–N(2)	2.134(2) 2.107(2)	$Ti(1) \cdots Cp_{cent}$ C(1)-N(1)	2.079 1.327(4)
Ti(1) - N(3)	1.748(2)	C(1)–N(2)	1.346 (4)
Bond angles/°			
Ti(1)–N(3)–C(14)	165.9(2)	$Cp_{cent} \cdots Ti(1) - N(2)$	119.6
$Cp_{cent} \cdots Ti(1) - N(1)$	120.5	$Cp_{cent} \cdots Ti(1) - N(3)$	121.8

Selected bond distances and angles are given in Table 1 and are very similar to those for 7 and are within the previously reported ranges for titanium(IV) complexes of the three types of ligand present.⁷²⁻⁷⁸ The approximately linear $Ti=N-C_{ipso}$ linkage suggests that the arylimido nitrogen N(3) is formally sp hybridized and able to act as 4 electron donor to the titanium centre, which achieves an overall valence electron count of 16.

The rest of this contribution describes the various reactions of cyclopentadienyl-amidinate imido complexes with CO_2 as a function of the imido *N*-substitutents and the overall steric properties of the complexes.

Reactions of aryl imido compounds with CO2: cycloaddition

Reactions of the 2,6-dimethylphenyl imido compounds Ti(n- C_5R_4Me)(N-2,6- $C_6H_3Me_2$){ $R^2C(NR^1)_2$ } (R = Me: R^1 , $R^2 = {}^iPr$, Me (7) or SiMe₃, Ph (14); R = H: R^1 , $R^2 = {}^{i}Pr$, Me (11) or SiMe₃, Ph (12) with an excess of CO₂ at room temperature yielded the corresponding cherry-red N,O-bound carbamate derivatives $Ti(\eta - C_5 R_4 Me) \{N(-2, 6 - C_6 H_3 Me_2)C(O)O\} \{R^2 C(NR^1)_2\} (R = Me:$ R^{1} , $R^{2} = {}^{i}Pr$, Me (15) or SiMe₃, Ph (16); R = H: R^{1} , $R^{2} =$ ^{*i*}Pr, Me (17) or SiMe₃, Ph (18)) in 50–96% yield (Scheme 2). The IR spectra of 15–18 contain intense new v(C=O) stretches in the range 1667-1671 cm⁻¹, consistent with presence of the proposed N,O-bound carbamate ligand,^{47,48,68} and the structures proposed in Scheme 2 are analogous to that crystallographically determined for the pendant arm amidinate homologue $Ti(\eta$ - C_5Me_5 $\{N(Bu)C(O)O\}$ $\{Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2\}$. The compounds are stable in solution at room temperature and only decompose at elevated temperatures. Thus heating a solution of 15 in benzene-d₆ at 80 °C for 8 h led to a mixture of products, including the corresponding aryl isocyanate and the oxo-bridged dimer *trans*-[Ti(η -C₅Me₅)(μ -O}{MeC(NⁱPr)₂}]₂ (see below).

The ¹H NMR spectra of **15** and **16** are sharp at room temperature and clearly show a loss of molecular C_s symmetry (*e.g.* inequivalent amidinate N–R groups) upon their formation. In addition, the presence of two sharp resonances (each with a relative integral of 3 H) for the *ortho*-methyl groups of the *N*-aryl rings indicate restricted rotation about the N–C_{ipso} bonds. However, warming a solution of **15** to 60 °C in toluened₈ led to broadening and mutual pairwise exchange (k_{exch} 4.2 s⁻¹ at 60 °C) between the amidinate *iso*-propyl methine and methyl groups, as well as between the *ortho*-methyl groups of the 2,6-C₆H₃Me₂ substituent at the same rate, implying that the same mechanism links the two exchange events. Determination⁷⁹ of five exchange rate constants in the range 49–71 °C (toluene-d₈) and an Eyring



Scheme 2

analysis⁸⁰ (see ESI[†]) gave the activation parameters $\Delta H^{\ddagger} = 62.1 \pm 0.8 \text{ kJ mol}^{-1}$ and $\Delta S^{\ddagger} = -45 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$, which correspond to $\Delta G^{\ddagger} = 75.5 \pm 2.3 \text{ kJ mol}^{-1}$ at 298 K. The somewhat negative activation entropy suggests a rather ordered transition state for the rate limiting step for exchange.⁸¹

In contrast to the sharp NMR spectra of 15 and 16, the room temperature spectra of the less sterically encumbered complexes 17 and 18 showed rapid pairwise exchange of the *ortho*-methyl groups of the 2,6-C₆H₃Me₂ substituents, the amidinate ligand N-substituents and C₅H₄Me ring hydrogens (apparent AA'BB' spin system) at room temperature on the NMR timescale. However, the low temperature limiting spectra (213–223 K in CD₂Cl₂) are sharp and consistent with the structures proposed in Scheme 2 (inequivalent ortho methyl groups and amidinate N-substituents, as well as four inequivalent C₅H₄Me ring C-H resonances). An Eyring analysis (see ESI[†]) of five rate constants for SiMe₃ group exchange in 18 (toluene- d_8 ; range -5 to -25 °C) gave the activation parameters $\Delta H^{\ddagger} = 51.6 \pm 1.0 \text{ kJ mol}^{-1}$ and $\Delta S^{\ddagger} = -10 \pm 5 \text{ J}$ mol⁻¹ K⁻¹, which correspond to $\Delta G^{\ddagger} = 54.5 \pm 3.9$ kJ mol⁻¹ at 298 K. In comparison with the data for 15, the lower value of ΔH^{\ddagger} for 18 is consistent with reduced unfavourable steric interactions at the transition state geometry, and the less negative ΔS^{\ddagger} suggests that less ordering is necessary in the transition state.

The dynamic NMR data for 15-18 are consistent with the overall equilibrium in eqn (2), which represents the interconversion of two enantiomeric forms. In principle these equilibria could proceed *via* the corresponding monomeric oxo compounds

Ti(η -C₅R₄Me)(O){R¹C(NR²)₂} and free ArNCO (Ar = 2,6-C₆H₃Me₂). However, the negative ΔS^{\dagger} values determined for **15** and **18** militate against a dissociative process on the NMR timescale.



Reactions of aryl imido compounds with CO_2 : insertion of a 2nd molecule of CO_2

In the presence of an excess of CO_2 (ca. 1.1 atm), compounds 15–18 slowly react to form the C_s symmetrical dicarboxylate (azamalonate) complexes $Ti(\eta - C_5 R_4 Me) \{OC(O)N(-2,6 C_6H_3Me_2)C(O)O$ { $R^2C(NR^1)_2$ } (R = Me: R¹, R² = ^{*i*}Pr, Me (19); R = H: R^1 , $R^2 = {}^{i}Pr$, Me (20) or SiMe₃, Ph (21)) in 33-82% isolated yields (Scheme 2). A pure dicarboxylate derivative could not be obtained for the bulkiest carbamate, 16. The IR spectra of 19, 20 and 21 are consistent with the incorporation of a second carbonyl group into the molecule and each contains two bands in the carbonyl stretching region (1694-1703 and 1651–1657 cm⁻¹) corresponding to in- and out-of-phase v(C=O)stretching modes. The EI mass spectra of compounds 19 and 20 showed the expected parent ion and compounds 19 and 21 have been structurally characterised. The NMR spectra are consistent with $C_{\rm s}$ symmetrical products. The *o*-methyl groups of the 2,6-C₆H₃Me₂ substituents appeared as two singlets, indicative of restricted rotation about the N-Cipso bonds.

The molecular structures of **19** and **21** are shown in Fig. 2 and selected bond lengths and angles are given in Table 2. Each contains a titanium atom in a four-legged piano stool geometry.

19	21						
Bond angles/Å							
2.064(2)	2.079 (3)						
2.071(2)	2.095 (3)						
1.932(2)	1.925 (2)						
1.931(2)	1.915 (2)						
2.046	2.026						
1.213(3)	1.211(4)						
1.210(3)	1.206(4)						
118.9	117.2						
111.8	115.7						
110.8	110.9						
112.2	113.1						
64.09(7)	64.9(1)						
83.38(6)	83.6 (1)						
	19 2.064(2) 2.071(2) 1.932(2) 1.931(2) 2.046 1.213(3) 1.210(3)						



Fig. 2 Displacement ellipsoid plots (25% probability) of $Ti(\eta_{5}Me_{3})$ -{OC(O)N(-2,6-₆H₃Me₂)C(O)O}{MeC(N'Pr)_{2}} (19, top) and $Ti(\eta$ -C₃H₄-Me){OC(O)N(-2,6-C₆H₃Me₂)C(O)O}{PhC(NSiMe_{3})_{2}} (21, bottom). H atoms omitted for clarity.

In addition to a η^5 -bound cyclopentadienyl ring and bidentate amidinate ligand, there is a bidentate azamalonate group. As far as we are aware, this is a new type of ligand in transition metal chemistry. The structures unambiguously confirm the complete cleavage of the Ti=N_{imide} bonds of the original starting complexes 7 and 12 and the "double-insertion" of two CO₂ molecules. Overall, the two structures are very similar, with Ti–C, Ti–N and Ti–O distances lying within the expected ranges.^{72,73} The atoms of the hitherto unknown titana-azamalonate ring are approximately planar. The C(1)–O(2) (1.213(3) and 1.211(4) Å for 19 and 21, respectively) and C(2)–O(4) (1.210(3) and 1.206(4) Å) distances are consistent with double bond (carbonyl) character in agreement with the IR data discussed above. The 2,6-C₆H₃Me₂ rings lie perpendicular to the titana-azamalonate ring as expected from the NMR data.

When followed by NMR spectroscopy, it was found that the rates of reaction of **15–18** with CO₂ follow the pattern expected on steric grounds, with the more encumbered carbamates reacting most slowly. Thus, the reaction of $Ti(\eta$ -C₃H₄Me){N(-2,6-C₆H₃Me₂)C(O)O}{MeC(NⁱPr)₂} (**17**) was complete within 12 h whereas $Ti(\eta$ -C₅Me₅){N(-2,6-C₆H₃Me₂)C(O)O}{MeC(NⁱPr)₂} (**15**) requires 2 d. With the most crowded carbamate, $Ti(\eta$ -C₅Me₅){N(-2,6-C₆H₃Me₂)C(O)O}{PhC(NSiMe₃)₂} (**16**), reaction with CO₂ eventually occurred after many days at room

temperature. As mentioned above, a pure product could not be obtained on a preparative scale.

The double substrate insertion reactions of these aryl imido complexes (i.e. complete cleavage of the Ti=NAr bond) are very uncommon in transition metal imido chemistry. Apart from our own recently reported examples with certain isocyanates for cyclopentadienyl-amidinate systems,56 the only well-defined examples involving M=NR cycloaddition reactions are for the iridium compound Cp*Ir(N'Bu) which reacts with two equivalents of $C_2(CO_2Me)_2$ to form $Cp*Ir{\eta^4-C_4(CO_2Me)_4N'Bu}$.⁶⁸ A double activation type reaction was implied in the isocyanate exchange reaction between the unsymmetrical ureate complex $Ti(Me_4taa){N(Ph)C(O)N(Tol)}$ and an excess of PhNCO, which vields Ti(Me₄taa){N(Ph)C(O)N(Ph)} and TolNCO via a putative biuret intermediate (not directly observed).47 Bergman recently reported related heterocumulene insertion reactions of iridium ureate and guanidinate complexes, although these did not originate from metal imido complexes.82 This group has also recently shown that certain alkynes and carbodiimides can be sequentially coupled with a Zr=NR bond to form six-membered metallacycles.⁸³ However, one should recall that the insertion of CO₂ into a metal-nitrogen single bond is in general very well precedented and has been the subject of experimental, mechanistic and computational investigations.69,84-93

In order to gain a better understanding of the second (insertion) step of the reaction a series of kinetic experiments was carried out. The rate of reaction of the *p*-tolylcarbamate $Ti(\eta$ - C_5Me_5 {N(Tol)C(O)O} {MeC(N'Pr)} (22) with CO₂ at room temperature makes this a convenient system for determining the rate expression. NMR samples in benzene-d₆ were exposed to CO₂ at ambient temperature and then transferred to an NMR spectrometer probe maintained at 25 °C, and spectra were recorded over at least three half-lives of 22. Studies were carried out at 5 different CO₂ pressures under pseudo-first order conditions in which at least a 10-fold excess of CO₂ was present at the lowest pressure studied (0.25 atm). The concentrations of the carbamate 22 and the product dicarboxylate 23 were monitored over time and the results fitted first-order exponential relationships; the observed rate constants k_{obs} were extracted from linear plots of $\ln(I/I_0)$ vs. reaction time (see Fig. 3 for $pCO_2 = 0.50$ atm and the ESI for other systems studied).[†] The k_{obs} values are summarised in Table 3. The exponential decay of carbamate and evolution of dicarboxylate product indicate that the rate determining step is first order in 22.

Table 3 Pseudo-first order rate constants k_{obs} and associated half-lives $(t_{1/2})$ for the CO₂ insertion reaction of the carbamate complexes Ti(η -C₅Me₅){N(-4-C₆H₄X)C(O)O}{MeC(N'Pr)₂} (X = Me (22), CF₃ (24) or NMe₂ (25))

Carbamate	<i>p</i> CO ₂ /atm	$k \times 10^4/\mathrm{s}^{-1}$
22	0.25	0.95 ± 0.02
	0.5	2.9 ± 0.03
	0.75	4.1 ± 0.06
	1.0	5.7 ± 0.09
	1.6	9.0 ± 0.09
	1.6	9.0 ± 0.09
24	1.6	9.3 ± 0.05
	1.6	8.9 ± 0.07
25	1.6	11.4 ± 0.07
	1.6	14.4 ± 0.17



Fig. 3 Plot of normalized concentrations against time for the insertion reaction of $Ti(\eta-C_5Me_5)\{N(Tol)C(O)O\}\{MeC(N'Pr)_2\}$ (22) with CO₂ (0.5 atm) (top). Values are given for starting carbamate 22 (represented as solid points) and product dicarboxy-late $Ti(\eta-C_5Me_5)\{OC(O)N(4-C_6H_4Me)C(O)O\}\{MeC(N'Pr)_2\}$ (23, represented as hollow points). Plot of $In(I/I_0)$ vs. reaction time for the consumption of $Ti(\eta-C_5Me_5)\{N(Tol)C(O)O\}\{MeC(N'Pr)_2\}$ (22) (0.5 atm CO₂) where "*I*" and " I_0 " represent the normalized [22] at the reaction time indicated or at time = 0 s, respectively (bottom).

The linear dependence of k_{obs} on CO₂ pressure (Fig. 4 and Table 3) shows that it is also first order in CO₂ and hence the overall rate expression is bi-molecular.



Fig. 4 Plot of k_{obs} vs. CO₂ pressure for the reaction of Ti(η -C₅Me₅)-{N(Tol)C(O)O}{MeC(N'Pr)_2} (22) with CO₂.

The effect of carbamate *N*-substituent electronic factors in these reactions was also evaluated by comparing the reaction rates for two other carbamate complexes $Ti(\eta-C_5Me_5)\{N(-4-C_6H_4X)C(O)O\}\{MeC(N'Pr)_2\}$ (X = CF₃ (**24**) or NMe₂ (**25**)) in which only the *para*-phenyl substituents were varied so that the steric effects at the metal centre were the same. The substituents

chosen have very different electron-donating or -withdrawing properties. The pseudo-first order reactions of **24** and **25** with CO_2 ($pCO_2 = 1.6$ atm) to form the dicarboxylates **26** and **27**, respectively, (Scheme 2) were assessed as for **22** above. Rate constants k_{obs} are shown in Table 3 together with those for **22**. They are effectively independent of the *N*-phenyl *para*-substituent, and do not fit a simple relationship with Hammett parameters.

Reactions of tert-butyl imido compounds with CO2

We have previously reported the reactions of CO_2 with pendant arm functionalised amidinates of the type 1 and 2 (Chart 1), together with some DFT studies of the model compound Ti(η- C_5H_5 (NMe){MeC(NMe)₂}.⁵³ For 2 (containing no pendant amine donor), CO₂ cycloaddition to Ti=N'Bu occurred readily at -78 °C, whereas for 1a (R = H; pendant arm = CH₂CH₂NMe₂) no significant reaction occurred below -35 °C. Both systems formed N,O-bound carbamates, which rapidly extruded 'BuNCO above -25 °C to form oxo-bridged dimers. There was no significant effect of the nature of the pendant arm on the extrusion process, the rates of which were first order in carbamate and concentration-independent. Although monomeric oxo intermediates were proposed, no direct evidence for their existence was advanced. The carbamate formed from the bulkier amidinate Ti(n- C_5Me_5 (N'Bu) {Me_3SiNC(Ph)NCH_2CH_2NMe_2} (1b) was more stable to extrusion of 'BuNCO, which took place comparatively slowly at room temperature ($t_{1/2} = 30 \text{ min}$). There was no evidence for double CO_2 addition reactions of the type shown in Scheme 2. Given the contrasting behaviour of 1a and 1b, and of the N-aryl substituted carbamates (Scheme 2), we decided to explore further the reactions of tert-butyl imido compounds with CO₂.

Reaction of the compounds $Ti(\eta-C_5Me_5)(N'Bu)\{PhC-(NSiMe_3)_2\}$ (3) and $Ti(\eta-C_5Me_5)(N'Bu)\{PhC(N'Pr)_2\}$ (4) with CO_2 (*ca.*1.1 atm) at room temperature, followed by immediate isolation, yielded the cherry-red N,O-bound carbamates $Ti(\eta-C_5Me_5)\{N('Bu)C(O)O\}\{PhC(NSiMe_3)_2\}$ (28) and $Ti(\eta-C_5Me_5)\{N('Bu)C(O)O\}\{MeC(N'Pr)_2\}$ (29) in 95 and 65% yields, respectively, (Scheme 3). The NMR spectra of 28 and 29 are consistent with the proposed structures and the IR spectra contain intense new stretches at 1660 cm⁻¹ and 1662 cm⁻¹, respectively, consistent with the incorporation of a new carbonyl unit into the molecule. These values are slightly lower that those for the aryl imido-derived homologues (*e.g.* 1667–1671 cm⁻¹ for 15–18) and similar values and trends have been found previously.⁴⁷

In contrast to their aryl imido-derived analogues 15–18, the carbamates 28 and 29 are unstable in solution at ambient temperature and cleanly eliminate *tert*-butyl isocyanate to form *trans*-[Ti(η -C₅Me₅)(μ -O){PhC(NSiMe₃)₂}]₂ (30) and *trans*-[Ti(η -C₅Me₅)(μ -O){MeC(N'Pr)₂}]₂ (31). The absence of terminal Ti=O stretching bands in the IR spectra of 30 and 31 are consistent with the formation of dimeric oxo-bridged structures, and 31 has been crystallographically characterised (see below). The 'BuNCO extrusion reaction still proceeds in the presence of an excess of CO₂ and there is no evidence for insertion of a second molecule of CO₂ into the Ti–N_{carbamate} bonds of 28 or 29. The rates of disappearance of 28 and 29 are markedly dependent upon the ancillary ligand set. Thus the acetamidinate-supported compound 29 decays in benzene-d₆ solution at room temperature within 24 h, while 28 (having the more bulky *N*,*N'*-bis(trimethylsilyl)benzamidinate



ligand) requires about a week to undergo complete conversion when followed by NMR spectroscopy.

The monomethylcyclopentadienyl complex **5** also reacts rapidly with CO₂ in benzene at room temperature. When the reaction was followed by ¹H NMR spectroscopy in benzene-d₆ the spectrum after 5 min revealed that *ca.* 80% of the parent imido complex had been consumed, while a new set of resonances indicated the formation of a new carbamate complex Ti(η -C₅H₄Me){N('Bu)C(O)O}{PhC(NSiMe_3)_2} (**33**, Scheme 3). However, the onset of 'BuNCO extrusion from **33** also starts to occur in this period, and after 30 min the only resonances visible were for the oxo complexes **32** and **32a** and 'BuNCO. Because of the rapid rate at which **33** undergoes extrusion, it could not be isolated on a preparative scale.

In contrast to the very fluxional *N*-aryl homologue Ti(η -C₅H₄Me){N(-2,6-C₆H₃Me₂)C(O)O}{PhC(NSiMe₃)₂}(18), the ¹H NMR resonances for 33 are *sharp* at room temperature, showing two clear SiMe₃ groups (δ –0.04 and –0.08 ppm) and four C₅H₄Me ring hydrogen resonances. The NMR spectra for the more sterically crowded C₅Me₅ homologues 28 and 29 are also non-fluxional. Thus 28, 29 and 33 do not appear to undergo the enantiomer interconversion process summarised in eqn (2) for the *N*-aryl homologues 15–18, at least on the NMR timescale.

The oxo-bridged dimer formed from 33 exists as a mixture of *trans*- (32) and *cis*- (32a) isomers according to the ¹H NMR spectrum of the product mixture. This revealed twice as many resonances as would be expected for a single product. The

formation of two isomers is possible because of the less sterically demanding nature of the methylcyclopentadienyl ligands. Heating the mixture of isomers in benzene- d_6 to 80 °C for 30 min resulted in quantitative conversion of **32a** to the *trans* isomer **32**, which has been crystallographically characterized (see below).

Exposure of a benzene-d₆ solution of the least sterically protected imide $Ti(\eta-C_3H_4Me)(N'Bu)\{MeC(N'Pr)_2\}$ (6) to CO_2 (1 atm) resulted in an extremely rapid reaction sequence. The solution briefly became cherry-red (consistent with a putative carbamate intermediate) but lightened to dark amber almost immediately. The ¹H NMR spectrum recorded after 3 min reaction time revealed complete consumption of 6 and resonances attributable to 'BuNCO and the isomeric oxo species *cis*- and *trans*- $[Ti(\eta-C_3H_4Me)(\mu-O)\{MeC(N'Pr)_2\}]_2$ (34 and 34a). These were isolated on the preparative scale in 58% yield. The *trans* isomer was successfully separated from the reaction mixture by fractional crystallisation.

The X-ray structures of trans-[Ti(η -C₅Me₅)(μ -O){MeC-(NⁱPr)₂}]₂ (**31**) and trans-[Ti(η -C₅H₄Me)(μ -O){PhC(NSiMe₃)₂}]₂ (**32**) have been determined. The molecular structures are shown in Fig. 5 and selected distances and angles and listed in Table 4. Both compounds have a pseudo-four-legged piano stool geometry about titanium and a *trans* arrangement of the cyclopentadienyl rings. Compounds with Ti₂(μ -O)₂ cores are well established, and a number have been crystallographically characterized.^{72,73} The bond lengths and angles for the two compounds are of comparable magnitudes, with the metal–ligand distances in **31** on average being slightly longer than in **32**. This is attributed to the presence of the more sterically demanding η -C₅Me₅ ligand in the former case.

Further aspects of the CO₂ cycloaddition/isocyanate extrusion reaction

The oxo-bridged dimers formed by isocyanate extrusion from *tert*-butyl carbamate complexes are probably preceded by short-lived monomeric terminal oxo intermediates. This is illustrated in Scheme 4 for the formation of dimeric **31** from **29** *via* a putative monomeric oxide **35**. To explore the chemistry of these systems further, a series of NMR tube scale reactions

Table 4 Selected bond lengths (Å) and angles (°) for *trans*- $[Ti(\eta-C_5Me_5)(\mu-O)\{MeC(N^iPr)_2\}]_2$ (**31**) and *trans*- $[Ti(\eta-C_5H_4Me)(\mu-O)\{PhC(NSiMe_3)_2\}]_2$ (**32**). Cp_{cent} refers to the C₅Me₅ or C₅H₄Me ring carbon centroid

Parameter	31	32					
Bond lengths/Å							
Ti(1)-N(1)	2.188(3)	2.154(1)					
Ti(1)–N(2)	2.168(3)	2.163(1)					
Ti(1)–O(1)	1.855(2)	1.842(1)					
Ti(1)-O(1B)	1.869(2)	1.859(1)					
Ti(1)-Cp _{cent}	2.130	2.087					
Bond angles/°							
Cp _{cent} -Ti(1)-N(1)	109.4	111.2					
Cp_{cent} -Ti(1)-N(2)	110.0	109.2					
Cp_{cent} -Ti(1)-O(1)	117.8	117.7					
Cp_{cent} -Ti(1)-O(1B)	115.9	115.5					
Ti(1)-O(1)-Ti(1B)	98.59(9)	97.01(4)					



Fig. 5 Displacement ellipsoid plots (25% probability) of *trans*-[Ti(η -C₅-Me₅)(μ -O){MeC(N^tPr)₂}]₂ (31, top) and *trans*-[Ti(η -C₅H₄Me)(μ -O)-{PhC(NSiMe₃)₂}]₂ (32, bottom). H atoms omitted for clarity.

on the representative tolyl and *tert*-butyl carbamates $Ti(\eta - C_5Me_5)\{N(R)C(O)O\}\{MeC(N'Pr)_2\}$ (R = Tol (22) or 'Bu (29) were carried out as summarized in Schemes 4 and 5.

To probe for any reversibility of 'BuNCO extrusion reaction, the effect of an excess of 'BuNCO on the extent and rate of decay of **29** was examined. In the absence of any added 'BuNCO, compound **29** underwent 30 and 70% conversion to 'BuNCO and the oxo bridged dimer **31** after 3 and 16 h, respectively, in benzene-d₆. In the presence of an excess of 'BuNCO (5 equiv.) the extents of conversion were 28 and 69%, respectively. Hence, there is negligible back reaction of the terminal oxo species **35** with 'BuNCO.

We have shown previously⁴⁷ that TolNCO reacts rapidly with the terminal Ti=O group of Ti(Me₄taa)(O) (**36**) to form Ti(Me₄taa){N(Tol)C(O)O} (**37**) as summarized in eqn (3) (the



corresponding reaction of **36** with 'BuNCO gave only 70% conversion to Ti(Me₄taa){N('Bu)C(O)O} after 17 d). In the hope that an aryl isocyanate could likewise trap the transient oxo species **35**, TolNCO (5 equiv.) was added to a sample of **29** in benzene-d₆. As before, 'BuNCO was slowly eliminated but in this instance Ti(η -C₅Me₅){OC(O)N(Tol)C(Tol)O}{MeC(N'Pr)_2} (**38**, Scheme 4) was the only organometallic product and no oxobridged dimer **31** was observed. Compound **38** was characterised by comparison with an authentic sample independently prepared from Ti(η -C₅Me₅){N(Tol)C(O)O}{MeC(N'Pr)_2} (**22**) and TolNCO.⁵⁶ The formation of **38** (*via* **22**) provides firm evidence for the the intermediate **35**. Note that the oxo-bridged dimer **31** is unreactive towards both 'BuNCO and TolNCO. Furthermore, **29**

itself does not react with TolNCO under these conditions, whereas 22 reacts wth TolNCO very rapidly, accounting for the formation of 38 since an excess of TolNCO was used.⁵⁶



These NMR experiments show that 'BuNCO elimination from **29** (and probably all of the *N-tert*-butyl carbamates described above) is irreversible. However, they also raise the possibility that the *N*-aryl carbamates (e.g. **22**) could exist in equilibrium with trace amounts of monomeric oxo species **35** which might, in turn, react back more readily with ArNCO than another terminal oxo species (leading to irreversible formation of dimeric oxo species).

In a further NMR experiment, a small excess (3 equiv.) of $Ti(Me_4taa)(O)$ (36) was therefore added to a sample of 22 in benzene-d₆. We have previously shown that $Ti(O)(Me_4taa)$ is an efficient trap for TolNCO, reacting rapidly to form the carbamate $Ti(Me_4taa){N(Tol)C(O)O}$ (37). Within 30 min, complete conversion of 22 to *trans*-[$Ti(\eta$ -C₅Me₅)(μ -O){MeC(N'Pr)₂}]₂ (31) and 37 had occurred. As illustrated in Scheme 5 this reaction probably proceeds *via* the transient terminal oxo compound 35. In a control experiment, a solution of pure 22 gave no formation of 31 over 24 h at room temperature under otherwise identical conditions.

Computational studies

The difference in reactivity with CO₂ of the alkyl and aryl imido complexes prompted us to carry a detailed DFT study of the reaction mechanisms. The CO₂ cycloaddition/isocyanate extrusion reaction of Ti(η -C₅H₅)(NMe){MeC(NMe)₂}, **1-Me**, was previously computed.⁵³ The mechanism proceeds with an almost barrier-less cycloaddition reaction of CO₂ ($\Delta E^{\#} = 0.7$ kJ mol⁻¹, **TS12-Me**) to yield the carbamate Ti(η -C₅H₅){N(Me)C(O)O}{MeC(NMe)₂},



Scheme 5

Published on 27 April 2009. Downloaded by University of Illinois at Chicago on 25/10/2014 20:19:27.

2-Me, which is a reasonably exothermic process ($\Delta E = -113.1 \text{ kJ mol}^{-1}$). This intermediate evolves into the oxo intermediate Ti(η -C₃H₃)(O){MeC(NMe)₂}, **3-O**, and MeNCO in an endothermic step ($\Delta E = 87.7 \text{ kJ mol}^{-1}$) with an activation energy through **TS23-Me** of 88 kJ mol⁻¹. When Gibbs free energies are considered, the energy diagram shown in Fig. 6 is obtained. The carbamate **2-Me** is more stable than the two extrusion pathways **1-Me** + CO₂ or **3-O** + MeNCO, the latter being favoured over the former. As a result, the overall transformation **1-Me** + CO₂ \rightarrow **3-O** + MeNCO is exergonic ($\Delta G = -32.2 \text{ kJ mol}^{-1}$). Once the oxo complex **3-O** is formed, it is known experimentally to convert in an irreversible step into the oxo-bridged dimer. We did not try to optimize the oxo-bridged dimer as it would have been computationally prohibitive.



Fig. 6 Gibbs free energy diagram (kJ mol⁻¹) for CO₂ cycloaddition/isocyanate extrusion (solid lines) and second CO₂ insertion (dotted lines) for the methyl imido complex **1-Me** ($\mathbf{R} = \mathbf{Me}$, black lines) and the phenyl imido complex **1-Ph** ($\mathbf{R} = \mathbf{Ph}$, blue lines).

The CO₂ cycloaddition/isocyanate extrusion pathway was also computed for CO₂ reacting with Ti(η -C₃H₃)(NPh){MeC(NMe)₂}, **1-Ph**, where the *iso*-propyl groups on the experimental acetamidinate ligand have been modelled by methyl groups to concentrate on the basic electronic features of the reaction. The geometries of the imido complex **1-Ph**, the TS for CO₂ cycloaddition **TS12-Ph**, and the carbamate product **2-Ph** are shown in Fig. 7, together with the HOMO of the system in each case. The electronic and Gibbs free energies (expressed with respect to separated



Fig. 7 Optimized geometry for 1-Ph, TS12-Ph, and 2-Ph and the corresponding HOMO in each case.

reactants) are given in Table 5. The activation barrier for CO₂ cycloaddition to 1-Ph is larger than that obtained with 1-Me, but still very low (10.6 kJ mol⁻¹ vs. 0.7 kJ mol⁻¹, see Table 5), and the reaction is less exothermic (-91.9 kJ mol⁻¹ vs. -113.1 kJ mol⁻¹, see Table 5). The transition state for cycloaddition is earlier with 1-Me. As a consequence, TS12-Me and TS12-Ph present significant differences in terms of geometrical parameters. The forming $Ti \cdots O$ and $N \cdots C$ bonds are significantly longer in TS12-Me (2.442 Å and 2.476 Å, respectively) than in TS12-Ph (2.285 Å and 2.277 Å). Interestingly, the orientation of the phenyl ring in TS12-Ph is different than in the reactant 1-Ph and the product 2-Ph (Fig. 7). In the imido complex 1-Ph, the orientation of the phenyl ring (lying in the plane bisecting the Cp-Ti-amidinate angle) allows the less stable out-of-plane 2p lone pair (LP_{π}) on N to interact with a high lying accepting orbital on Ti (HOMO of 1-Ph, Fig. 7), whereas the more stable in-plane 2p lone pair (LP_{π}) interacts with a low lying accepting orbital on Ti. Rotating the phenyl group by 90° in **TS12-Ph** allows LP_{π} on the nitrogen to interact with the incoming CO₂ molecule as illustrated by the HOMO of TS12-Ph (Fig. 7). This rotation also reduces steric interactions between the phenyl ortho C-H with the approaching CO_2 .

The reaction can thus be described as a nucleophilic attack by the imido nitrogen on the carbon atom of CO₂. Furthermore, the size of the activation barrier for CO₂ cycloaddition is influenced by the nature of the *para* substituent on the phenyl ring. Three different *para*-substituted aryl imido complexes Ti(η -C₅H₅)(NAr){MeC(NMe)₂}, **1-PhX**, have been considered (Ar = 4-C₆H₄Me, **X** = Me; Ar = 4-C₆H₄CF₃, **X** = CF₃; Ar = 4-C₆H₄MMe₂,

Table 5 Electronic energy (E) and Gibbs free energy (G) of the various extrema located expressed with respect to the separated reactants **1-R** and CO_2 . Energies are in kJ mol⁻¹, and for $R = {}^{i}Bu$, **3-O** is **3'-O**

	TS12-R		2-R		TS23-R		3-0		TS24-R		4-R	
	$\overline{\Delta E^{\#}}$	$\Delta G^{\#}$	ΔE	ΔG	$\Delta E^{\#}$	$\Delta G^{\#}$	ΔE	ΔG	$\Delta E^{\#}$	$\Delta G^{\#}$	ΔE	ΔG
R = Me	0.7	51.7	-113.1	-55.4	-25.1	29.7	-25.4	-32.2	-77.5	34.1	-212.8	-99.6
R = Ph	10.6	68.0	-91.9	-21.5	2.0	65.0	-1.6	-3.7	-45.9	73.8	-151.8	-31.6
$R = PhNMe_2$	7.4	57.6	-93.1	-27.9	-5.3	52.6	-8.6	-16.5	-49.6	65.7	-158.4	-44.0
R = PhMe	10.0	65.9	-91.4	-24.5	0.2	62.2	-3.2	-7.4	-46.7	74.8	-153.7	-34.5
$R = PhCF_3$	13.1	66.1	-88.8	-23.5	12.9	72.5	8.7	2.0	-43.5	73.2	-145.5	-27.2
$R = {}^{t}Bu$	16.5	74.9	-101.6	-39.5	-7.7	49.1	-33.4	-49.1	-20.1	101.0	-171.4	-53.1

X = NMe₂). The calculated activation and reaction energies are given in Table 5 together with the corresponding Gibbs free energy values. The more electron releasing the *para* substituent (NMe₂, $\sigma_p = -0.63$; Me, $\sigma_p = -0.14$; CF₃, $\sigma_p = 0.53$) the lower the activation barrier, in agreement with the reaction being a nucleophilic attack of the imido nitrogen on CO₂.

Formation of the carbamate is less exothermic for the aryl imido complexes than for the methyl case (Table 5). The HOMO of **2-Ph** (Fig. 7) shows that the lone pair LP_{π} on nitrogen interacts both with an empty d orbital on Ti and with a π -accepting orbital on C=O. In the starting imido complex 1-Ph, the two lone pairs LP_{π} and LP_{π} ' are interacting with Ti, while in the product **2-Ph**, LP_{π} ' is used to make the new N–C bond. The magnitude of the reaction energy (Table 5) originates mainly from the creation of two new σ -bonds (Ti–O and N–C) at the expense of two π -bonds (C=O and Ti=N). This negative value is further altered by the reorganization of the framework of π interactions in the product (2-Me or 2-Ph) with respect to the reactant (1-Me or 1-Ph). The Ti-N bond becomes longer in the carbamate intermediate as a result of the cycloaddition, but the increase is larger for the aryl case (Ti-N = 1.688 Å, 1-Me; Ti-N = 1.710 Å, 1-Ph; Ti-N = 1.916 Å, 2-Me;Ti–N = 2.005 Å, **2-Ph**). There is thus a larger loss of π -donation from N to Ti in 2-Ph than in 2-Me. This is only partly compensated by increased π -donation from N to C=O in the carbamate as illustrated by the shorter N-C bond in 2-Ph (1.384 Å) than in **2-Me** (1.394 Å), and also by the lower v_{co} vibrational frequency in the carbamate (1825.6 cm⁻¹, 2-Me; 1823.0 cm⁻¹, 2-Ph). This analysis is supported by the results for the *para*-substituted aryls (Table 5) where the reaction energy is more exothermic for the more electron releasing groups, and the $v_{\rm CO}$ stretching frequencies show the expected trend (1817.9 cm⁻¹, **2-PhNMe**₂; 1820.7 cm⁻¹, **2-PhMe**; 1823.4 cm⁻¹, **2-PhCF**₃).

The geometry of the TS for extrusion of PhNCO, **TS23-Ph**, is shown in Fig. 8 and the electronic and Gibbs free energies associated with this process are given in Table 5 (see also Fig. 6). The transition state **TS23-Ph** (leading to **3-O** and PhNCO) could be described as an N-adduct of PhNCO (Ti \cdots N = 2.304 Å) on the terminal oxo **3-O**, and features a short C \cdots O contact (2.254 Å). The geometry is typical of a [2 + 2] cycloaddition product (PhNCO extrusion being the reverse of Ti=O + PhNCO cycloaddition) and the C_{ipso}-N-CO angle in this TS (122°) is *ca*. 20° less than in PhNCO itself (141°). The activation barrier for the extrusion process is slightly larger than in the methyl case ($\Delta E^{\#} = 88$ kJ mol⁻¹, **TS23-Me**; $\Delta E^{\#} = 93.9$ kJ mol⁻¹, **TS23-Ph**), and consequently the reaction is slightly more endothermic ($\Delta E =$

Fig. 8 Optimized geometry of the TS for PhNCO extrusion TS23-Ph, the TS for second CO_2 insertion TS24-Ph, and the product of second CO_2 insertion 4-Ph.

87.7 kJ mol⁻¹, **3-O** + MeNCO; $\Delta E = 90.3$ kJ mol⁻¹, **3-O** + PhNCO). In contrast to the situation for the methyl imide **1-Me**, the pathway for CO₂ or PhNCO extrusion from **2-Ph** are competitive in terms of activation barriers and reaction energies ($\Delta E^{\#} = 102.5$ kJ mol⁻¹, $\Delta E = 91.9$ kJ mol⁻¹, **2-Ph** \rightarrow **1-Ph** + CO₂; $\Delta E^{\#} = 93.9$ kJ mol⁻¹, $\Delta E = 90.3$ kJ mol⁻¹, **2-Ph** \rightarrow **3-O** + PhNCO). As a result, the reaction **1-Ph** + CO₂ \rightarrow **3-O** + PhNCO is only slightly exergonic ($\Delta G = -3.7$ kJ mol⁻¹). The Gibbs free energy diagram for the CO₂ cycloaddition/PhNCO extrusion reaction of **1-Ph** is shown in Fig. 6 for a comparison with the results for **1-Me**.

Estimation of the turnover frequency (TOF) at room temperature of the two consecutive processes with the procedure proposed by Kozuch and Shaik^{94,95} yielded similar values (0.78 10^{-2} s⁻¹, **1-Me**; 0.20 10^{-2} s⁻¹, **1-Ph**). This shows that even though the TS's are at higher energy in the phenyl case (Fig. 6), formation of a less stable carbamate intermediate compensates and the overall rates are similar. However, in stark contrast to these predictions, the experimental results are different for the real *tert*-butyl and aryl imido complexes. In the former cases, extrusion of 'BuNCO is observed. In the aryl cases, no extrusion of ArNCO is observed, except under forcing conditions. Furthermore, in the presence of an excess of CO₂, insertion of a second CO₂ molecule is generally observed.

We therefore searched for a mechanism associated with the insertion of CO₂ into the Ti-N_{Ph} bond of the carbamate 2-Ph to form the azamalonato complex 4-Ph. The geometries of the TS for the second CO₂ insertion, TS24-Ph, and of the product of insertion, 4-Ph, are shown in Fig. 8. The electronic and Gibbs free energies are given in Table 5. In TS24-Ph, the carbamate moiety is twisted out of the "equatorial" plane of $Ti(\eta - C_5H_5)$ {MeC(NMe)₂} to allow attack by CO₂. In the transition state, the forming $N \cdots C$ bond is 2.295 Å and the oxygen atom interacts with Ti $(Ti \cdots O = 2.36 \text{ Å})$. As for the first insertion, the reaction is best described as a nucleophilic attack by the nitrogen lone pair on the carbon atom of CO_2 . However, due to the steric interactions imposed by the geometry of TS24-Ph, the reacting lone pair on nitrogen is not conjugated with the phenyl ring as efficiently as it was in TS12-Ph. The electronic activation barrier is thus larger (46 kJ mol⁻¹ vs. 10.6 kJ mol⁻¹, Table 5) but is still indicative of a facile process. Moreover, the formation of the product 4-Ph is thermodynamically favoured ($\Delta E = -59.9 \text{ kJ mol}^{-1}$ with respect to 2-Ph and -151.8 kJ mol⁻¹ with respect to 1-Ph). The transition state for the second CO₂ insertion was also computed for the parasubstituted phenyl groups and the activation barriers are very close (43.5 kJ mol⁻¹, **TS24-PhNMe**₂; 44.7 kJ mol⁻¹, **TS24-PhMe**; 45.3 kJ mol⁻¹, **TS24-PhCF**₃). There is thus a weaker influence of the *para*-substituent on the second CO₂ insertion ($\Delta \Delta E^{\#} \approx$ 2.5 kJ mol⁻¹) than on the first one ($\Delta\Delta E^{\#} \approx 4.5$ kJ mol⁻¹) because of the change of hybridisation at the nitrogen atom rendering the lone pair less conjugated with the phenyl ring. This is in agreement with the experimental results on k_{obs} (Table 3) where no particular influence of the para group was observed.

The Gibbs free energy diagram for the second CO_2 insertion on **2-Ph** is given in Fig. 6 for comparison with the PhNCO extrusion process. Even though the activation barrier for the second insertion is *ca*. 10 kJ mol⁻¹ larger than the activation barrier for extrusion ($\Delta G^{\#} = 86.5$ kJ mol⁻¹, **2-Ph** \rightarrow **3-O** + PhNCO; $\Delta G^{\#} = 95.3$ kJ mol⁻¹, **2-Ph** + CO₂ \rightarrow **4-Ph**, Table 5), there is a clear thermodynamic driving force toward insertion of



the second CO₂ molecule ($\Delta G = 17.8 \text{ kJ mol}^{-1}$, 2-Ph \rightarrow 3-O + PhNCO; $\Delta G = -10.1 \text{ kJ mol}^{-1}$, **2-Ph** + CO₂ \rightarrow **4-Ph**, Table 5). In the present case, comparison is made between processes in which the changes of molecularity of each steps are different. Extrusion of PhNCO is associated with creation of degrees of freedom, whereas insertion of the second CO₂ corresponds to annihilation of degrees of freedom. As the major contributor to G in the calculations is the loss or gain of translational entropy, the $\Delta G^{\#}$ values should be only taken as qualitative indicators of the respective reactivity. Nevertheless, the calculated values indicate that the processes of CO₂ cycloaddition/PhNCO extrusion and CO_2 cycloaddition/second CO_2 insertion are competitive and are both likely to occur at similar rates. The final outcome here is dictated by the relative stability of the products with respect to 2-Ph, specifically the thermodynamically favourable formation of the azamalonato complex 4-Ph and the unfavourable formation of 3-O and PhNCO. As a matter of fact the extrusion of PhNCO is reversible ($\Delta G > 0$) as illustrated by the trapping experiment shown in Scheme 4 with TolNCO cycloaddition on the unobserved oxo complex 35. Moreover the large excess of CO_2 is likely to reduce the effective activation barrier leading to 4-Ph.

The results of the second CO₂ insertion on the aryl carbamate **2-Ph** prompted us to study the potential insertion of CO_2 into the Ti-N_{Me} bond of the carbamate 2-Me. A transition state, TS24-Me, similar to TS24-Ph, was located 35.6 kJ mol⁻¹ above 2-Me + CO_2 (Table 5, Fig. 6). In this TS, the C \cdots N forming bond is 2.30 Å, whereas the $Ti \cdots O$ contact is longer than in TS24-Ph (2.515 Å vs. 2.36 Å). The TS is thus earlier in the methyl case and this is confirmed by the value of the reaction energy $\Delta E =$ -99.7 kJ mol⁻¹, much larger than for the aryl case (-59.9 kJ mol⁻¹, Table 5). There is thus a strong electronic thermodynamic driving force toward the insertion of a second CO₂ molecule on the carbamate 2-Me as illustrated by the Gibbs free energy profile on Fig. 6. Thus, placed under the same experimental conditions of excess of CO₂, the methyl carbamate 2-Me should insert easily a second CO₂ molecule to yield 4-Me. However, such an outcome was not observed experimentally and only 'BuNCO extrusion was observed. Moreover, in the actual experimental systems, the steric bulk has an influence on the reactivity. With the tert-butyl imido complexes 3-6 (Scheme 3), the carbamate intermediate was isolated only for the larger systems (28 and 29), while for the smaller systems the carbamate was either only observed by NMR (33) or not observed at all at room temperature. In all cases, the system evolves to the oxo-bridged dimers (30-32, 34) after ^tBuNCO extrusion.

In order to address the influence of the steric bulk on the reactivity of the alkyl imido complexes toward CO₂, DFT calculations were carried out on the model system Ti(η -C₃H₃)(N'Bu){MeC(NⁱPr)₂}, **1-'Bu**. This model is very close to the experimental system **6** where the Cp ring has a single methyl substituent, and differs from **4** by the use of Cp instead of Cp*. The electronic and Gibbs free energies of the extrema located along the pathway for CO₂ cycloaddition/'BuNCO extrusion are given in Table 5.

As expected, the activation barrier for CO₂ cycloaddition on 1-^{*i*}**Bu** to form the carbamate 2-'**Bu** is larger than with 1-Me ($\Delta E^{\#} =$ 16.5 kJ mol⁻¹, TS12-'**Bu**; $\Delta E^{\#} = 0.7$ kJ mol⁻¹, TS12-Me). The Ti ··· O and N ··· C forming bonds in TS12-'**Bu** are shorter than in the less bulky TS12-Me (Ti ··· O = 2.351 Å, N ··· C = 2.363 Å, **TS12-'Bu**; Ti ··· O = 2.442 Å, N··· C = 2.476 Å, **TS12-Me**). Based on these shorter contacts, the apparent stronger interaction of CO₂ with Ti in **TS12-'Bu** is necessary to compensate for the larger steric repulsion, thus allowing for a cycloaddition with still a low barrier. Interestingly, the carbamate intermediate **2-'Bu** is not particularly destabilized as the reaction energy $\Delta E = -101.6$ kJ mol⁻¹ is only *ca.* 10 kJ mol⁻¹ less exothermic than for the formation of **2-Me**.

The main difference between the two systems concerns the extrusion pathway and in Fig. 9 is shown a comparison of the Gibbs free energy diagram for 1-Me and 1-'Bu. Increasing the steric bulk results in a slightly larger activation barrier ($\Delta G^{\#} =$ 85.1 kJ mol⁻¹, **2-Me** \rightarrow **3-O** + MeNCO; $\Delta G^{\#} = 88.6$ kJ mol⁻¹, $2^{-t}Bu \rightarrow 3'-O + {}^{t}BuNCO$, but the main difference is the large increase of thermodynamic stability of the extrusion product. From the carbamate intermediate $2^{-t}Bu$, the extrusion reaction is now computed to be exergonic by $\Delta G = -9.6 \text{ kJ mol}^{-1}$ (Table 5). Consequently the overall reaction $1-Bu + CO_2 \rightarrow 3'-O + CO_2$ ^tBuNCO is now exergonic by $\Delta G = -49.1$ kJ mol⁻¹, and the calculated TOF is similar to that obtained with 1-Me (0.19 10^{-2} s⁻¹, 1^{-t} Bu; 0.78 10^{-2} s⁻¹, 1-Me). Compound 1^{-t} Bu is very close to the experimental system 6 whose reaction with CO_2 was extremely rapid at room temperature (completion in less than 3 min). The calculated TOF for 1-'Bu corresponds to a half-reaction time of ca. 6 min, qualitatively in very good agreement with the experimental observation. The high energy of TS23-'Bu with respect to **3'-O** + 'BuNCO (98.2 kJ mol⁻¹, which corresponds to $\Delta G^{\#}$ for the back-reaction 3'-O + 'BuNCO \rightarrow 2-'Bu) is consistent with the experimental observation that the rate of 'BuNCO extusion from $Ti(\eta-C_5Me_5){N(^tBu)C(O)O}{MeC(N^iPr)_2}$ (29) is unaffected by added 'BuNCO (Scheme 4).



Fig. 9 Gibbs free energy diagram (kJ mol⁻¹) of the CO₂ cycloaddition/isocyanate extrusion (solid lines) and second CO₂ insertion (dotted lines) for the methyl imido complex **1-Me** ($\mathbf{R} = \mathbf{Me}$, black lines) and the bulky *tert*-butyl imido complex **1-'Bu** ($\mathbf{R} = '\mathbf{Bu}$, blue lines). For $\mathbf{R} = '\mathbf{Bu}$ and $\mathbf{R'} = '\mathbf{Pr}$, the oxo complex is **3'-O**.

Not only does the steric bulk favour the isocyanate formation pathway by stabilizing the extrusion product, it also influences in a dramatic way the CO_2 insertion pathway. The transition state for CO₂ insertion, TS24-'Bu, in the carbamate 2-'Bu was located on the potential energy surface together with the azamalonato complex 4-'Bu. The electronic and Gibbs free energies are given in Table 5 and the Gibbs free energy diagram is shown in Fig. 9 for comparison with the extrusion pathway. In order to achieve the required $N \cdots C$ interactions between the carbamate and CO_2 in TS24-'Bu, the tert-butyl group has to move toward the amidinate ligand where the isopropyl groups exert some steric pressure. Consequently, strong steric repulsion develops in the TS and the activation barrier is dramatically increased ($\Delta E^{\#} = 35.6 \text{ kJ mol}^{-1}$, **TS24-Me**; $\Delta E^{\#} = 81.5 \text{ kJ mol}^{-1}$, **TS24-**'**Bu**). This translates into a very unfavourable $\Delta G^{\#} = 140.1 \text{ kJ mol}^{-1}$ from the carbamate (Fig. 9). Even though the second CO_2 insertion is an exergonic reaction ($\Delta G = -13.6 \text{ kJ mol}^{-1}$), the activation barrier is too high for the process to be effective. This is reflected qualitatively by the calculated TOF value for the process $1\text{-}{'Bu} \rightarrow 2\text{-}{'Bu} \rightarrow 4\text{-}$ ^{*t*}**Bu** of 0.16×10^{-11} s⁻¹ that would correspond to an extrusion reaction being $ca. 10^7$ times faster than insertion. In the case of the alkyl imido complexes, the steric bulk, in particular at the imido ('Bu), results in a complete shut down of the second CO₂ insertion pathway.

As a further attempt to probe the influence of the steric bulk on the extrusion pathway, the experimental system 29 was computed together with the TS for 'BuNCO extrusion. The activation barrier is larger than from 2-'Bu ($\Delta G^{\#} = 88.6 \text{ kJ mol}^{-1}$, TS23-'Bu; $\Delta G^{\#} =$ 96.6 kJ mol⁻¹, 29 \rightarrow oxo complex + 'BuNCO) and the reaction is more exergonic ($\Delta G = -9.6 \text{ kJ mol}^{-1}$ vs. $\Delta G = -40.7 \text{ kJ mol}^{-1}$). As expected there is a stronger thermodynamic driving force for 'BuNCO extrusion when steric bulk is increased. However, this is not accompanied by a lowering of the activation barrier. As already described for TS23-Ph (Fig. 8), the TS for RNCO extrusion could again be described as an N-adduct on the Ti centre of the oxo complex. Therefore any increase of the steric bulk at the nitrogen atom would result in a longer $Ti \cdots N$ bond in the transition state and thus to a higher barrier. This could be compensated only in part by a stronger $C \cdots O$ interaction in the TS. This analysis is confirmed by the evolution of the $Ti \cdots N$ and $C \cdots O$ bond distances in the TS for extrusion (Ti \cdots N = 2.224 Å, C · · · O = 2.161 Å, **TS23-Me**; Ti · · · N = 2.350 Å, C · · · O = 2.152 Å, **TS23-**'**Bu**; Ti \cdots N = 2.660 Å, C \cdots O = 2.082 Å, TS from 29). Increasing the steric bulk at the cyclopentadienyl ring has resulted in an increase of the activation barrier by 8 kJ mol⁻¹, which translates at room temperature into a reaction ca. 25 times less rapid. This is in qualitative agreement with the experimental results where 29 decays at room temperature within 24 h, whereas reaction of 6 with CO₂ to form 34 is complete within 3 min without observation of the carbamate intermediate.

We return finally to the difference in dynamic NMR behaviour of the aryl carbamates **15–18** (fluxional but dependent on steric factors) and the *tert*-butyl carbamates **28**, **29** and **33** (apparently non-fluxional). The proposed fluxional process in eqn (2) appears to proceed *via* a net rotation about the Ti \cdots C_{carbamate} vector. This motion is the same as that which brings the model carbamates **2-R** to the second insertion transition states **TS24-R** (*e.g.*, Fig. 8 for **TS24-Ph**). The higher barrier for the fluxional process in the bulkier carbonates **15** and **16**, and the absence of fluxionality in the *tert*-butyl carbamates, are therefore consistent with the calculations described above.

Conclusions

We have carried out a comprehensive experimental and computational study of the reaction of titanium alkyl and aryl imido complexes with CO₂. These complement our previous studies with isocyanate and related unsaturated substrates.⁵⁶ Experimentally, the two reaction outcomes, namely CO₂ cycloaddition/isocyanate extrusion and CO₂ cycloaddition/second CO₂ insertion are found to differ dramatically depending on whether tert-butyl or aryl imides are under consideration. A second important factor is the steric demands of the supporting ligand sets ($C_5H_4Me vs. C_5Me_5$ and PhC(NSiMe₃)₂ vs. MeC(NⁱPr)₂). The DFT calculations reproduce the experimental data and reveal that the intrinsic electronic differences between alkyl and phenyl imides (when modelled by non-sterically demanding groups) are small in comparison with the major changes to transition state and product energies which occur upon introducing tert-butyl in place of methyl on the imido nitrogen. Similarly, the electronic effects of para substituents in the series $Ti(\eta - C_5 R_5)(N-4-C_6 H_4 X) \{MeC(NR')_2\}$ are relatively minor.

Experimental

General methods and instrumentation

All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon or of dinitrogen. Solvents were pre-dried over 4 Å molecular sieves and were refluxed over appropriate drying agents under a dinitrogen atmosphere and collected by distillation. Deuterated solvents were dried over appropriate drying agents, distilled under reduced pressure and stored under dinitrogen in Teflon valve ampoules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ¹H, ¹³C{¹H} and ¹³C NMR spectra were recorded on Varian Unity Plus 500 and Varian Mercury spectrometers. ¹H and ¹³C assignments were confirmed where necessary with the use of NOE, DEPT-135, DEPT90, DEPT-45, and two dimensional ¹H-¹H and ¹³C⁻¹H NMR experiments. All spectra were referenced internally to residual protio-solvent (1H) or solvent (13C) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in Hertz. Infrared spectra were prepared as Nujol mulls or thin films between KBr or NaCl plates and were recorded on Perkin-Elmer 1600 and 1700 series spectrometers. Infrared data are quoted in wavenumbers (cm⁻¹). Mass spectra were recorded by the mass spectrometry service of the University of Oxford's Inorganic Chemistry Laboratory. Combustion analyses were recorded by the analytical services of the University of Oxford's Inorganic Chemistry Laboratory.

Starting materials and literature preparations

The compounds $Ti(\eta-C_5Me_5)(N'Bu)\{PhC(NSiMe_3)_2\}$ (3),⁵⁶ $Ti(\eta-C_5Me_5)(N'Bu)\{MeC(N'Pr)_2\}$ (4),⁵⁶ $Ti(\eta-C_5H_4Me)(N'Bu)$ $\{PhC(NSiMe_3)_2\}$ (5),⁵⁶ $Ti(\eta-C_5H_4Me)(N'Bu)\{MeC(N'Pr)_2\}$ (6),⁵⁶ $Ti(\eta-C_5Me_5)(N-2,6-C_6H_3Me_2)\{MeC(N'Pr)_2\}$ (7),⁵⁶ $Ti(\eta-C_5Me_5)(NTol)\{MeC(N'Pr)_2\}$ (8),⁵⁶ $Ti(\eta-C_5Me_5)(N-2,6-C_6H_3-Me_2)Cl(py)$ (13)⁷¹ and $Li[PhC(NSiMe_3)_2]^{96}$ were prepared according to published methods. All other compounds and reagents were purchased and used without further purification.

(9). 680 $Ti(\eta-C_5Me_5)(N-4-C_6H_4CF_3)\{MeC(N'Pr)_2\}$ mg (1.73 mmol) Ti(η -C₅Me₅)(N'Bu){MeC(N'Pr)₂} (4) was dissolved in ca. 15 mL benzene to give a red solution. To this was added dropwise a solution of 217 µL (278 mg, 1.73 mmol) 4-(trifluoromethyl)aniline in ca. 5 mL benzene over 5 min to give a green solution. After 18 h, all volatiles were removed under reduced pressure. Compound 9 was isolated as a brown powder. Yield: 728 mg (87%). ¹H NMR data (benzene-d₆, 500.0 MHz, 298 K) δ : 7.34 (2 H, d, J = 8.0 Hz, m-(N-4-C₆H₄CF₃)), 6.56 (2 H, d, J = 8.0 Hz, o-(N-4-C₆H₄CF₃)), 3.46 (2 H, apparent sept., J =6.4 Hz, NCHMeMe), 1.98 (15 H, s, C₅Me₅), 1.47 (3 H, s, MeCN₂), 0.96 (6 H, d, J = 6.4 Hz, NCHMeMe), 0.91 (6 H, d, J = 6.6 Hz, NCHMeMe).¹³C– $\{^{1}H\}$ NMR data (benzene-d₆, 75.5 MHz, 298 K) δ: 164.2 (CN₂), 162.8 (*i*-N-4-C₆H₄CF₃), 126.3 (*p*-N-4- $C_6H_4CF_3$), 125.9 (*m*-N-4- $C_6H_4CF_3$), 123.0 (*o*-N-4- $C_6H_4CF_3$), 121.8 (C₅Me₅), 49.8 (NCHMeMe), 26.5 (NCHMeMe), 25.4 (NCHMeMe), 12.8 (C₅Me₅), 12.1 (MeCN₂). CF₃ resonance not observed. ¹⁹F NMR data (benzene-d₆, 282.4 MHz, 298 K) δ : -61.0 (CF₃). IR data (KBr plates, Nujol mull, cm⁻¹) 2726 (w), 2670 (w), 1892 (w), 1654 (m), 1601 (s), 1499 (s, br), 1412 (m), 1317 (s), 1275 (m, br), 1213 (m), 1159 (s), 1115 (s), 1066 (s), 1020 (w), 964 (m), 890 (w), 849 (m), 838 (m), 812 (w), 793 (w), 772 (w), 723 (m), 687 (m), 664 (w), 644 (w), 633 (w), 581 (w), 473 (w), 440 (w), 402 (w). Anal. found (calcd for C₂₅H₃₆F₃N₃Ti): C 61.8 (62.1) H 7.5 (7.5) N 8.9 (8.7)%. Mass spec. (E.I.) m/z 483 [M]⁺, 464 [M – $F]^+$, 445 $[M - 2F]^+$, 426 $[M - 3F]^+$.

 $Ti(\eta-C_5Me_5)(N-4-C_6H_4NMe_2){MeC(N^iPr)_2}$ (10). 549 mg (1.40 mmol) Ti(η -C₅Me₅)(N^tBu){MeC(N^tPr)₂} (4) was dissolved in ca. 15 mL benzene to give a red solution. To this was added 189 mg (1.39 mmol) freshly sublimed N,N-dimethyl-1,4phenylenediamine in ca. 15 mL benzene to afford a red solution that quickly turned green. After 1 h, all volatiles were removed under reduced pressure to give 10 as a green-brown solid. Yield: 555 mg (87%). ¹H NMR data (benzene- d_6 , 500.0 MHz, 298 K) δ : 6.80 (2 H, d, J = 9.0 Hz, m-N-4-C₆H₄NMe₂), 6.56 (2 H, d, J =9.0 Hz, o-N-4-C₆H₄NMe₂), 3.58 (2 H, apparent sept., J = 6.4 Hz, NCHMeMe), 2.51 (6 H, s, NMe₂), 2.11 (15 H, s, C₅Me₅), 1.55 (3 H, s, MeCN₂), 1.16 (6 H, d, J = 6.4 Hz, NCHMeMe), 1.00 (6 H, d, J = 6.4 Hz, NCHMeMe). ¹³C–{¹H} NMR data (benzene-d₆, 75.5 MHz, 298 K) δ: 162.9 (CN₂), 153.7 (*i*-N-4-C₆H₄NMe₂) 144.6 (p-N-4-C₆H₄NMe₂), 124.1 (m-N-4-C₆H₄NMe₂), 120.1 (C₅Me₅), 113.9 (o-N-4-C₆H₄NMe₂), 49.6 (NCHMeMe), 41.7 (NMe₂), 26.7 (NCHMeMe), 25.7 (NCHMeMe), 12.8 (C₅Me₅), 12.0 (MeCN₂). IR data (KBr plates, Nujol mull, cm⁻¹) 2956 (s), 2724 (w), 1655 (w), 1599 (w), 1499 (s), 1337 (w), 1313 (m), 1261 (m), 1218 (m), 1171 (w), 1123 (w), 1060 (w), 1021 (w), 969 (w), 947 (w), 858 (w), 814 (s), 753 (w), 724 (w), 625 (w), 555 (w), 470 (w). Anal. found (calcd for C₂₆H₄₂N₄Ti): C 67.2 (68.1) H 9.2 (9.2) N 12.2 (12.2)%. Mass spec. (E.I.) m/z 458 [M]⁺.

[Ti(η -C₅H₄Me)(N-2,6-C₆H₃Me₂){MeC(NⁱPr)₂}] (11). To 600 mg (1.77 mmol) Ti(η -C₅H₄Me)(NⁱBu){MeC(NⁱPr)₂} (6) in 60 mL benzene was added 220 µL (216 mg, 1.79 mmol) 2,6dimethylaniline *via* microlitre syringe, resulting in an immediate colour change from red to green. After 1 h, all volatiles were removed under reduced pressure to give a dark green oil. This was purified *via* tube distillation (130 °C, 1 × 10⁻⁵ Torr, 4 h) to afford **11** as a green oil. Yield: 485 mg (71%). ¹H NMR data (benzene-d₆, 500.0 MHz, 298 K) δ : 7.01 (2 H, d, J = 7.5 Hz, m-2,6-C₆H₃Me₂), 6.72 (1 H, t, J = 7.5 Hz, p-2,6-C₆H₃Me₂), 6.37 (2 H, virtual t, J = 2.7 Hz, $C_2H_2(\beta)C_2H_2(\alpha)CMe$), 5.92 (2 H, virtual t, J = 2.7 Hz, $C_2H_2(\beta)C_2H_2(\alpha)CMe$), 3.50 (2 H, apparent sept., J = 6.4 Hz, NCHMeMe), 2.38 (6 H, s, 2,6-C₆H₃Me₂), 2.10 $(3 \text{ H}, \text{ s}, \text{C}_2\text{H}_2(\beta)\text{C}_2\text{H}_2(\alpha)\text{C}Me), 1.53 (3 \text{ H}, \text{ s}, \text{MeCN}_2), 1.01 (6 \text{ H}, \text{d}, \text{d})$ J = 6.4 Hz, NCH*Me*Me), 0.86 (6 H, d, J = 6.4 Hz, NCHMe*Me*). ¹³C–{¹H} NMR data (benzene-d₆, 125.7 MHz, 298 K) δ : 160.3 (CN₂), 131.6 (*i*-2,6-C₆H₃Me₂), 128.3 (*o*-2,6-C₆H₃Me₂), 127.6 (*m*-2,6-C₆H₃Me₂), 125.0 (*p*-2,6-C₆H₃Me₂), 119.5 (C₂(β)C₂(α)CMe), $(C_2(\beta)C_2(\alpha)CMe),$ 111.8 $(C_2(\beta)C_2(\alpha)CMe),$ 113.6 48.8 (NCHMeMe), 25.6 (NCHMeMe), 25.4 (NCHMeMe), 20.6 $(N-2,6-C_6H_3Me_2)$, 15.1 $(C_2(\beta)C_2(\alpha)CMe)$, 10.6 $(MeCN_2)$. IR data (KBr plates, neat thin film, cm⁻¹) 3170 (w), 3054 (m), 3028 (m), 2965 (s), 2927 (s), 2868 (s), 2720 (w), 2601 (w), 2365 (w), 2053 (w), 1827 (w), 1765 (w), 1640 (w, br), 1587 (m), 1467 (s, br), 1408 (s), 1378 (s), 1361 (s), 1336 (s), 1308 (s, br), 1227 (s), 1173 (m), 1143 (m), 1123 (m), 1094 (m), 1057 (m), 1049 (m), 1032 (m), 1019 (m), 980 (m), 963 (m), 936 (w), 915 (w), 885 (w), 845 (m), 816 (s), 786 (s), 758 (s), 742 (m), 624 (m), 585 (m), 564 (w), 550 (w), 503 (w), 435 (m). Anal. found (calcd for C₂₂H₃₃N₃Ti): C 66.0 (68.2); H 8.7 (8.6); N 10.8 (10.9)%. Mass spec. (E.I.) m/z 387 [M]⁺.

 $Ti(\eta-C_5H_4Me)(N-2,6-C_6H_3Me_2){PhC(NSiMe_3)_2}$ (12). 1.48 g (3.21 mmol) Ti(η -C₅H₄Me)(N'Bu){PhC(NSiMe₃)₂} (5) was dissolved in ca. 60 mL pentane, and to this was added 400 µL (394 mg, 3.25 mmol) 2,6-dimethylaniline via microlitre syringe. After 16 h, all volatiles were removed under reduced pressure, and the residue taken up in a minimum of pentane and cooled to -30 °C. 576 mg (36% yield) was obtained from the first batch of crystals. Total yield after a second crop was obtained: 943 mg (58%). ¹H NMR data (benzene-d₆, 500.0 MHz, 298 K) δ: 7.14–7.09 (3 H, m, aryl-H), 7.00-6.95 (5 H, m, aryl-H), 6.74 (2 H, virtual t, $C_5H_2(\beta)H_2(\alpha)Me$), 5.86 (2 H, virtual t, $C_5H_2(\beta)H_2(\alpha)Me$), 2.56 (6 H, s, N-2,6- $C_6H_3Me_2$), 2.10 (3 H, s, $C_5H_2(\beta)H_2(\alpha)Me$), -0.15 (18 H, s, SiMe₃).¹³C–{¹H} NMR data (benzene-d₆, 125.7 MHz, 298 K) δ : 171.0 (CN₂), 159.6 (i-2,6-C₆H₃Me₂), 138.6 (i-C₆H₅CN₂), 132.4 (o-2,6-C₆H₃Me₂), 128.9 (o-C₆H₅CN₂), 127.6 (m-2,6-C₆H₃Me₂), 127.5 $(p-C_6H_5CN_2)$, 125.2 $(p-2,6-C_6H_3Me_2)$, 119.9 $(C_2(\beta)C_2(\alpha)CMe)$, 114.5 ($C_2(\beta)C_2(\alpha)CMe$), 111.7 ($C_2(\beta)C_2(\alpha)CMe$), 20.6 (N-2,6- $C_6H_3Me_2$, 14.9 ($C_2(\beta)C_2(\alpha)CMe$), 2.2 (SiMe₃). IR data (KBr plates, Nujol mull, cm⁻¹) 2726 (w), 1589 (w), 1406 (m, br), 1308 (m, br), 1249 (s), 1171 (w, br), 1094 (w), 1033 (w), 1006 (m), 996 (m), 919 (w), 840 (s), 793 (m), 781 (m), 760 (m), 723 (w), 702 (w), 643 (w), 517 (m). Anal. found (calcd for $C_{27}H_{39}N_3Si_2Ti$): C 63.3 (63.6); H 8.3 (7.7); N 8.2 (8.2)%. Mass spec. (E.I.) m/z 509 [M]+, 495 [M - Me]+.

Ti(η-C₅Me₅)(N-2,6-C₆H₃Me₂){PhC(NSiMe₃)₂} (14). 409 mg (0.98 mmol) Ti(η-C₅Me₅)(N-2,6-C₆H₃Me₂)Cl(py) (13 and 267 mg (0.99 mmol) Li[PhC(NSiMe₃)₂] were dissolved in *ca.* 40 mL benzene and heated to 90 °C for 3 h. Volatiles were removed under reduced pressure, and the residue extracted with 25 mL benzene and filtered. The volatiles were again removed under reduced pressure, the residue extracted into a minimum amount of pentane, and the compound further purified by crystallisation at -30 °C to afford 14 as a green powder. Yield: 225 mg (36%). ¹H NMR data (benzene-d₆, 500.0 MHz, 298 K) δ: 7.17–7.13 (3 H, m, *o*-, *p*-C₆H₅), 7.03-7.00 (4 H, m, *m*-C₆H₅, *m*-2,6-C₆H₃Me₂), 6.73 (1 H, t, *J* = 7.4 Hz, *p*-2,6-C₆H₃Me₂), 2.36 (6 H, s, 2,6-C₆H₃Me₂), 2.02 (15 H, s, C₅Me₅), -0.08 (18 H, s, SiMe₃). ¹³C–{1H} NMR

data (benzene-d₆, 125.7 MHz, 298 K) δ : 174.7 (CN₂), 158.5 (*i*-2,6-C₆H₃Me₂), 138.9 (*i*-C₆H₅CN₂), 132.0 (*o*-2,6-C₆H₃Me₂), 128.9 (one CH from *o*-, *p*-Ph or *m*-Me₂C₆H₃), 128.5 (*m*-C₆H₅), 128.0 (one CH from *o*-, *p*-Ph or *m*-Me₂C₆H₃), 127.4 (one CH from *o*-, *p*-Ph or *m*-Me₂C₆H₃), 127.4 (one CH from *o*-, *p*-Ph or *m*-Me₂C₆H₃), 127.4 (one CH from *o*-, *p*-Ph or *m*-Me₂C₆H₃), 128.5 (*c*₅Me₅), 119.2 (*p*-C₆H₃Me₂), 20.8 (C₆H₃Me₂), 12.5 (C₅Me₅), 3.3 (SiMe₃). IR data (KBr discs, Nujol mull, cm⁻¹) 2726 (w), 1881 (w), 1651 (w), 1586 (w), 1307 (s), 1293 (s), 1248 (s), 1162 (w), 1093 (m), 1077 (w), 1031 (w), 1005 (m), 996 (m), 961 (w), 932 (w), 839 (s), 781 (m), 756 (s), 743 (s), 706 (m), 623 (w), 581 (w), 563 (w), 511 (m), 438 (m). Anal. found (calcd for C₃₁H₄₇N₃Si₂Ti:): C 65.6 (65.8); H 8.6 (8.4); N 7.3 (7.4)%. Mass spec. (E.I.) *m*/*z* 565 [M]⁺.

 $Ti(\eta-C_5Me_5){N(-2,6-C_6H_3Me_2)C(O)O}{MeC(N'Pr)_2}$ (15). 198 mg (0.45 mmol) Ti(η -C₅Me₅)(N-2,6-C₆H₃Me₂){MeC(NⁱPr)₂} (7) was dissolved in ca. 10 mL pentane, the headspace evacuated, and the solution exposed to CO_2 at a pressure of 1 atm for 10 min. Volatiles were then removed under reduced pressure to afford 15 as a brown powder. Yield: 71 mg (79%). ¹H NMR data (benzene-d₆, 500.0 MHz, 298 K) & 6.95-7.00 (3 H, m, *m*-, *p*- 2,6-C₆H₃Me₂), 3.23 (1 H, m, NCH_aMeMe), 3.05 (1 H, m, NCH_bMeMe), 2.24 (3 H, s, 2,6-C₆H₃MeMe), 1.97 (3 H, s, 2,6-C₆H₃MeMe), 1.95 (15 H, s, C₅Me₅), 1.41 (3 H, s, MeCN₂), 1.06 (3 H, d, J = 6.6 Hz, NCH_aMe_aMe), 1.00 (3 H, d, J =6.6 Hz), NCH_aMe Me_b (0.79, 3 H, d, J = 6.4 Hz) NCH_b Me_a Me $(0.52, 3 \text{ H}, d, J = 6.4 \text{ Hz}, \text{NCH}_{b}\text{Me}Me_{b})$. ¹³C-{¹H} NMR data (benzene-d₆, 125.7 MHz, 298 K) δ: 168.5 (OCO), 159.2 (MeCN₂), 147.1 (i- C₆H₃Me₂), 134.2 (o- C₆H₃Me₂), 133.6 (m- C₆H₃Me₂), 129.4 (p- C₆H₃Me₂), 124.7 (C₅Me₅), 50.5 (NCH_aMeMe), 49.3 (NCH_bMeMe), 25.7 (NCH_bMe_aMe), 24.6 (NCH_aMeMe_b), 24.2 (NCH_aMe_aMe) , 24.0 (NCH_bMeMe_b) , 19.7 $(2,6-C_6H_3MeMe)$, 19.2 (2,6-C₆H₃MeMe), 13.6 (MeCN₂), 13.0 (C₅Me₅). IR data (KBr plates, Nujol mull, cm⁻¹) 2955 (s), 2726 (w), 1669 (s, br), 1577 (w), 1405 (w), 1328 (w), 1309 (m), 1282 (m), 1247 (m), 1207 (m), 1172 (s, br), 1116 (w), 1002 (w), 910 (m), 821 (m), 790 (m), 762 (m), 723 (m, br), 687 (w), 631 (w), 587 (w), 549 (w), 467 (m), 443 (m). Anal. found (calcd for C₂₇H₄₇N₃Si₂Ti): C 61.0 (62.6), H 9.2 (9.2), N 7.6 (8.1)%.

 $Ti(\eta - C_5Me_5) \{N(-2, 6-C_6H_3Me_2)C(O)O\} \{PhC(NSiMe_3)_2\}$ (16). 57.3 mg (0.10 mmol) $Ti(\eta-C_5Me_5)(N-2,6-C_6H_3Me_2)$ - $\{PhC(NSiMe_3)_2\}$ (14) was dissolved in *ca*. 5 mL benzene, the headspace evacuated, and the solution exposed to CO₂ at a pressure of 1 atm, which resulted in a colour change from dark green to cherry red within 1 min. After 16 h, all volatiles were removed under reduced pressure, affording 16 as a red powder. Yield: 59.1 mg (96%). ¹H NMR data (benzene-d₆, 500.0 MHz, 298 K) δ : 7.25 (1 H, d, J = 7.6 Hz, m-2,6-C₆H₃Me₂), 7.08 (1 H, d, J =7.6 Hz, m-2,6-C₆H₃Me₂), 7.02 (1 H, t, J = 7.6 Hz, p-2,6-C₆H₃Me₂), 7.02–6.94 (5 H, m, C_6H_5), 2.28 (3 H, s, 2,6- C_6H_3MeMe (a)), 2.26 (3 H, s, 2,6-C₆H₃MeMe (b)), 1.99 (15 H, s, C₅Me₅), -0.11 (9 H, s, SiMe₃), -0.36 (9 H, s, SiMe₃). ¹³C-{¹H} NMR data (benzened₆, 125.7 MHz, 298 K) δ: 177.3 (OCO), 158.8 (PhCN₂), 147.1 (*i*-2,6-C₆H₃Me₂), 137.2 (*i*-C₆H₅), 134.7 (*o*-2,6-C₆H₃Me₂ (a)), 133.5 (o- 2,6-C₆H₃Me₂ (b)), 130.1 (C₅Me₅), 129.6 (o-C₆H₅), 128.2 (m-C₆H₅), 128.0 (*p*-2,6-C₆H₃Me₂), 127.9 (*m*-2,6-C₆H₃Me₂ (a)), 127.3 (m-2,6-C₆H₃Me₂ (b)), 125.0 (p-C₆H₅), 20.7 (2,6-C₆H₃MeMe), 19.6 $(2,6-C_6H_3MeMe)$, 13.3 (C_5Me_5) , 3.4 $(SiMe_3)$, 3.0 $(SiMe_3)$. IR data (KBr plates, Nujol mull): 2727 (w), 2669 (w), 2208 (w), 1671 (s), 1634 (m), 1608 (m), 1577 (m), 1277 (s), 1260 (s), 1248 (s), 1171

(s), 1158 (m), 1098 (m), 1076 (m), 1004 (s), 991 (s), 913 (s), 841 (s, br), 808 (s), 788 (s), 760 (s), 748 (s), 725 (s), 687 (m), 640 (w), 627 (w), 590 (w), 557 (w), 512 (w), 469 (w), 441 (w) cm⁻¹. Mass spec. (E.I.) $m/z = 609 [M]^+$. A satisfactory elemental analysis was not obtained.

 $Ti(\eta - C_5H_4Me) \{N(-2, 6-C_6H_3Me_2)C(O)O\} \{MeC(N'Pr)_2\}$ (17). 100 mg (0.26 mmol) $Ti(\eta-C_5H_4Me)(N-2,6-C_6H_3Me_2)$ - ${MeC(N^{i}Pr)_{2}}$ (11) was dissolved in 10 mL benzene to give a green solution. The headspace was evacuated, and the solution exposed to CO₂ at a pressure of 1 atm, resulting in an immediate colour change to deep red. After 5 min, all volatiles were removed under reduced pressure to afford 17 as an olive-green powder. Yield: 82 mg (74%). ¹H NMR data (dichloromethane-d₂, 500.0 MHz, 213 K) δ : 6.93 (1 H, t, J = 4.7 Hz, p-2,6-C₆H₃Me₂), 6.86 (2 H, d, J = 4.7 Hz, $m-2,6-C_6H_3Me_2$), 6.80 (1 H, m, $CH(\beta_1)CH(\beta_2)C_2H_2(\alpha)CMe)$, 6.49 (1 H, m, $CH(\beta_1)CH(\beta_2)$ - $C_2H_2(\alpha)CMe$, 6.35 (1 H, m, $C_2H_2(\beta)CH(\alpha_1)CH(\alpha_2)CMe$), 6.23 $(1H, m, C_2H_2(\beta)CH(\alpha_1)CH(\alpha_2)CMe), 3.50 (2H, m, NCHMeMe),$ 2.43 (3 H, s, C₅H₄Me), 2.07 (3 H, s, 2,6-C₆H₃MeMe), 1.88 (3 H, s, MeCN₂), 1.75 (3 H, s, 2,6-C₆H₃MeMe), 1.11 (3 H, d, J = 6.7 Hz, NCH_aMeMe), 1.09 (3 H, d, J = 6.7 Hz, NCH_bMeMe), 0.95 (3 H, d, J = 6.7 Hz, NCH_aMeMe), 0.23 $(3 \text{ H}, d, J = 6.7 \text{ Hz}, \text{NCH}_{b}\text{MeMe})$. ¹³C-{¹H} NMR data (dichloromethane-d₂, 125.7 MHz, 213 K) δ: 166.4 (OCO), 159.2 (MeCN₂), 144.8 (i-2,6-C₆H₃Me₂), 135.7 (o-2,6-C₆H₃Me₂), 133.5 $(o-2,6-C_6H_3Me_2)$, 132.5 $(i-C_5H_4Me)$, 128.1 $(m-2,6-C_6H_3Me_2)$ $C_6H_3Me_2$), 127.2 (*p*-2,6- $C_6H_3Me_2$), 124.5 (*m*-2,6- $C_6H_3Me_2$), 119.8 $(C_2H_2(\beta)CH(\alpha_1)CH(\alpha_2)CMe)$, 117.7 $(CH(\beta_1)CH(\beta_2) C_2H_2(\alpha)CMe$, 117.3 ($CH(\beta_1)CH(\beta_2)C_2H_2(\alpha)CMe$), 115.5 $(C_2H_2(\beta)CH(\alpha_1)CH(\alpha_2)CMe),$ 50.1 (NCHMeMe), 49.4 (NCHMeMe), 24.2 (NCH_aMeMe), 24.0 (NCH_bMeMe), 23.7 (NCH_aMeMe), 22.9 (NCH_bMeMe), 19.0 (2,6-C₆H₃MeMe), 18.1 (2,6-C₆H₃MeMe), 15.3 (C₅H₄Me), 11.0 (MeCN₂). IR data (KBr plates, Nujol mull): 2955 (s), 2726 (w), 2669 (w), 1733 (w), 1670 (s, br), 1615 (w), 1577 (w), 1499 (m), 1339 (m), 1309 (m), 1294 (m), 1261 (w), 1248 (w), 1218 (m), 1173 (w), 1138 (w), 1120 (w), 1096 (w), 1073 (w), 1020 (w), 1003 (w), 926 (w), 911 (w), 829 (m), 819 (m), 805 (m), 791 (m), 779 (w), 767 (w), 723 (m), 688 (w), 69 (w), 628 (w), 617 (w), 586 (w), 552 (w), 469 (w), 441 (w), 417 (w) cm⁻¹. A satisfactory elemental analysis was not obtained.

 $Ti(\eta-C_5H_4Me)\{N(-2,6-C_6H_3Me_2)C(O)O\}\{PhC(NSiMe_3)_2\}$ (18). 167 mg (0.33 mmol) $Ti(\eta-C_5H_4Me)(N-2,6-C_6H_3Me_2)$ - ${PhC(NSiMe_3)_2}$ (12) was dissolved in *ca.* 10 mL benzene to give a brown solution. The headspace was evacuated, and the solution exposed to CO_2 at a pressure of 1 atm. A colour change from brown to red was observed. After 5 min, volatiles were removed under reduced pressure to afford 18 as a hard brown solid. This was triturated with ca. 5 mL pentane. 90 mg (50% yield). ¹H NMR data (dichloromethane-d₂, 500.0 MHz, 223 K) δ : 7.40–7.46 (3 H, m, *m*-, *p*- C₆H₅), 7.20 (1 H, d, J = 6.6 Hz, $o-C_6H_5(\alpha)$), 7.14 (1 H, d, J = 5.4 Hz, $o-C_6H_5(\beta)$), 6.97 (2 H, d, J = 7.6 Hz, *m*-N-2,6-C₆H₃Me₂), 6.92 (1 H, t, J = 6.6 Hz, $p-N-2, 6-C_6H_3Me_2$, 6.86 (1 H, s, $CH(\beta_1)CH(\beta_2)C_2H_2(\alpha)CMe$), 6.63 (1 H, s, $CH(\beta_1)CH(\beta_2)C_2H_2(\alpha)CMe$), 6.53 (1 H, s, $C_2H_2(\beta)$ - $CH(\alpha_1)CH(\alpha_2)CMe)$, 6.20 (1 H, s, $C_2H_2(\beta)CH(\alpha_1)CH(\alpha_2)CMe)$, 2.46 (3 H, s, C_5H_4Me), 2.13 (3 H, s, N-2,6- C_6H_3MeMe (a)), 2.04 (3 H, s, N-2,6-C₆H₃MeMe (b)), -0.22 (9 H,s, SiMe₃), -0.48 (9 H, s, SiMe₃). ¹³C-{¹H} NMR data (dichloromethane-d₂, 125.7 MHz, 223 K) δ : 173.2 (OCO), 159.1 (C₆H₅CN₂), 144.6 (*i*-2,6-C₆H₃Me₂), 135.3 (*i*-C₆H₅), 134.3 (*o*-2,6-C₆H₃Me₂ (a)), 133.5 (*o*-2,6-C₆H₃Me₂ (b)), 132.8 (C₅Me₅), 129.5 (*m*-/*p*-C₆H₅), 128.4 (*p*-/*m*-C₆H₅), 127.5 (*m*-2,6-C₆H₃Me₂), 126.7 (*o*-C₆H₅ (β)), 125.8 (*o*-C₆H₅ (α)), 125.0 (*p*-2,6-C₆H₃Me₂), 121.9 (C₂H₂(β)CH(α₁)CH(α₂)CMe), 120.5 (CH(β₁)CH(β₂)C₂H₂(α)CMe), 116.8 (CH(β₁)CH(β₂)-C₂H₂(α)CMe) 116.3 (C₂H₂(β)CH(α₁)CH(α₂)CMe), 19.0 (2,6-C₆H₃MeMe), 18.5 (2,6-C₆H₃MeMe), 15.6 (C₅H₄Me), 0.9 (SiMe₃ (× 2)), *i*-C₅H₄Me resonance not observed. IR data (KBr plates, Nujol mull, cm⁻¹): 2954 (s), 2725 (w), 2670 (w), 2361 (w), 2209 (w), 1667 (s), 1610 (m), 1590 (m), 1571 (m), 1496 (m), 1289 (s), 1246 (s), 1185 (w), 1165 (m), 1097 (w), 1067 (w), 1034 (m), 1004 (s), 994 (m), 927 (m), 914 (m), 838 (s), 785 (m), 763 (s), 723 (s), 687 (s), 614 (w), 587 (w), 518 (m), 461 (m), 444 (m) cm⁻¹. Anal. found (calcd for C₂₈H₃₉N₃O₂Si₂Ti): C 60.5 (60.7); H 7.1 (7.1); N 7.3 (7.6)%.

 $Ti(\eta-C_5Me_5){OC(O)N(-2,6-C_6H_3Me_2)C(O)O}{MeC(N'Pr)_2}$ (19). 125 mg (0.28 mmol) $Ti(\eta-C_5Me_5)(N-2,6-C_6H_3Me_2)$ - ${MeC(N'Pr)_2}$ (7) was dissolved in *ca.* 10 mL benzene, the headspace evacuated, and the solution exposed to CO₂ at a pressure of 1 atm for a period of 24 h. Volatiles were then removed under reduced pressure to afford 19 as a red powder. Yield: 122 mg (82%). ¹H NMR data (benzene-d₆, 300.0 MHz, 298 K) δ : 7.12 $(1 \text{ H}, d, J = 8.0 \text{ Hz}, H_a), 7.09 (1 \text{ H}, t, J = 8.0 \text{ Hz}, H_b), 7.04$ $(1 \text{ H}, d, J = 8.0 \text{ Hz}, H_c), 3.51 (2 \text{ H}, \text{ apparent sept, NCHMeMe}),$ 2.55 (3 H, s, Me_a), 2.20 (3 H, s, Me_b), 1.97 (15 H, s, C₅Me₅), 1.42 $(3 \text{ H}, \text{ s}, MeCN_2), 1.12 (6 \text{ H}, d, J = 7.0 \text{ Hz}), NCHMeMe (1.07,)$ 6 H, d, J = 7.0 Hz, NCHMeMe). ¹³C-{¹H} NMR data (benzene d_6 , 125.7 MHz, 298 K) δ : 169.4 (MeCN₂), 153.3 ({O(CO)}₂N), 139.6 (*i*-N-2,6-C₆H₃Me₂), 136.3 (*o*-N-2,6-C₆H₃Me₂ (adj. Me_a)), 135.9 (o-N-2,6-C₆H₃Me₂ (adj. Me_b)), 130.9 (C₅Me₅), 128.6 (m-N-2,6-C₆H₃Me₂ (adj. Me_a)), 128.4 (*m*-N-2,6-C₆H₃Me₂ (adj. Me_b)), 127.2 (p-N-2,6-C₆H₃Me₂), 50.5 (NCHMeMe), 24.2 (NCHMeMe), 23.3 (NCHMeMe), 18.7 (Me_a), 18.1 (Me_b), 14.4 (MeCN₂), 12.7 (C₅Me₅). IR data (KBr plates, Nujol mull): 2725 (w), 1694 (s), 1651 (s), 1556 (w), 1314 (w), 1262 (w, br), 1234 (w), 1206 (m), 1173 (m), 1158 (m), 1124 (w), 1030 (w), 1004 (s), 811 (m), 782 (w), 771 (m), 742 (w), 724 (m), 685 (w), 652 (w), 611 (m), 587 (w), 528 (m), 511 (w), 453 (m, br) cm⁻¹. Mass spec. (E.I.): $m/z = 531 [M]^+$. Anal. found (calcd for C₂₈H₄₁N₃O₄Ti): C 63.4 (63.3); H 7.3 (7.8); N 8.1 (7.9)%.

 $Ti(\eta-C_5H_4Me)\{OC(O)N(\textbf{-2,6-}C_6H_3Me_2)C(O)O\}\{MeC(N^{i}Pr)_2\}$ (20). 100 mg (0.26 mmol) $Ti(\eta-C_5H_4Me)(N-2,6-C_6H_3Me_2)$ - ${MeC(N'Pr)_2}$ (11) was dissolved in 10 mL benzene to give a green solution. The headspace was evacuated, and the solution exposed to CO_2 at a pressure of 1 atm, resulting in an immediate colour change to dark red. After 24 h, all volatiles were removed to afford 20 as a red-brown solid. Yield: 75 mg (61%). ¹H NMR data δ : (benzene-d₆, 300.0 MHz, 298 K): 7.10 (1 H, d, J = 7.2 Hz, H_a), 7.08 (1 H, t, J = 7.2 Hz, H_b), 7.03 (2 H, d, J =7.2 Hz, H_c), 6.30 (2 H, virtual t, J = 2.7 Hz, $C_5 H_2(\beta) H_2(\alpha) Me$), 5.96 (2 H, virtual t, J = 2.7 Hz, $C_5H_2(\beta)H_2(\alpha)Me$), 3.16 (2 H, sept, J = 6.4 Hz, NCHMeMe), 2.46 (3 H, s, Me_a), 2.19 (3 H, s, $Me_{\rm b}$), 2.12 (3 H, s, $C_5H_2(\beta)H_2(\alpha)Me$), 1.13 (3 H, s, $MeCN_2$), 1.11 (6 H, d, J = 6.4 Hz, NCHMeMe), 1.04 (6 H, d, J = 6.4 Hz, NCHMeMe). ${}^{13}C-{}^{1}H$ NMR data (benzene-d₆, 125.7 MHz, 298 K) δ :167.1 (MeCN₂), 152.9 ({O(CO)}₂N), 139.3 (*i*-2,6-C₆H₃Me₂), 136.1 (o-2,6-C₆H₃Me₂ (adj. Me_a)), 136.0 (o-2,6-C₆H₃Me₂ (adj. Me_b)), 134.2 ($C_2H_2(\beta)C_2H_2(\alpha)CMe$), 128.6 (*m*-N-2,6-C₆H₃Me₂)

(adj. Me_a)), 128.5 (*m*-N-2,6-C₆H₃Me₂ (adj. Me_b)), 127.4 (*p*-N-2,6-C₆H₃Me₂), 119.5 (C₂(β)C₂(α)CMe), 119.4 (C₂(β)C₂(α)CMe), 50.6 (NCHMeMe), 23.7 (NCH*Me*Me), 23.4 (NCHMe*Me*), 18.5 (*Me*_a), 18.4 (*Me*_b), 18.0 (*Me*CN₂), 9.9 (C₂(β)C₂(α)C*Me*). IR data (KBr plates, Nujol mull): 2956 (s), 2726 (w), 2671 (w), 1700 (s), 1651 (s, br), 1611 (m), 1583 (m), 1557 (m), 1262 (m), 1244 (m), 1216 (s), 1173 (s), 1122 (m), 1085 (m), 1071 (m), 1031 (m), 1003 (m), 936 (w), 920 (w), 811 (s), 767 (m), 722 (s), 703 (m), 585 (w), 549 (w), 532 9w), 458 (w), 426 (w) cm⁻¹. Anal. found (calcd for C₂₄H₃₃N₃O₄Ti): C 61.0 (60.6); H 7.4 (7.0); N 9.1 (8.8)%. Mass spec. (E.I.): *m/z* = 475 [M]⁺.

 $Ti(\eta-C_5H_4Me){OC(O)N(-2,6-C_6H_3Me_2)C(O)O}{PhC(NSi Me_{3}_{2}$ (21). 142 mg (0.28 mmol) $Ti(\eta-C_{5}H_{4}Me)(N-2,6 C_6H_3Me_2$ {PhC(NSiMe_3)₂} (12) was dissolved in *ca.* 15 mLbenzene to give a brown solution. The headspace was evacuated, and the solution exposed to CO₂ at a pressure of 1 atm, resulting in an immediate colour change to red. After 43 h, all volatiles were removed under reduced pressure, and the residue triturated with ca. 5 mL pentane. Compound 21 was obtained as a brown powder. Yield: 55 mg (33%). ¹H NMR data (benzene d_6 , 500.0 MHz, 298 K) δ : 7.12 (1 H, d, J = 7.3 Hz, H_a), 7.09 $(1 \text{ H}, \text{ t}, J = 7.3 \text{ Hz}, H_{\text{b}}), 7.04 (1 \text{ H}, \text{ d}, J = 7.3 \text{ Hz}, H_{\text{c}}),$ 6.95–6.90 (3 H, m, o-, p-C₆H₅), 6.86–6.81 (2 H, m, m-C₆H₅), 6.43 (2 H, virtual t, J = 2.7 Hz, $C_5H_2(\beta)H_2(\alpha)Me$), 6.05 (2 H, virtual t, J = 2.7 Hz, $C_5H_2(\beta)H_2(\alpha)Me$, 2.48 (3 H, s, Me_a), 2.34 (3 H, s, Me_b), 2.12 (3 H, s, $C_5H_2(\beta)H_2(\alpha)Me$), -0.02 (18 H, s, SiMe₃). ${}^{13}C-{}^{1}H$ NMR data (benzene-d₆, 125.7 MHz, 298 K) δ:175.0 (C₆H₅CN₂), 152.8 (OCO), 139.1 (*i*-2,6-C₆H₃Me₂), 136.6 (*i*-C₆H₅), 136.0 (*o*-2,6-C₆H₃Me₂ (adj. Me_a)), 135.9 (*o*-2,6- $C_6H_3Me_2$ (adj. Me_b)), 133.8 ($C_2(\beta)C_2(\alpha)CMe$), 128.6 (*m*-2,6-C₆H₃Me₂ (adj. Me_a)), 128.3 (*m*-2,6-C₆H₃Me₂ (adj. Me_b)), 128.2 $(m-C_6H_5)$, 128.1 $(o-/p-C_6H_5)$, 127.9 $(p-/o-C_6H_5)$, 127.5 (p-2,6- $C_6H_3Me_2$, 120.7 ($C_2(\beta)C_2(\alpha)CMe$), 119.8 ($C_2(\beta)C_2(\alpha)CMe$), 18.5 (Me_a), 18.0 (Me_b), 15.7 (C₂(β)C₂(α)CMe), 1.7 (SiMe₃). IR data (KBr plates, Nujol mull): 3106 (w), 2728 (w), 2671 (w), 2336 (w), 2273 (w), 1944 (w), 1703 (s), 1657 (s), 1624 (m), 1590 (m), 1558 (m), 1524 (m), 1500 (m), 1407 (s), 1366 (s), 1301 (s), 1248 (s), 1229 (m), 1172 (m), 1094 (m), 1075 (m), 1032 (m), 1003 (s), 992 (s), 913 (s, br), 842 (s, br), 812 (s), 780 (s), 765 (s), 724 (s), 637 (w), 615 (w), 587 (w), 536 (w), 519 (w), 438 (w) cm^{-1.} Anal. found (calcd for C₂₉H₃₉N₃O₄Si₂Ti): C 58.4 (58.3); H 6.5 (6.6); N 6.8 (7.0)%.

 $Ti(\eta-C_5Me_5){N(Tol)C(O)O}{MeC(N'Pr)_2}$ (22). 371 mg (0.87 mmol) Ti(η -C₅Me₅)(NTol){MeC(NⁱPr)₂} (8) was dissolved in ca. 30 mL benzene. The solution was frozen at -196 °C, and the headspace evacuated. 0.86 mmol CO₂ was condensed onto the frozen solution using a volumetrically calibrated manifold, and the solution warmed to room temperature. Volatiles were removed under reduced pressure after ca. 10 min to afford the product as a red powder. Yield: 225 mg (55%). ¹H NMR data (benzene-d₆, 500.0 MHz, 298 K) δ : 7.35 (2 H, d, J = 8.5 Hz, m-4-C₆H₄Me), 7.03 (2 H, d, J = 8.5 Hz, o-4-C₆H₄Me), 3.65 (1 H, m, br, NCH_aMeMe), 3.29 (1 H, m, br, NCH_bMeMe), 2.14 (3 H, s, ArMe), 1.94 (15 H, s, C₅Me₅), 1.35 (3 H, s, MeCN₂), 1.08 (6 H, d, J = 6.2 Hz, NCH_bMeMe), 0.98 (3 H, d, J = 5.9 Hz, NCH_a*Me*Me), 0.64 (3 H, d, J = 6.1 Hz, NCH_aMe*Me*. ¹³C-{¹H} NMR data (125.7 MHz, 298 K, benzene- d_6) δ : 169.9 (MeCN₂), 157.7 (OCO), 146.1 (*i*-4-C₆H₄Me), 131.0 (*p*-4-C₆H₄Me), 129.4 $(o-4-C_6H_4Me)$, 129.0 (C_5Me_5) , 122.6 $(m-4-C_6H_4Me)$, 50.5 Published on 27 April 2009. Downloaded by University of Illinois at Chicago on 25/10/2014 20:19:27.

(NCH_bMeMe), 49.5 (NCH_aMeMe), 24.3 (NCH_aMeMe), 24.1 (NCH_aMeMe), 23.9 (NCH_bMeMe), 20.9 (ArMe), 15.0 (MeCN₂), 12.6 (C₅Me₅). IR data (KBr plates, Nujol mull): 2955 (s), 2726 (w), 2673 (w), 2360 (w), 1701 (w), 1672 (s), 1609 (w, br), 1575 (w), 1508 (s), 1339 (w), 1307 (m), 1207 (m), 1177 (w), 1160 (w), 1128 (w), 1064 (w), 1006 (m), 934 (w), 915 (m), 818 (m), 791 (m), 724 (s), 681 (w), 612 (w), 586 (w), 516 (w), 476 (m), 424 (w) cm⁻¹. Anal. found (calcd for $C_{26}H_{39}N_3O_2Ti$): C 65.8 (65.6); H 8.1 (8.3); N 8.4 (8.9)%.

 $Ti(\eta-C_5Me_5){OC(O)N(Tol)C(O)O}{MeC(N^iPr)_2}$ (23). 197 mg (0.46 mmol) Ti(η -C₅Me₅)(NTol){MeC(N^{*i*}Pr)₂} (8) was dissolved in ca. 15 mL benzene to give a green solution. The headspace was evacuated, and the solution exposed to CO_2 at a pressure of 1 atm for a period of 16 h. The volatiles were then removed under reduced pressure to afford 23 as a brown solid. Yield: 145 mg (61%). ¹H NMR data (benzene-d₆, 300.0 MHz, 298 K): 7.39 (2 H, d, J = 8.4 Hz, $o-C_6H_4Me$), 7.04 (2 H, d, J = 8.4 Hz, m-C₆H₄Me), 3.42 (1 H, apparent sept, J = 6.8 Hz, NCHMeMe), 2.05 (3 H, s, C₆H₄Me), 1.94 (15 H, s, C₅Me₅), 1.32 $(3 H, s, MeCN_2), 1.10 (6 H, d, J = 6.8 Hz, NCHMeMe), 1.07 (6 H, d, J = 6.8 Hz), 1.07 (6 H, d, J = 6$ d, J = 6.8 Hz, NCHMeMe). ¹³C–{¹H} NMR data (benzene-d₆, 125.7 MHz, 298 K) δ : 169.5 (MeCN₂), 154.4 ({O(CO)}₂N), 139.2 (i-4-C₆H₄Me), 136.3 (p-4-C₆H₄Me), 130.9 (C₅Me₅), 129.4 (o-4-C₆H₄Me), 129.3 (o-4-C₆H₄Me), 128.3 (m-4-C₆H₄Me), 50.5 (NCHMeMe), 24.0 (NCHMeMe), 23.8 (NCHMeMe), 21.0 (C₆H₄Me), 13.2 (MeCN₂), 12.7 (C₅Me₅). IR data (KBr plates, Nujol mull): 2955 (s), 1698 (m), 1656 (m), 1265 (m), 1206 (w), 1154 (m), 1124 (w), 1005 (m), 784 (w), 723 (w), 610 (w), 526 (w) cm⁻¹. Anal. found (calcd for $C_{27}H_{39}N_3O_4Ti$): C 63.0 (62.7); H 7.9 (7.6); N 7.9 (8.1)%.

 $Ti(\eta-C_5Me_5)\{N(-4-C_6H_4CF_3)C(O)O\}\{MeC(N^iPr)_2\}$ (24). 153 mg (0.31 mmol) Ti(η -C₅Me₅)(N-4-C₆H₄CF₃){MeC(NⁱPr)₂} (9) was dissolved in ca. 10 mL benzene to give a dark green solution. The headspace was evacuated, and the solution exposed to CO₂ at a pressure of 1 atm, resulting in an immediate colour change to red. After 25 s, all volatiles were removed under reduced pressure to afford 24 as a brown solid. Yield: 110 mg (67%). ¹H NMR data (benzene-d₆, 500.0 MHz, 298 K) δ: 7.47 $(2 \text{ H}, \text{ d}, J = 8.5 \text{ Hz}, m-4-C_6H_4CF_3), 7.43 (2 \text{ H}, \text{ d}, J = 8.8 \text{ Hz},$ $o-4-C_6H_4CF_3$), 3.57 (1 H, m, J = 6.6 Hz, NCH_aMeMe), 3.22 (1 H, m, J = 6.6 Hz, NCH_bMeMe), 1.85 (15 H, s, C₅Me₅), 1.29 $(3 \text{ H}, \text{ s}, MeCN_2), 1.04 (3 \text{ H}, \text{d}, \text{J} = 6.6 \text{ Hz}, \text{NCH}_{b}MeMe), 1.01$ $(3 \text{ H}, d, J = 6.6 \text{ Hz}, \text{NCH}_{b}\text{MeMe}), 0.98 (3 \text{ H}, d, J = 6.6 \text{ Hz})$ NCH_aMeMe), 0.44 (3 H, d, J = 6.6 Hz, NCH_aMeMe). ¹⁹F NMR data (benzene-d₆, 282.4 MHz, 298 K): -61.33 (CF₃). ¹³C-{¹H} NMR data (benzene-d₆, 125.7 MHz, 298 K) δ: 169.6 (MeCN₂), 151.3 (OCO), 130.4 (i-/p- 4-C₆H₄CF₃), 128.5 (C₅Me₅), 125.8 $(o-4-C_6H_4CF_3)$, 121.5 $(m-4-C_6H_4CF_3)$, 50.9 (NCH_bMeMe) , 49.8 (NCH_aMeMe), 24.3 (NCH_aMeMe), 24.2 (NCH_bMeMe), 23.7 (NCH_aMeMe), 15.8 (MeCN₂), 13.0 (C_5Me_5). IR data (KBr plates, Nujol mull): 2727 (w), 1655 (m), 1603 (m), 1499 (m), 1322 (s), 1208 (m), 1160 (m), 1108 (m), 1066 (s), 1012 (m), 914 (w), 890 (w), 846 (w), 789 (w), 723 (w), 678 (w), 663 (w), 644 (w), 632 (w), 580 (w), 508 (w), 469 (w) cm⁻¹. Anal. found (calcd for C₂₆H₃₆F₃N₃O₂Ti): C 59.5 (59.2); H 7.0 (6.9); N 7.7 (8.0)%.

 $Ti(\eta-C_{5}Me_{5})\{N(-4-C_{6}H_{4}NMe_{2})C(O)O\}\{MeC(N^{i}Pr)_{2}\}$ (25). 111 mg (0.24 mmol) Ti(η -C_{5}Me_{5})(N-4-C_{6}H_{4}NMe_{2})\{MeC(N^{i}Pr)_{2}\} (10) was dissolved in ca. 10 mL benzene to give a green solution. The headspace was evacuated, and the solution exposed to CO_2 at a pressure of 1 atm, resulting in an immediate colour change to cherry red. After 20 s, all volatiles were removed under reduced pressure to afford 25 as a dark red solid which was triturated with ca. 5 mL pentane and dried in vacuo. Yield: 60 mg (50%). ¹H NMR data (benzene-d₆, 500.0 MHz, 298 K) δ : 7.31 (2 H, d, J = 9.0 Hz, m-4-C₆H₄NMe₂), 6.66 (2 H, d, J = 9.0 Hz, o-4-C₆H₄NMe₂) 3.62 (1 H, m, br, NCH₄MeMe), 3.27 (1 H, m, br, NCH_bMeMe), 2.54 (6 H, s, NMe₂), 1.98 (15 H, s, C₅Me₅), 1.40 (3 H, s, MeCN₂), 1.15 (3 H, d, br, NCH_bMeMe), 1.11 (3 H, d, br, NCH_bMeMe), 0.98 (3 H, d, br, NCH_aMeMe), 0.73 (3 H, d, br, NCH_aMeMe). ${}^{13}C-{}^{1}H$ NMR data (benzene-d₆, 75.5 MHz, 298 K) d: 169.8 (MeCN₂), 158.2 (OCO), 146.9 (*i*-4-C₆H₄NMe₂), 139.8 (p-4-C₆H₄NMe₂), 130.0 (o-4-C₆H₄NMe₂), 129.0 (C₅Me₅), 123.8 (m-4-C₆H₄NMe₂), 50.8 (NCH_bMeMe), 49.8 (NCH_aMeMe), 41.3 (NMe2), 24.6 (NCHaMeMe), 24.5 (NCHaMeMe), 24.3 $(NCH_{b}MeMe)$, 15.0 $(MeCN_{2})$, 13.1 $(C_{5}Me_{5})$. IR data (KBr plates, Nujol mull): 2726 (w), 2671 (w), 1656 (m), 1603 (m), 1511 (s), 1341 (s), 1309 (s), 1261 (m), 1206 (m), 1162 (m), 1129 (m), 1065 (w), 1022 (w), 947 (m), 908 (w), 817 (m), 789 (w), 723 (m), 596 (w), 533 (w), 464 (w), 404 (w) cm⁻¹. Anal. found (calcd for C₂₇H₄₂N₄O₂Ti): C 64.2 (64.5); H 8.3 (8.4); N 10.7 (11.2)%.

 $Ti(\eta-C_5Me_5){OC(O)N(-4-C_6H_4CF_3)C(O)O}{MeC(N'Pr)_2}$ (26). 117 mg (0.24 mmol) $Ti(\eta-C_5Me_5)(N-4-C_6H_4CF_3)$ - ${MeC(N^{i}Pr)_{2}}$ (9) was dissolved in *ca*. 5 mL benzene to give a dark green solution. The headspace was evacuated, and the solution exposed to CO_2 at a pressure of 1 atm for a period of 4 h. All volatiles were removed under reduced pressure to afford 26 as an oily brown solid. Yield: 85 mg (62%). ¹H NMR data (benzene-d₆, 500.0 MHz, 298 K) δ : 7.40 (2 H, d, J = 8.5 Hz, $o-4-C_6H_4CF_3$), 7.34 (2 H, d, J = 8.5 Hz, $m-4-C_6H_4CF_3$), 3.41 (2 H, apparent sept, J = 6.5 Hz, NCHMeMe), 1.92 (15 H, s, C_5Me_5), 1.31 (3 H, s, MeCN₂), 1.08 (6 H, d, J = 6.5 Hz, NCH*Me*Me), 1.05 (6 H, d, J = 6.5 Hz, NCHMe*Me*). ¹⁹F NMR data (benzene-d₆, 282.4 MHz, 298 K) δ : -62.40 (CF₃). ¹³C-{¹H} NMR data (benzene- d_6 , 125.7 MHz, 298 K) δ : 169.5 (MeCN₂), 153.8 ($\{O(CO)\}_2N$), 144.7 (*i*-4-C₆H₄CF₃), 131.5 (C_5Me_5), 130.1 (o-4-C₆H₄CF₃), 125.8 (m-4-C₆H₄CF₃), 50.6 (NCHMeMe), 24.0 (NCHMeMe), 23.7 (NCHMeMe), 14.1 (MeCN₂), 12.7 (C₅Me₅), CF₃, p-4-C₆H₄CF₃ resonances not observed. IR data (CsBr plates, Nujol mull): 2955 (s), 2728 (w), 1704 (s), 1658 (s), 1642 (s), 1632 (s), 1604 (s), 1548 (m), 1513 (m), 1494 (s), 1411 (s), 1323 (s), 1261 (s), 1208 (m), 1159 (s), 1107 (s), 1067 (s), 1007 (m), 918 (w), 890 (w), 846 (w), 795 (m), 723 (w), 677 (w), 663 (w), 633 (w), 595 (w), 534 (w), 454 (w), 409 (w) cm⁻¹. Anal. found (calcd for $C_{27}H_{36}F_{3}N_{3}O_{4}Ti \cdot 0.20(C_{6}H_{6}))$: C 57.6 (57.7); H 6.6 (6.4); N 7.0 (7.2)%.

Ti(η-C₅Me₅){**OC**(**O**)N(-4-C₆H₄NMe₂)**C**(**O**)**O**}{**MeC**(NⁱPr)₂} (27). 110 mg (0.24 mmol) Ti(η-C₅Me₅)(N-4-C₆H₄NMe₂)-{MeC(NⁱPr)₂} (10) was dissolved in *ca*. 5 mL benzene to give a green solution. The headspace was evacuated, and the solution exposed to CO₂ at a pressure of 1 atm for a period of 4 h. All volatiles were then removed under reduced pressure to give a dark red solid. Trituration with *ca*. 2 mL pentane afforded the product as a very fine red-brown powder. Yield: 71 mg (54%). ¹H NMR data (benzene-d₆, 500.0 MHz, 298 K) δ: 7.43 (2 H, d, *J* = 8.9 Hz *o*-4-C₆H₄NMe₂), 6.62 (2 H, d, *J* = 8.9 Hz, $m-4-C_6H_4NMe_2$), 3.43 (2 H, apparent sept, J = 6.8 Hz, NCHMeMe), 2.44 (6 H, s, NMe₂), 1.97 (15 H, s, C₅Me₅), 1.32 (3 H, s, MeCN₂), 1.11 (6 H, d, J = 6.8 Hz, NCHMeMe), 1.08 (6 H, d, J = 6.8 Hz, NCHMeMe). ¹³C-{¹H} NMR data (benzene-d₆, 125.7 MHz, 298 K) δ : 154.8 ({O(CO)}₂N), 131.1 (*i*-4-C₆H₄NMe₂), 130.7 $(p-4-C_6H_4NMe_2)$, 129.8 $(o-4-C_6H_4NMe_2)$, 124.7 (C_5Me_5) , 113.0 (m-4-C₆H₄NMe₂), 50.5 (NCHMeMe), 40.4 (NMe₂), 24.1 (NCHMeMe), 23.9 (NCHMeMe), 14.1 (MeCN₂), 12.7 (C₅Me₅), MeCN₂ resonance not observed. IR data (KBr plates, Nujol mull): 2727 (w), 1774 (w), 1698 (s), 1653 (s), 1614 (m), 1558 (w), 1521 (m), 1263 (m), 1212 (m), 1183 (m), 1157 (m), 1129 (m), 1067 (m), 1025 (w), 998 (m), 947 (w), 918 (w), 820 (m), 790 (s), 751 (w), 723 (m), 676 (w), 596 (m), 533 (m), 454 (m) cm⁻¹. Anal. found (calcd for C₂₈H₄₂N₄O₄Ti): C 62.0 (61.5); H 7.8 (7.8); N 10.7 (10.3)%. Mass spec. (E.I.): $m/z = 546 \text{ [M]}^+$. Accurate mass E.I. mass spectrum found (calcd for C₂₈H₄₂N₄O₄Ti): 546.2689 (546.2686).

 $Ti(\eta-C_5Me_5){N('Bu)C(O)O}{PhC(NSiMe_3)_2}$ (28). 184 mg (0.36 mmol) $Ti(\eta-C_5Me_5)(N'Bu)\{PhC(NSiMe_3)_2\}$ (3) was dissolved in ca. 5 mL benzene, the headspace evacuated, and the solution exposed to CO_2 at a pressure of 1 atm for 20 min. The volatiles were then removed under reduced pressure to afford 28 as a red powder. Yield: 189 mg (95%). ¹H NMR data (benzene-d₆, 500.0 MHz, 298 K) δ: 7.00–7.03 (1 H, m, *p*-C₆H₅), 6.95–6.99 (2 H, m, o-C₆H₅), 6.84-6.91 (2 H, m, m-C₆H₅), 1.99 (15 H, s, C₅Me₅), 1.49 (9 H, s, N^tBu), 0.03 (9 H, s, SiMe₃ (NOE ^tBu)), -0.10 (9 H, s, SiMe₃). ${}^{13}C-{}^{1}H$ NMR data (benzene-d₆, 125.7 MHz, 298 K) δ : 180.5 (OC(O)), 159.4 (CN₂), 138.0 (*i*-C₆H₅), 129.6 (C₅Me₅), $129.2, 128.7 (o-C_6H_5), 128.5, 127.7 (m-C_6H_5), 127.4 (p-C_6H_5), 57.8$ (NCMe₃), 31.5 (NCMe₃), 13.0 (C₅Me₅), 5.7 (SiMe₃), 2.4 (SiMe₃). IR data (CsBr plates, Nujol mull, cm⁻¹) 2855 (s, br), 2726 (w), 2360 (w), 1854 (w), 1839 (w), 1807 (w), 1787 (w), 1766 (w), 1739 (w), 1726 (w), 1711 (w), 1660 (s), 1592 (m), 1549 (w), 1513 (w), 1250 (m, br), 1157 (w, br), 1065 (w), 1002 (w), 988 (m), 938 (m), 920 (w), 838 (s), 798 (w), 787 (w), 767 (m, br), 721 (s), 675 (m), 596 (w), 514 (m), 465 (m), 404 (w). Anal. found (calcd for $C_{28}H_{47}N_3O_2Si_2Ti$): C 59.8 (59.9); H 8.5 (8.4), 6.4 (7.5)%.

 $Ti(\eta-C_5Me_5)\{N(^{t}Bu)C(O)O\}\{MeC(N^{t}Pr)_2\}$ (29). 127 mg (0.32 mmol) Ti(η -C₅Me₅)(N'Bu){MeC(N'Pr)₂} (4)was dissolved in ca. 10 mL pentane and cooled to -78 °C (CO₂-acetone bath). The headspace was evacuated, and the solution exposed to CO₂ at a pressure of 1 atm for 2 min, during which time the solution was removed from the cold bath. Volatiles were then immediately removed under reduced pressure to give 29 as a dark red powder. Yield: 92 mg (65%). ¹H NMR data (benzene-d₆, 500.0 MHz, 298 K) δ : 3.73 (1 H, apparent sept., J = 6.4 Hz, NCH_bMe_aMe_b), 3.47 (1 H, apparent sept., J = 6.4 Hz, NCH_aMe_aMe_b), 1.90 (15 H, s, C₅Me₅), 1.50 (3 H, s, MeCN₂), 1.39 (9 H, s, C₅Me₅), 1.15 (3 H, d, J = 6.4 Hz, NCH_bMe_aMe_b), 1.13 (3 H, d, J = $6.4 \text{ Hz}, \text{NCH}_{a}\text{Me}_{a}Me_{b}$), $1.05 (3 \text{ H}, d, J = 6.4 \text{ Hz}, \text{NCH}_{b}Me_{a}\text{Me}_{b})$, 1.04 (3 H, d, J = 6.4 Hz, $NCH_aMe_aMe_b$). ¹³C-{¹H} NMR data (benzene-d₆, 125.7 MHz, 298 K) δ: 172.4 (OC(O)), 158.8 (CN_2) , 127.7 (C_5Me_5) , 57.5 $(NCMe_3)$, 50.2 $(NCH_aMe_aMe_b)$, 48.3 (NCH_bMe_aMe_b), 30.7 (NCMe₃), 24.8 (NCH_bMe_aMe_b), 24.5 $(NCH_bMe_aMe_b)$, 23.7 $(NCH_aMe_aMe_b)$, 22.9 $(NCH_aMe_aMe_b)$, 16.7 (MeCN₂), 12.5 (C₅Me₅). IR data (KBr plates, Nujol mull, cm⁻¹) 2723 (w), 1662 (s), 1646 (s, br), 1589 (m), 1494 (m), 1355 (s), 1313 (w), 1243 (m), 1208 (m), 1174 (w), 1127 (m), 1066 (w), 1024 (w, br), 940 (m), 923 (w), 826 (w), 797 (m), 782 (w), 722

(m,br), 681 (w), 656 (w, br), 597 (w), 578 (w), 527 (w, br), 466 (s), 431 (w), 410 (m). Anal. found (calcd for $C_{23}H_{41}N_3O_2Ti$): C 62.7 (62.9) H 9.3 (9.4) N 9.1 (9.6)%. Mass spec. (E.I.) m/z 439 [M]⁺.

 $[Ti(\eta-C_5Me_5)(\mu-O){PhC(NSiMe_3)_2}]_2$ **(30).** 497 mg (0.96 mmol) $[Ti(\eta-C_5Me_5)(N'Bu){PhC(NSiMe_3)_2}]$ (3) was dissolved in 25 mL benzene, the headspace evacuated, and the solution exposed to CO₂ at 1 atm. Immediate colour change of the solution from red to cherry red occurred, followed by a further colour change to brown over ca. 2 d. After 2 d, the brown solution was removed by decantation and the remaining yellow powder was washed with pentane $(3 \times 10 \text{ mL})$. Drying under vacuum yielded the product (a mixture of cis and trans isomers) as a yellow solid. Yield: 80 mg (19%). IR data (KBr plates, Nujol mull, cm⁻¹) 2955 (s), 2720 (w), 2359 (w), 1952 (w), 1816 (w), 1771 (w), 1682 (w), 1651 (w), 1615 (w), 1575 (w), 1456 (s), 1258 (m), 1244 (m), 1162 (w), 1074 (w), 1020 (w), 1002 (m), 985 (m), 908 (m), 837 (m), 781 (m), 762 (m), 722 (m), 680 (w), 639 (m), 628 (m), 609 (m), 597 (m), 491 (m), 430 (m). Anal. found (calcd for $C_{46}H_{76}N_4O_2Si_4Ti_2): C \ 60.1 \ (59.7); \ H \ 8.6 \ (8.3); \ N \ 5.5 \ (6.1)\%.$

Trans-[Ti(η -C₅Me₅)(μ -O){MeC(NⁱPr)₂}]₂ **(31).** 250 mg (0.64 mmol) $Ti(\eta-C_5Me_5)(N^tBu)\{MeC(N^tPr)_2\}$ (4) was dissolved in ca. 5 mL benzene. The headspace was evacuated, and the solution was exposed to CO_2 at a pressure of 1 atm, resulting in an immediate colour change from red to cherry red. The solution was left standing for 72 h, after which time all volatiles were removed under reduced pressure. The residue was washed with 2×5 mL pentane, to afford 31 as a yellow powder. Yield: 152 mg (70%). ¹H NMR data (benzene-d₆, 500.0 MHz, 298 K) δ : 3.46 (2 H, apparent sept., J = 6.4 Hz, NCHMeMe), 2.01 (15 H, s, C₅Me₅), 1.61 (3 H, s, MeCN₂), 1.40 (6 H, d, J = 6.4 Hz, NCHMeMe), 1.16 (6 H, d, J = 6.4 Hz, NCHMeMe). ¹³C-{¹H} NMR data (benzene-d₆, 125.7 MHz, 298 K) δ: 170.0 (CN₂), 121.9 (C₅Me₅), 48.7 (NCHMeMe), 26.4 (NCHMeMe), 24.4 (NCHMeMe), 14.2 (C_5Me_5) , 13.2 (MeCN₂). IR data (NaCl plates, Nujol mull, cm⁻¹) 2360 (w), 2342 (w), 1652 (w), 1495 (m), 1325 (m), 1306 (m), 1261 (m), 1201 (m), 1172 (w), 1094 (m, br), 1012 (m), 809 (s), 722 (w), 637 (m), 611 (w), 557 (w), 442 (w), 423 (w). Anal. found (calcd for C₃₆H₆₄N₄O₂Ti₂): C 63.8 (63.5); H 9.3 (9.5); N 8.3 (8.2)%. Mass spec. (E.I.) m/z 340 $[1/_2M]^+$.

Trans- and *cis*-[Ti(η -C₅H₄Me)(μ -O){PhC(NSiMe₃)₂}]₂ (32 and 32a). 242 mg (0.52 mmol) $Ti(\eta-C_5H_4Me)(N'Bu)$ {PhC- $(NSiMe_3)_2$ (6) was dissolved in *ca*. 5 mL benzene, the headspace evacuated, and the solution exposed to CO₂ at a pressure of 1 atm for 1 h. Volatiles were then removed under reduced pressure to afford the product (a mixture of cis and trans isomers) as a very fine beige powder. Yield: 194 mg (91%). Full conversion to the trans isomer 32 was effected by dissolution in benzene and heating to 80 °C for 1 h. Trans-[Ti(n- C_5H_4Me)(μ -O){PhC(NSiMe_3)₂}]₂ (32). ¹H NMR data (benzened₆, 500.0 MHz, 298 K) δ: 7.31 (4 H, m, m-C₆H₅), 7.04 (6 H, m, o-, p-C₆H₅), 6.54 (4 H, virtual t, J = 2.6 Hz, C₅H₂(β)H₂(α)Me), 6.22 (4 H, virtual t, J = 2.6 Hz, $C_5H_2(\beta)H_2(\alpha)Me$), 2.35 (6 H, s, C_5H_4Me), 0.12 (36 H, s, SiMe₃). ¹³C-{¹H} NMR data (benzene-d₆, 75.5 MHz, 298 K) δ: 177.9 (CN₂), 140.9 (i- $C_6H_5CN_2$, 128.5 (*o*- $C_6H_5CN_2$), 126.9 (*m*- $C_6H_5CN_2$), 126.5 (*p*- $C_6H_5CN_2$), 114.0 ($C_2(\beta)C_2(\alpha)CMe$), 112.5 ($C_2(\beta)C_2(\alpha)CMe$), 16.1 $(C_2(\beta)C_2(\alpha)CMe)$, 2.5 SiMe₃. Resonance from $C_2(\beta)C_2(\alpha)CMe$ not observed. Cis-[Ti(η -C₅H₄Me)(μ -O){PhC(NSiMe₃)₂}]₂ (32a) ¹H NMR data (benzene-d₆, 500.0 MHz, 298 K) δ: 7.46 (4 H, d, J = 7.8 Hz, $m-C_6H_5$), 7.04 (6 H, m, o-, $p-C_6H_5$), 6.46 (4 H, virtual t, J = 2.6 Hz, $C_5 H_2(\beta) H_2(\alpha) Me$), 6.12 (4 H, virtual t, J =2.6 Hz, C₅H₂(β)H₂(α)Me), 2.30 (6 H, s, C₅H₄Me), 0.08 (36 H, s, SiMe₃). ¹³C–{¹H} NMR data (benzene-d₆, 75.5 MHz, 298 K) δ : 177.1 (CN₂), 141.4 (*i*-C₆H₅CN₂), 128.5 (*o*-C₆H₅CN₂), 126.7 (*m*- $C_6H_5CN_2$, 126.4 (*p*- $C_6H_5CN_2$), 113.7 (*C*₂(β)C₂(α)CMe), 112.3 $(C_2(\beta)C_2(\alpha)CMe)$, 15.3 $(C_2(\beta)C_2(\alpha)CMe)$, 2.2 (SiMe₃). Resonance from $C_2(\beta)C_2(\alpha)CMe$ not observed. IR data on isomeric mixture (KBr plates, Nujol mull, cm⁻¹) 2726 (w), 2671 (w), 2094 (w), 1733 (w), 1576 (w), 1500 (m), 1305 (m, br), 1260 (m), 1246 (m), 1175 (w), 1074 (w), 1055 (w), 1038 (w), 1002 (m), 990 (m), 938 (w), 918 (w), 890 (w), 840 (s), 795 (m), 784 (w), 760 (m), 740 (w), 723 (s), 700 (w), 677 (m), 634 (w), 616 (w), 591 (m, br), 503 (s), 433 (w). Anal. found (calcd for C₃₈H₆₀N₄O₂Si₄Ti₂): C 56.0 (56.1), H 7.3 (7.4), N 6.7 (6.9). Anal. found (calcd for C₃₈H₆₀N₄O₂Si₄Ti₂): C 56.0 (56.1), H 7.3 (7.4), N 6.7 (6.9)%.

NMR tube scale synthesis of Ti(η-C₅H₄Me){N('Bu)-C(O)O}{PhC(NSiMe₃)₂} (33). 55.9 mg (0.12 mmol) Ti(η-C₅H₄Me)(N'Bu){PhC(NSiMe₃)₂} (5) was dissolved in 0.6 mL benzene-d₆, and freeze-pump-thawed three times. The solution was then exposed to CO₂ at a pressure of *ca*. 0.5 atm, resulting in an immediate colour change to cherry red. The product **33** formed quantitatively and characterized by ¹H NMR spectroscopy. ¹H NMR data (benzene-d₆, 500.0 MHz, 298 K) δ: 6.95 (1 H, d, J = 7.3 Hz, $CH(\beta_1)CH(\beta_2)C_2H_2(\alpha)CMe)$, 6.92 (3 H, m, *o*-, *p*-C₆H₅), 6.80 (1 H, d, J = 7.3 Hz, $CH(\beta_1)CH(\beta_2)C_2H_2(\alpha)CMe)$, 6.15 (1 H, d, J = 2.4 Hz, $C_2H_2(\beta)CH(\alpha_1)CH(\alpha_2)CMe)$, 6.01 (1 H, d, J = 2.4 Hz, $C_2H_2(\beta)CH(\alpha_1)CH(\alpha_2)CMe)$, 2.19 (3 H, s, C_5H_4Me), 1.42 (9 H, s, N'Bu), -0.04 (9 H, s, SiMe₃), -0.08 (9 H, s, SiMe₃).

Trans- and *cis*- $[Ti(\eta-C_5H_4Me)(\mu-O){MeC(N'Pr)_2}]_2$ (34 & 34a). 250 mg (0.74 mmol) [Ti(η -C₅H₄Me)(N^tBu){MeC(N^tPr)₂} (6) was dissolved in 25 mL benzene, the headspace evacuated, and the solution exposed to CO₂ at 1 atm. Immediate colour change of the solution from red to cherry red occurred, followed by a further colour change to brown over ca. 2 min. After 16 h, all volatiles were removed under reduced pressure, and the residue triturated with ca. 10 mL pentane. The product (a mixture of cis and trans isomers) was afforded as a light brown solid. Yield: 121 mg (58%). Trans-[Ti(η-C₅H₄Me)(μ-O){MeC(N^{*i*}Pr)₂}]₂ (34). ¹H NMR data (benzene-d₆, 500.0 MHz, 298 K) δ : 6.33 (4 H, virtual t, J = 2.7 Hz, $C_5 H_2(\beta) H_2(\alpha) Me$), 6.09 (4 H, virtual t, J = 2.7 Hz, $C_5H_2(\beta)H_2(\alpha)Me$), 3.47 (4 H, virtual sept, J = 6.4 Hz, NCHMeMe), 2.18 (6 H, s, C₅H₂(β)H₂(α)Me), 1.52 (6 H, s, MeCN₂), 1.27 (12 H, d, J = 6.4 Hz, NCHMeMe), 1.13 (12 H, d, J = 6.4 Hz, NCHMeMe). ${}^{13}C-{}^{1}H$ NMR data (benzene-d₆, 75.5 MHz, 298 K) δ : 167.9 (MeCN₂), 126.2 (C₂(β)C₂(α)CMe), 112.7 $(C2(\beta)C_2(\alpha)CMe)$, 112.1 $(C_2(\beta)C_2(\alpha)CMe)$, 48.4 (NCHMeMe), 25.2 (NCHMeMe), 24.9 (NCHMeMe), 15.8 (C₂(β)C₂(α)CMe), 10.5 (MeCN₂). Cis-[Ti(η -C₅H₄Me)(μ -O){MeC(NⁱPr)₂}]₂ (34a). ¹H NMR data (benzene-d₆, 500.0 MHz, 298 K) δ : 6.44 (4 H, virtual t, J = 2.7 Hz, 2.4 Hz, $C_5 H_2(\beta) H_2(\alpha) Me$), 6.08 (4 H, virtual t, J = 2.7 Hz, 2.4 Hz, $C_5H_2(\beta)H_2(\alpha)Me$, 3.36 (4 H, virtual sept, J =6.4 Hz, NCHMeMe), 2.15 (6 H, s, C₅H₄Me), 1.45 (6 H, s, MeCN₂), 1.17 (12 H, d, J = 6.3 Hz, NCHMeMe), 1.13 (12 H, d, J = 6.3 Hz,

NCHMe*Me*). ¹³C–{¹H} NMR data (benzene-d₆, 75.5 MHz, 298 K) δ : 167.8 (MeCN₂), 126.3 (C₂(β)C₂(α)CMe), 113.1 (C₂(β)C₂(α)CMe), 111.5 (C₂(β)C₂(α)CMe), 48.1 (NCHMeMe), 25.0 (NCH*Me*Me), 23.9 (NCHMe*Me*), 15.1 (C₂(β)C₂(α)C*Me*), 10.0 (*Me*CN₂). IR data on mixture of isomers (KBr plates, Nujol mull, cm⁻¹) 2726 (w), 1652 (w), 1338 (m), 1310 (m), 1216 (m), 1173 (w), 1037 (w), 847 (w), 793 (m), 679 (w), 590 (w), 445 (w), 421 (w) cm⁻¹. Anal. found (calcd for C₂₈H₄₈N₄O₂Ti₂): C 59.5 (59.2), H 8.4 (8.5), N 9.8 (9.9)%.

Reaction of Ti(η -C₅Me₅){N(Tol)C(O)O}{MeC(NⁱPr)₂} (22) with Ti(Me₄taa)(O) (36). A solution of 22 in CD₂Cl₂ (0.6 ml) was prepared *in situ* in an NMR tube equipped with a J. Young Teflon valve from 8 (8.4 mg, 2.0 × 10⁻⁵ mol) and CO₂ (1 atm). To this was added. Ti(Me₄taa)(O) (36, 3.0 equiv, 23.7 mg, 6.0 × 10⁻⁵ mol). The ¹H NMR spectrum recorded after 30 min contained no resonances for 22 but new resonances attributed to the previously reported Ti(Me₄taa){N(Tol)C(O)O} (37) and *trans*-[Ti(η -C₅Me₅)(μ -O){MeC(NⁱPr)₂}]₂ (31).

Crystal structure determinations of Ti(n-C5Me5)(N-2,6- $C_{6}H_{3}Me_{2}$ {PhC(NSiMe_{3})₂}(14), Ti(η -C₅H₄Me){OC(O)N(-2,6- $C_6H_3Me_2C(O)O$ {PhC(NSiMe_3)₂} (21) and *trans*-[Ti(η - C_5H_4Me)(μ -O){PhC(NSiMe_3)₂}]₂ (32). Crystal data collection and processing parameters are given in Table 6. Crystals were mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150 or 175 K in a stream of cold N₂. Diffraction data were measured using either an Enraf-Nonius DIP2000 or KappaCCD diffractometer. Intensity data were processed using the DENZO package.97 The structures were solved with SIR9298 and subsequent full-matrix least-squares refinements were carried out using CRYSTALS.99 Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were placed in calculated positions. Further details of the structure solution and refinements are given in the Supporting Information (CIF data). A full listing of atomic coordinates, bond lengths and angles and displacement parameters for all the structures have been deposited at the Cambridge Crystallographic Data Centre. Details of the X-ray structures of 19 and 31 have been reported previously.70

Computational details

All calculations were performed with the Gaussian 03 set of programs¹⁰⁰ within the framework of hybrid DFT (B3PW91).^{101,102} The titanium atom was represented by the relativistic effective core potential (RECP) from the Stuttgart group (12 valence electrons) and its associated basis set,¹⁰³ augmented by an f polarization function ($\alpha = 0.869$).¹⁰⁴ The remaining atoms (C, H, N, O) were represented by a 6-31G(d,p) basis set.¹⁰⁵ Full optimizations of geometry without any constraint were performed, followed by analytical computation of the Hessian matrix to confirm the nature of the located extrema as minima or transition states. The nature of the reactants and products connected by a given transition state was checked by optimizations of the transition state vector. Calculations of TOF values were performed on the gas phase Gibbs free energies at room temperature (298.15 K).

 $\begin{array}{l} \textbf{Table 6} \quad X-Ray \ data \ collection \ and \ processing \ parameters \ for \ Ti(\eta-C_5Me_5)(N-2,6-C_6H_3Me_2)\{PhC(NSiMe_3)_2\}(\textbf{14}), \ Ti(\eta-C_5H_4Me)\{OC(O)N(-2,6-C_6H_3Me_2)C(O)O\}\{PhC(NSiMe_3)_2\}(\textbf{21}), \ and \ trans-[Ti(\eta-C_5H_4Me)(\mu-O)\{PhC(NSiMe_3)_2\}_2(\textbf{32})\} \\ \end{array}$

Compound	14	21	32	
Empirical formula	$C_{31}H_{47}N_3Si_2Ti$	$C_{29}H_{39}N_3O_4Si_2Ti$	$C_{50}H_{72}N_4O_2Si_4Ti_2$	
$FW/g mol^{-1}$	565.81	597.72	969.30	
T/K	150	150	150	
λ/Å	0.71073	0.71073	0.71073	
Space group	$P2_{1}/n$	$P2_1/n$	$P\overline{1}$	
a/Å	11.672(5)	10.7126(2)	10.1320(4)	
b/Å	15.361(2)	17.2231(4)	10.4210(7)	
c/Å	18.018(7)	16.6483(4)	15.3100(11)	
$\alpha /^{\circ}$	90	90	92.248(4)	
$\beta/^{\circ}$	100.92(4)	90.704	104.045(5)	
γ/°	90	90	118.207(4)	
$V/Å^3$	3172(1)	3071.5	1359.4(2)	
Reflections measured	18 449	11 752	22 600	
Data completeness (%)	88	99	89	
Unique reflections	6934	7025	5134	
R _{int}	0.04	0.05	0.02	
Z	4	4	1	
$D_{\rm calcd}/{ m Mg}~{ m m}^{-3}$	1.18	1.29	1.184	
μ/mm^{-1}	0.37	0.39	0.421	
R indices R_1 , $R_w [I > 3\sigma(I)]^a$	$R_1 = 0.0401$	$R_1 = 0.0396$	$R_1 = 0.0694$	
	$R_{\rm w} = 0.0489$	$R_{\rm w} = 0.0478$	$R_{\rm w} = 0.0432$	
GOF	1.06	0.98	1.03	
${}^{a}R_{1}\sum_{w} F_{o} - F_{c} /\sum_{w} F_{o} ; R_{w} = \sqrt{2}$	$\Sigma W(F_{o} - F_{c})^{2} / \Sigma (W F_{o} ^{2})$			

Acknowledgements

We thank the EPSRC and the CNRS for support, Dr N H Rees for assistance with the VT NMR analysis and Dr A R Cowley for help with the crystallography. E C and P M thank the Royal Society of Chemistry for International Authors Travelling Grants and the British Council for support. We acknowledge the use of the EPSRC National Service for Computational Chemistry Software and the UK Computational Chemistry Facility.

References

- 1 J. E. Hill, R. D. Profilet, P. E. Fanwick and I. P. Rothwell, Angew. Chem., Int. Ed. Engl., 1990, 29, 664.
- 2 H. W. Roesky, H. Velker, M. Witt and M. Noltemeyer, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 669.
- 3 C. C. Cummins, C. P. Schaller, G. D. Van Duyne, P. T. Wolczanski, A. W. E. Chan and R. Hoffmann, J. Am. Chem. Soc., 1991, 113, 2985.
- 4 P. L. McGrane, M. Jensen and T. Livinghouse, *J. Am. Chem. Soc.*, 1992, **114**, 5459.
- 5 N. Adams, A. R. Cowley, S. R. Dubberley, A. J. Sealey, M. E. G. Skinner and P. Mountford, *Chem. Commun.*, 2001, 2738.
- 6 N. Adams, H. R. Bigmore, T. L. Blundell, C. L. Boyd, S. R. Dubberley, A. J. Sealey, A. R. Cowley, M. E. G. Skinner and P. Mountford, *Inorg. Chem.*, 2005, 44, 2882.
- 7 T. R. Cundari, Chem. Rev., 2000, 100, 807.
- 8 A. J. Blake, A. R. Cowley, S. C. Dunn, J. C. Green, N. Hazari, N. M. Jones, A. G. Moody and P. Mountford, *Chem.–Eur. J.*, 2005, 2111.
- 9 N. Kaltsoyannis and P. Mountford, J. Chem. Soc., Dalton Trans., 1999, 781.
- 10 P. E. Collier, S. C. Dunn, P. Mountford, O. V. Shishkin and D. Swallow, J. Chem. Soc., Dalton Trans., 1995, 3743.
- 11 T. E. Hanna, I. Keresztes, E. Lobkovsky, W. H. Bernskoetter and P. J. Chirik, Organometallics, 2004, 23, 3448.
- 12 P. D. Bolton, E. Clot, A. R. Cowley and P. Mountford, *Chem. Commun.*, 2005, 3313.
- 13 P. D. Bolton, E. Clot, A. R. Cowley and P. Mountford, J. Am. Chem. Soc., 2006, 128, 15005.
- 14 N. A. H. Male, M. E. G. Skinner, S. Y. Bylikin, P. J. Wilson, P. Mountford and M. Schroder, *Inorg. Chem.*, 2000, 39, 5483.

- 15 A. J. Nielson, M. W. Glenny and C. E. F. Rickard, J. Chem. Soc., Dalton Trans., 2001, 232.
- 16 N. Adams, H. J. Arts, P. D. Bolton, D. Cowell, S. R. Dubberley, N. Friedrichs, C. M. Grant, M. Kranenburg, A. J. Sealey, B. Wang, P. J. Wilson, A. R. Cowley, P. Mountford and M. Schroder, *Chem. Commun.*, 2004, 434.
- 17 P. D. Bolton and P. Mountford, Adv. Synth. Catal., 2005, 355.
- 18 N. Adams, H. J. Arts, P. D. Bolton, D. Cowell, S. R. Dubberley, N. Friederichs, C. M. Grant, M. Kranenburg, A. J. Sealey, B. Wang, P. J. Wilson, M. A. Zuideveld, A. J. Blake, M. Schröder and P. Mountford, *Organometallics*, 2006, 25, 3888.
- 19 H. R. Bigmore, S. R. Dubberley, M. Kranenburg, S. C. Lawrence, A. J. Sealey, J. D. Selby, M. Zuideveld, A. R. Cowley and P. Mountford, *Chem. Commun.*, 2006, 436.
- 20 C. T. Owen, P. D. Bolton, A. R. Cowley and P. Mountford, Organometallics, 2007, 26, 83.
- 21 G. J. Hayday, C. Wang, N. H. Rees and P. Mountford, *Dalton Trans.*, 2008, 3301.
- 22 C. J. Carmalt, A. Newport, I. P. Parkin, A. J. Sealey and S. R. Dubberley, J. Mater. Chem., 2003, 13, 84.
- 23 C. J. Carmalt, S. R. Whaley, P. S. Lall, A. H. Cowley, R. A. Jones, B. G. McBurnett and J. G. Ekdert, J. Chem. Soc., Dalton Trans., 1998, 553.
- 24 T. S. Lewkebandara, P. H. Sheridan, M. J. Heeg, A. L. Rheingold and C. H. Winter, *Inorg. Chem.*, 1994, 33, 5879.
- 25 C. H. Winter, P. H. Sheridan, T. S. Lewkebandara, M. J. Heeg and J. W. Proscia, J. Am. Chem. Soc., 1992, 114, 1095.
- 26 P. J. McKarns, G. P. A. Yap, A. L. Rheingold and C. H. Winter, *Inorg. Chem.*, 1999, 35, 5968.
- 27 C. J. Carmalt, A. Newport, I. P. Parkin, A. J. P. White and D. J. Williams, J. Chem. Soc., Dalton Trans., 2002, 4055.
- 28 D. E. Wigley, Prog. Inorg. Chem., 1994, 42, 239.
- 29 P. Mountford, Chem. Commun., 1997, 2127 (feature article review).
- 30 L. H. Gade and P. Mountford, Coord. Chem. Rev., 2001, 216-217, 65.
- 31 N. Hazari and P. Mountford, Acc. Chem. Res., 2005, 38, 839.
- 32 A. R. Fout, U. J. Kilgore and D. J. Mindiola, *Chem.–Eur. J.*, 2007, **13**, 9428.
- 33 J. L. Bennett and P. T. Wolczanski, J. Am. Chem. Soc., 1994, 116, 2179.
- 34 A. Bashall, P. E. Collier, L. H. Gade, M. McPartlin, P. Mountford and D. J. M. Trosch, *Chem. Commun.*, 1998, 2555.
- 35 Y. Li, Y. Shi and A. L. Odom, J. Am. Chem. Soc., 2004, 126, 1794.
- 36 E. Haak, I. Bytsschkov and S. Doye, *Angew. Chem., Int. Ed.*, 1999, 38, 3389.

- 37 B. D. Ward, A. Maisse-Francois, P. Mountford and L. H. Gade, *Chem. Commun.*, 2004, 704.
- 38 N. Vujkovic, B. D. Ward, A. Maisse-Francois, H. Wadepohl, P. Mountford and L. H. Gade, *Organometallics*, 2007, 26, 5522.
- 39 N. Vujkovic, J. L. Fillol, B. D. Ward, H. Wadepohl, P. Mountford and L. H. Gade, *Organometallics*, 2008, 27, 2518.
- 40 S. M. Pugh, D. J. M. Trosch, D. J. Wilson, A. Bashall, F. G. N. Cloke, L. H. Gade, P. B. Hitchcock, M. McPartlin, J. F. Nixon and P. Mountford, *Organometallics*, 2000, **19**, 3205.
- 41 A. J. Blake, P. E. Collier, L. H. Gade, M. McPartlin, P. Mountford, M. Schubart and I. J. Scowen, *Chem. Commun.*, 1997, 1555.
- 42 A. Bashall, P. E. Collier, L. H. Gade, M. McPartlin, P. Mountford, S. M. Pugh, S. Radojevic, M. Schubart, I. J. Scowen and D. J. M. Trosch, *Organometallics*, 2000, **19**, 4784.
- 43 F. G. N. Cloke, P. B. Hitchcock, J. F. Nixon, D. J. Wilson and P. Mountford, *Chem. Commun.*, 1999, 661.
- 44 F. G. N. Cloke, P. B. Hitchcock, J. F. Nixon, D. J. Wilson, F. Tabellion, U. Fischbeck, F. Preuss, M. Regitz and L. Nyulaszi, *Chem. Commun.*, 1999, 2363.
- 45 S. M. F. Asmus and M. Regitz, Tetrahedron Lett., 2001, 42, 7543.
- 46 F. G. N. Cloke, J. C. Green, N. Hazari, P. B. Hitchcock, P. Mountford, J. F. Nixon and D. J. Wilson, *Organometallics*, 2006, 25, 3688.
- 47 A. J. Blake, J. M. McInnes, P. Mountford, G. I. Nikonov, D. Swallow and D. J. Watkin, J. Chem. Soc., Dalton Trans., 1999, 379.
- 48 S. R. Dubberley, A. Friedrich, D. A. Willman, P. Mountford and U. Radius, *Chem.-Eur. J.*, 2003, 9, 3634.
- 49 T.-G. Ong, G. P. Yap and D. S. Richeson, Chem. Commun., 2003, 2612.
- T. E. Hanna, I. Keresztes, E. Lobkovsky, W. H. Bernskoetter and P. J. Chirik, *Organometallics*, 2004, 23, 3448.
 S.-H. Hsu, C. Chang, C.-L. Lai, C.-H. Hu, H. M. Lee, G.-H. Lee,
- S.-M. Peng and J.-H. Huang, *Inorg. Chem.*, 2004, **43**, 6786.
- 52 H. Wang, H. Chan and Z. Xie, *Organometallics*, 2005, 24, 3772.
- 53 C. L. Boyd, E. Clot, A. E. Guiducci and P. Mountford, Organometallics, 2005, 24, 2347.
- 54 C. L. Boyd, T. Toupance, B. R. Tyrrell, B. D. Ward, C. R. Wilson, A. R. Cowley and P. Mountford, *Organometallics*, 2005, 24, 309.
- 55 S. C. Dunn, N. Hazari, A. R. Cowley, J. C. Green and P. Mountford, Organometallics, 2006, 25, 1755.
- 56 A. E. Guiducci, C. L. Boyd and P. Mountford, Organometallics, 2006, 26, 1167.
- 57 A. J. Blake, P. E. Collier, L. H. Gade, P. Mountford, J. Lloyd, S. M. Pugh, M. Schubart, M. E. G. Skinner and D. J. M. Trosch, *Inorg. Chem.*, 2001, 40, 870.
- 58 P. J. Stewart, A. J. Blake and P. Mountford, *Organometallics*, 1998, 17, 3271.
- 59 P. J. Stewart, A. J. Blake and P. Mountford, J. Organomet. Chem., 1998, 564, 209.
- 60 D. J. Darensbourg and R. A. Kudaroski, *Adv. Inorg. Chem.*, 1983, 22, 129.
- 61 D. A. Palmer and R. van Eldik, Chem. Rev., 1983, 83, 651.
- 62 H. Arakawa, M. Aresta, J. M. Armor, M. A. Barteau, E. J. Beckman, E. T. Bell, J. E. Bercaw, C. Creutz, E. Dinjus, D. A. Dixon, K. Domen, D. L. DuBois, J. Eckert, E. Fujita, G. H. Gibson, W. A. Goddard, D. W. Goodman, J. Keller, G. J. Kubas, H. H. Kung, J. E. Lyons, L. E. Manzer, T. J. Marks, K. Morokuma, K. M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielson, W. M. H. Sachtler, L. D. Schmidt, A. Sen, G. A. Somorjai, P. C. Stair, B. R. Stults and W. Tumas, *Chem. Rev.*, 2001, **101**, 953.
- 63 M. Torrent, M. Sola and G. Frenking, Chem. Rev., 2000, 100, 439.
- 64 W. Leitner, Coord. Chem. Rev., 1996, 153, 257.
- 65 X. Yin and J. R. Moss, Coord. Chem. Rev., 1999, 181, 27.
- 66 D. Gibson, *Chem. Rev.*, 1996, **96**, 2063. 67 R. E. Blake, D. M. Antonelli, L. M. Henling, W. P. Schaefer, K. I.
- Hardcastle and J. E. Bercaw, *Organometallics*, 1998, 17, 718.
 68 D. S. Glueck, J. Wu, F. J. Hollander and R. G. Bergman, *J. Am. Chem. Soc.*, 1991, 113, 2041.
- 69 B. D. Ward, G. Orde, E. Clot, A. H. Cowley, L. H. Gade and P. Mountford, Organometallics, 2005, 24, 2368.
- 70 A. E. Guiducci, A. R. Cowley, M. E. G. Skinner and P. Mountford, J. Chem. Soc., Dalton Trans., 2001, 1392.
- 71 A. E. Guiducci, D. Phil, Thesis, University of Oxford, 2002.
- 72 F. H. Allen and O. Kennard, *Chem. Des. Automat. News*, 1993, **8**, 1 and 31.
- 73 D. A. Fletcher, R. F. McMeeking and D. J. Parkin, J. Chem. Inf. Comput. Sci., 1996, 36, 746.

- 74 R. Gomez, R. Duchateau, A. N. Chernega, A. Meetsma, F. T. Edelmann, J. H. Teuben and M. L. H. Green, J. Chem. Soc., Dalton Trans., 1995, 217.
- 75 J. R. Babcock, C. Incarvito, A. L. Rheingold, J. C. Fettinger and L. Sita, *Organometallics*, 1999, 18, 5729.
- 76 L. A. Koterwas, J. C. Fettinger and L. Sita, *Organometallics*, 1999, 18, 4183.
- 77 W. J. van Meerendonk, K. Schroder, E. A. C. Brussee, A. Meetsma, B. Hessen and J. H. Teuben, *Eur. J. Inorg. Chem.*, 2003, 427.
- 78 M. Sotoodeh, I. Leichtweis, H. W. Roesky, M. Noltemeyer and H.-G. Schmidt, *Chem. Ber.*, 1993, **126**, 913.
- 79 P. H. M. Budzelaar, gNMR for Windows v4.1, Cherwell Scientific Ltd., Oxford, 1999.
- 80 J. Sandstrom, Dynamic NMR Spectroscopy, Academic Press, London, 1982.
- 81 R. B. Jordan, *Reaction Mechanisms of Inorganic and Organometallic Systems*, Oxford University Press, Oxford, 1998.
- 82 A. W. Holland and R. G. Bergman, J. Am. Chem. Soc., 2002, 124, 9010.
- 83 R. L. Zuckerman and R. G. Bergman, Organometallics, 2001, 20, 1792.
- 84 D. J. Darensbourg, B. J. Frost and D. L. Larkins, Inorg. Chem., 2001.
- 85 W. D. Mcghee, D. P. Riley, M. E. Christ and K. M. Christ, Organometallics, 1993, 40, 1993.
- 86 J. Fournier, C. Bruneau, P. H. Dixneuf and S. Lecolier, J. Org. Chem., 1991, 56, 4456.
- 87 W. D. Mcghee and D. P. Riley, Organometallics, 1992, 11, 900.
- 88 M. H. Chisolm and M. W. Extine, J. Am. Chem. Soc., 1977, 99, 782.
- 89 M. H. Chisolm and M. W. Extine, J. Am. Chem. Soc., 1977, 99, 792.
- 90 J. F. Hartwig, R. G. Bergman and R. A. Andersen, J. Am. Chem. Soc., 1991, 113, 6499.
- 91 S. Park, A. L. Rheingold and D. M. Roundhill, Organometallics, 1991, 10, 615.
- 92 P. Legzdins, S. J. Rettig and K. J. Ross, Organometallics, 1994, 13, 569.
- 93 M. H. Chisolm, F. A. Cotton, M. W. Extine and W. W. Reichert, J. Am. Chem. Soc., 1978, 100, 1727.
- 94 S. Kozuch and S. Shaik, J. Am. Chem. Soc., 2006, 128, 3355.
- 95 S. Kozuch and S. Shaik, J. Phys. Chem. A, 2008, 112, 6032.
- 96 R. T. Boere, R. T. Oakley and R. W. Reed, J. Organomet. Chem., 1987, 331, 161.
- 97 Z. Otwinowski and W. Minor, Processing of X-Ray Diffraction Data Collected in Oscillation Mode, Academic press, New York, 1997.
- 98 A. Altomare, G. Cascarano, J. R. Carrithers, P. W. Betteridge and R. I. Cooper, J. Appl. Crystallogr., 1994, 27, 435.
- 99 D. J. Watkin, C. K. Prout, J. R. Carruthers, P. W. Betteridge and R. I. Cooper, *CRYSTALS*, Chemical Crystallography Laboratory, Oxford, UK, 2001.
- 100 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, GAUSSIAN 03 (Revision C.02), Gaussian, Inc., Wallingford, CT, 2004.
- 101 A. D. Becke, J. Chem. Phys., 1992, 98, 5648.
- 102 J. P. Perdew and Y. Wang, Phys. Rev. B, 1992, 45, 13244.
- 103 D. Andrae, U. Haussermann, M. Dolg, H. Stoll and H. Preuss, *Theor. Chim. Acta*, 1990, **77**, 123.
- 104 A. W. Ehlers, M. Bohme, S. Dapprich, A. Gobbi, A. Hollwarth, V. Jonas, K. F. Kohler, R. Stegmann, A. Veldkamp and G. Frenking, *Chem. Phys. Lett.*, 1993, **208**, 111.
- 105 P. C. Hariharan and J. A. Pople, Theor. Chim. Acta, 1973, 28, 213.