RSCPublishing

Synthesis of ureas from titanium imido complexes using CO_2 as a C-1 reagent at ambient temperature and pressure†

James C. Anderson* and Rafael Bou Moreno
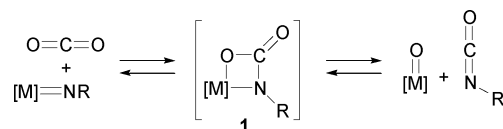
The coordinatively unsaturated 12-electron complex dichloro *t*-butylimido bispyridine titanium(IV) (**2a**) has been shown to react with CO_2 to give *N*,*N*-bis-*t*-butyl urea. Two analogous sterically hindered coordinatively saturated 14-electron complexes dichloro *t*-butylimido trispyridine titanium(IV) (**10a**) and dichloro 2,6-(*i*-Pr)$_2$phenylimido trispyridine titanium(IV) (**10b**) also gave their corresponding symmetrical ureas upon treatment with CO_2. Further experiments support the intermediary of metallocycles formed from heterocumulene metathesis reactions. The unsymmetrical urea *N*-benzyl, *N*-*t*-butyl urea (**11**) was produced from treatment of 2,6-(*i*-Pr)$_2$phenylimido trispyridine titanium(IV) (**10b**) with CO_2 and interception with $BnNH_2$. Equimolar quantities of *N*,*N*-bistrimethylsilybenzyl-amine or *N*,*N*-bistrimethylsilyphenethylamine were shown to promote the reaction between *t*-butylimido bispyridine titanium(IV) (**2a**) and CO_2 to give near quantitative yields of symmetrical urea. Other symmetrical ureas could be produced from $TiCl_4$, amine and CO_2 in moderate to quantitative yields depending on the stoichiometry of amine present.

Introduction

There is currently a search for alternatives to chemical feedstocks for the fine chemicals industry that do not rely upon oil. Carbon dioxide has emerged as a renewable candidate as it is abundant, non-toxic, non-flammable and is the waste product of many industrial processes. However, it is thermodynamically and kinetically very stable and its use as a general C-1 reagent poses significant problems.[1] Carbon dioxide is currently used industrially for the synthesis of urea, inorganic carbonates, methanol, salicylic acid, cyclic carbonates and polycarbonates. For these processes the CO_2 is always pressurised or is in the solid state.[1b,2] While there have been considerable advances in the activation and use of CO_2 as a renewable C-1 source in the copolymerisation of CO_2 and epoxides,[3] there is a need for the development of other processes that can function at ambient temperature and pressures of CO_2. The synthesis of ureas from primary and secondary amines with CO_2 at atmospheric pressure and ambient temperature still remains a challenge.[4]

We have been interested in heterocumulene synthesis through the direct combination of CO_2 as a C-1 reagent with metal imido complexes to form isocyanates (Scheme 1). The converse reaction, to generate a metal imido complex (and CO_2) from the combination of isocyanates and metal oxo complexes is a well known method for the synthesis of metal imido complexes.[5] The reactions proceed by a [2 + 2] cycloaddition to generate a titanium-

Department of Chemistry, University College London, 20 Gordon Street, London, UK, WC1H 0AJ. E-mail: j.c.anderson@ucl.ac.uk
† Electronic supplementary information (ESI) available: Experimental and full characterisation data. See DOI: 10.1039/c1ob06576a

Scheme 1 The formation of a carbamate metallocycle by [2 + 2] reactions.

carbamate metallocycle **1**. The lability of these sorts of complexes normally leads to the elimination of carbon dioxide. Examples of the forwards reaction described in Scheme 1 are rare,[6] but titanium has shown some general reactivity in this reaction.[7–9] Cycloaddition reactions of titanium imido complexes with CO_2 have been reported for a number of titanium complexes by Mountford[7] and others.[8,9] The formation of the thermodynamically stable titanium oxo complex is normally the driving force for the reaction and its isolation the focus of most studies.[6]

Mindiola and co-workers reported the formation of an iso-cyanate from the reaction between a latent low coordinate titanium imido complex and CO_2 (eqn (1)).[8] Unlike other imido systems, excess CO_2 did not lead to six-membered ring aryl imidodicarboxylates.[7e] Isocyanates are also known to react with titanium imido complexes to give carbodiimides.[7g,10] It has also been reported that certain titanium imido complexes react with carbodiimides to give symmetrical metallocyclo–guanidine complexes.[11] In this paper we report our studies between Mountford-like 12- and 14-electron titanium imido complexes with CO_2 to give ureas as a preparative reaction. Further experiments are presented that support a reaction mechanism involving the *in situ* formation of metallocycle intermediates *via* heterocumulene metathesis.

$$(1)$$
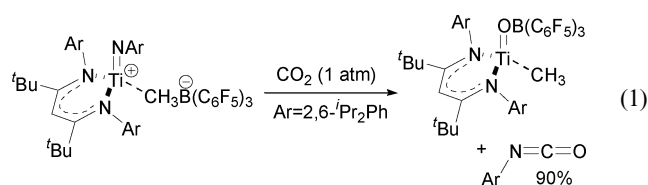
Results and Discussion

Recently we reported the synthesis of carbodiimides by a heterocumulene metathesis reaction between isocyanates and $Ti(N^tBu)Cl_2Py_2$ (**2a**),[12] which led us to explore the possible activation of CO_2 by this complex.[10b] We envisaged that reaction of **2a** with CO_2 could lead to an isocyanate like the Mindiola work (eqn (1)).[8] In the event, treatment of **2a** with 1.5 atm of CO_2 in CH_2Cl_2 at rt for 5 h followed by work up with 2 M HCl gave symmetrical urea **3a** in 8% yield after aqueous hydrolysis (eqn (2)). We inferred from this result that the central carbonyl carbon was derived from CO_2.


$$(2)$$
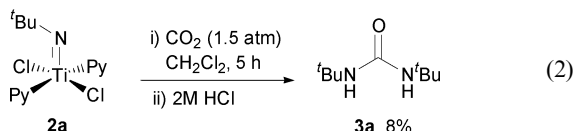
We presume the mechanism is similar to that formulated by Mindiola[8c] and which we had used to explain the formation of carbodiimides from isocyanates and $Ti(N^tBu)Cl_2Py_2$ (**2a**).[10b] Isocyanate **5** (and presumably **6**), formed from the collapse of metallo carbamate **4**, could react with **2** to form either of the two metallocycles **7** (from [2 + 2] cycloaddition across RN=C of **5**) or **8** (from [2 + 2] cycloaddition across C=O of **5**). Potentially complexes **7** and **8** could interconvert. Hydrolysis of **7** or **8** during work up would lead to symmetrical urea **3**. Alternatively, metallocycle **8** could break down to diimide **9** that could then be hydrolysed during work up to **3** (Scheme 2).
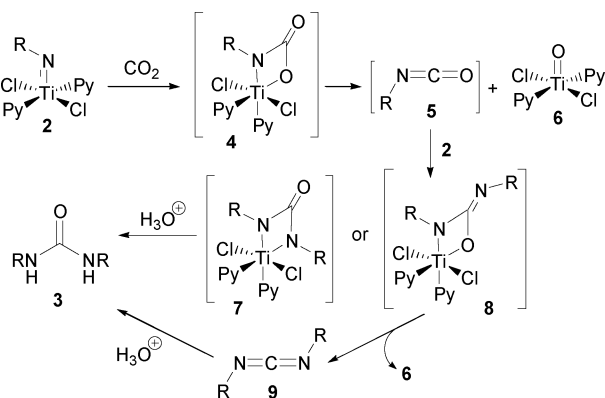
**Scheme 2** Possible mechanisms for the conversion of CO_2 to ureas.

In order to investigate whether analogous imido complexes of **2** performed this transformation we required a flexible synthesis. We found we could not purify other alkyl imido analogues of complex **2a** synthesised using the Mountford route to **2a**.[12] The use of anilines also gave no products. Attempted transimination of the 12-electron complex **2a** with alkyl amines and anilines was uniformly unsuccessful. We then investigated another method of Mountford[12] and prepared a range of coordinatively saturated 14

electron complexes **10** by transimination of *t*-butyl complex **10a** with anilines. Unfortunately, attempted transimination reactions with alkyl amines did not go to completion and we were unable to purify without degradation. Removal of the apical pyridine ligand under high vacuum had been demonstrated by Mountford for the conversion of certain sterically hindered titanium imido complexes, such as **10b** to **2b**.[12] From our work we found that the less sterically hindered imido complexes prepared by transimination did not undergo this reaction, only the sterically hindered imido complex **10a** lost a pyridine ligand under high vacuum to give complex **2a** (Scheme 3). Not surprisingly there seems to be a steric effect in this ligand loss, which for our purposes was preparatively restrictive.
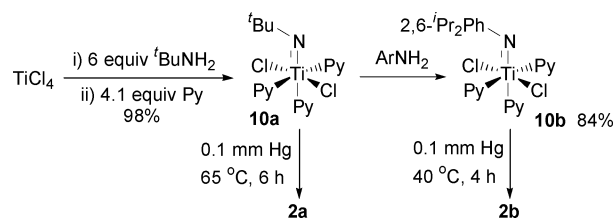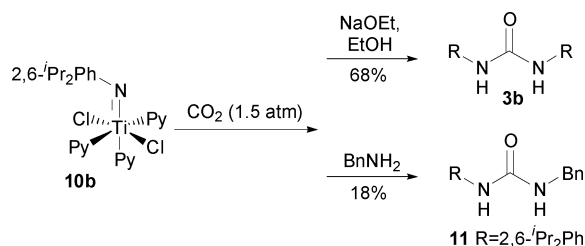

Scheme 3 The synthesis of 12-electron titanium imido complexes.

Treatment of coordinatively saturated 14 electron complexes **10** with CO_2 mostly gave no reaction except for the sterically hindered analogues **10a** and **10b** that gave symmetrical urea **3a** and **3b** in 14% and 98% unoptimised isolated yields, respectively (eqn (3)). We speculate that the reaction proceeds by the 12 electron imido complexes **2** and that loss of a pyridine ligand from **10a, b** occurs during the reaction as a consequence of steric compression from the large *t*-Bu and 2,6-(*i*-Pr)$_2$Ph groups on nitrogen. Loss of a pyridine ligand would be necessary to allow coordination of CO_2.

$$(3)$$
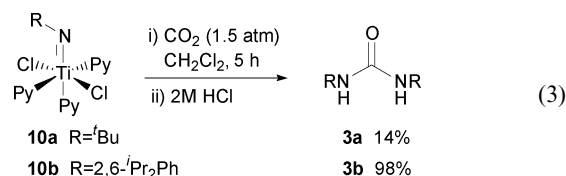
In order to try and decipher whether urea **3** was produced from hydrolysis of complexes **7** or **8**, or formed by hydrolysis of carbodimide **9** (Scheme 2) a range of nucleophiles were added to the reaction (eqn (3)). Complex **10b** was allowed to react with CO_2 as before and then treated separately with nucleophiles EtOH, H_2O and $BnNH_2$ in an attempt to intercept any intermediate before hydrolysis (Scheme 4). If these nucleophiles were to react with the imide type ligand of **7** or **8** in an acyl substitution type mechanism we would expect to isolate a carbamate, an amine


Scheme 4 Activation of CO_2 by **10b**.

This journal is © The Royal Society of Chemistry 2012

Org. Biomol. Chem., 2012, **10**, 1334–1338 | 1335

(*via* decarboxylation of carbamic acid) and an unsymmetrical urea, respectively. Reaction with EtOH led to degradation, but treatment with NaOEt led to symmetrical urea **3b** in 68% yield. Treatment with H_2O led to no reaction. The fact that no urea was observed by quenching with H_2O or EtOH suggests no carbodiimide **9** is present as these are favourable reactions. When the reaction was quenched by addition of benzylamine, unsymmetrical urea **11** was isolated in 18% yield.

Formation of the symmetrical urea **3b** from the treatment of **10b** with CO_2 and H_3O^+ work up suggests either hydrolysis of metallocycle **7** or **8** or hydrolysis of a symmetrical carbodiimide **9**. Formation of the same urea from treatment with ethoxide ion, however, suggests displacement of the imido ligand from **7** or **8** by the oxygen nucleophile (ethoxide ion). The fact that no carbamate was generated from this latter experiment suggests that any intermediate isocyanate **5** is consumed rapidly in the reaction, presumably by reaction with another molecule of imido complex **2**. The isolation of the unsymmetrical urea **11** from treatment with $BnNH_2$ suggests either the interception of a postulated metallocycle like **4**, which based on the results for the oxygen nucleophiles would seem unlikely, or more likely an acyl substitution type reaction with the analogous complexes **7** or **8**. The fact the oxygen nucleophiles react in a different manner may be a facet of titanium's oxophilicity.

Intermediate complexes **7** and **8** are identical to those postulated in our previous report for the synthesis of ureas from the reaction of complex **2a** and isocyanates.[10b] Treatment of **2a** with *tert*-butylisocyanate in an NMR experiment showed only a constant ~1 : 1 mixture of an intermediate, believed to be **7** or **8** and carbodiimide product over 16 h with no impurities [intermediate (30%) : **2a** (43%) : bis-*N*,*N*′-*t*butyl carbodiimide (23%) : **6** (3%)].[7b] Quenching an identical preparative experiment led to the isolation of symmetrical urea **3a** in 62% yield (Scheme 5).[13] When the reaction was quenched with NaOEt, **3a** was isolated in 82% yield, but when quenched with $BnNH_2$ unsymmetrical urea **12c** was isolated in 51% yield. No symmetrical urea **3a** was detected in the crude reaction mixture or isolated product of this latter reaction.
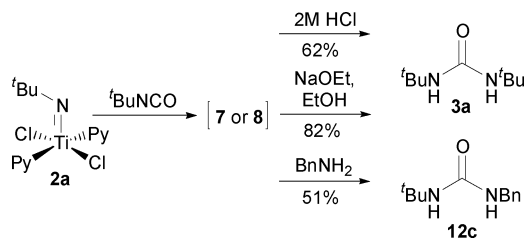
Scheme 5 The investigation of the intermediate.

The similarities in these two sets of experiments (Scheme 4 and 5) suggests a common intermediate, which we propose is either complex **7** or **8**. As supported by our previous work,[10b] the treatment of either **2a** or coordinatively saturated 14-electron complexes **10a, b** with CO_2 gave symmetrical ureas with no evidence for the formation of carbodiimide **9**.

To investigate the reaction further we decided to investigate the reaction of a mixture of complexes **10a** and **10b** with CO_2. Theoretically a mixture of 3 ureas **3a**, **3b** and **12b** could be expected (eqn (4)). In the event, treatment of 2 different mixtures of complexes **10a** and **10b** with CO_2 (1.5 atm) for 5 h at rt in CH_2Cl_2

Table 1 Evolution of eqn (4) with different ratios of **10a** and **10b**

Initial ratio 10a : 10b	16 h ratio 10a : 10b	40 h ratio 10a : 10b
20 : 80	4 : 96	0 : 100
28 : 72	12 : 88	0 : 100
52 : 48	37 : 63	26 : 74
48 : 52	40 : 60	29 : 71
60 : 40	50 : 50	43 : 57
77 : 23	70 : 30	64 : 36

Experiments were conducted in C_6D_6.

followed by workup with 2 M HCl led only to the unsymmetrical urea **12b**.

$$\text{(4)}$$

| 10a : 10b	
30 : 70	36%
36 : 64	21%
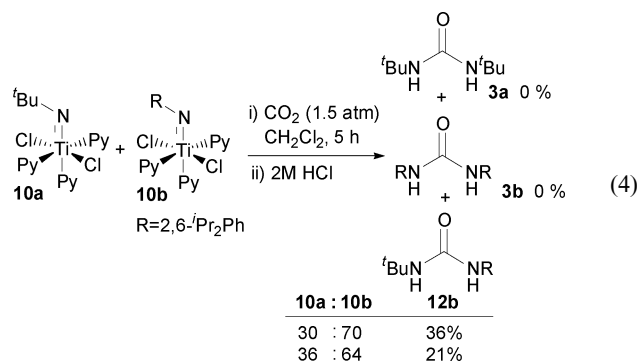
The formation of only **12b** suggests that one of the complexes reacts faster with CO_2 than the other. The isocyanate formed then reacts with the other complex to form a mixed urea after hydrolysis. In order to assess this a series of NMR experiments were conducted with varying ratios of complexes **10a** and **10b** (Table 1).

In all cases the proportion of complex **10b** increases with time. These results suggest that the *t*-butyl compex **10a** reacts quicker than **10b** with CO_2, presumably to produce *t*-butylisocyanate. Attempted isolation of the putative titanium oxo complex was never achieved in this or any other experiments and could be due to the propensity of Ti═O bonds to oligomerise.[6–9] Complex **10b** then reacts with the *t*-butylisocyanate, in preference to CO_2, to give complex **7** or **8** and upon hydrolysis **12b**. From experiments above (eqn (3) and Scheme 5) we also think the reaction between **10a** and *t*BuNCO is slow (*vide infra*).[13] In support of these conclusions, treatment of complex **10b** with CO_2 in an NMR tube (C_6D_6, rt, 16 h) led to the formation of only ~10% of 2,6-di-isopropylphenylisocyanate, indicating this is a slow reaction. Also treatment of **10b** with *t*-butylisocyanate in CH_2Cl_2 for 48 h at rt followed by quenching with dilute acid led to **12b** in 29% yield. Treatment of **10a** with 2,6-di-isopropylphenylisocyanate produced no urea after prolonged stirring. These control experiments were consistent with the proposed order of events.

The attempted synthesis of non aromatic 12- and 14-electron titanium imido complexes *via* transimination (Scheme 3) had proved unsuccessful. The reactions most often did not go to completion and we were unable to separate the new imido complexes without degradation. Due to these difficulties in purification we submitted some crude reaction mixtures to reaction with CO_2 (eqn (5)).

1336 | *Org. Biomol. Chem.*, 2012, **10**, 1334–1338

This journal is © The Royal Society of Chemistry 2012

$$(5)$$
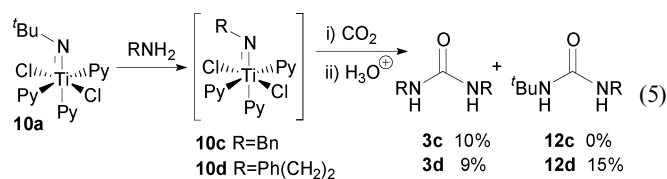
The yields were low and gave mixtures of ureas due to the mixtures of complexes present. Another known method of performing the desired transimination to form new complexes is to use bis-silylated amines.[14] Treatment of **10a** with either of two bistrimethylsilylamines (1 equivalent) and addition of CO_2 *in situ* generated symmetrical urea **3a** in almost quantitative yield (eqn (6)). Clearly no transimination took place, but the silylated amines are promoting the reaction in some way (compare with eqn (3)). Their exact role in this reaction remains unknown. A tertiary amine Et_3N (1 equivalent) was also found to activate the reaction, but less efficiently with a reduced yield of 37%.

$$(6)$$
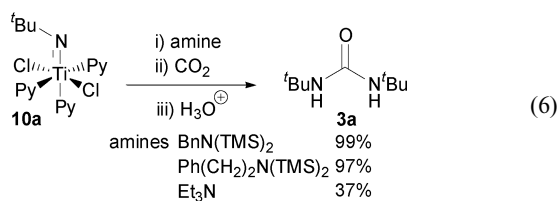
Another conceivable route to non-aromatic imido–titanium complexes is their generation from $TiCl_4$ and amines, similar to the method used by Mountford[12] and which we used to synthesize the *t*-butyl imido complex **2a**. This route gave us the desired complexes, but the formation of byproducts of similar solubility made their purification difficult. The crude complexes were thus treated with CO_2 *in situ* to give moderate yields of the symmetrical ureas (eqn (7) and Table 2). Three equivalents of amine were initially added as we believed at least two equivalents would be needed to sequester HCl. We postulate that a 12- or 14-electron titanium complex is formed followed by heterocumulene metathesis to form isocyanate. Heterocumulene metathesis between the formed isocyanate and another equivalent of complex would give a metallocycle intermediate (**7** or **8**) that upon hydrolysis gives symmetrical urea **3**. This mechanism requires 2 equivalents of $TiCl_4$ to form one equivalent of urea.
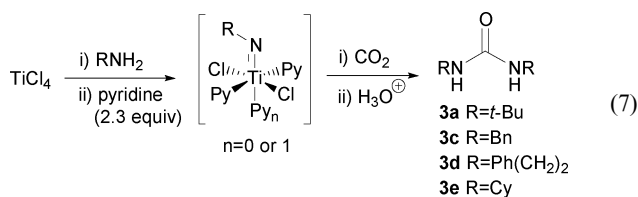

$$(7)$$

Using one equivalent of amine gave yields roughly one third of that when using 3 equivalents. Excess amine (6 equivalents) seemed to be deleterious to the reaction. Theoretically, excess amine could intercept the isocyanate and effectively 1 equivalent of $TiCl_4$ would only be needed. We found that a large excess of amine (300 equiv) and pyridine (230 equiv) gave near quantitative yields of symmetrical urea **3** based upon 1 equivalent of $TiCl_4$. Control experiments where the reactions were repeated in the absence of $TiCl_4$ led to no reaction.

If the mechanism for the formation of the urea is as we hypothesised (Scheme 3), then there exists an opportunity to try and encourage turnover of the titanium oxide byproduct to react with amine and form an imido complex and thus make the process catalytic in Ti. Preliminary experiments to activate the presumed Ti=O bond by the addition of varying amounts of TMSCl were unsuccessful, giving only stoichiometric quantitative yield as observed above (eqn (7)). Other Lewis acids, such as $Mg(OTf)_2$, Bu_3BOTf, Bu_3SnCl and $B(C_6F_5)_3$, were also tested under the same reaction conditions, but they inhibited the reaction and no urea or other identifiable organic adduct was formed.

Conclusions

Our initial observation that the 12-electron complex $Ti(N^tBu)Cl_2Py_2$ (**2a**) gave symmetrical urea **3a** upon treatment with CO_2 (eqn (2)) led us to investigate this reaction further. We found that only two sterically hindered 14-electron imido complexes $Ti(N^tBu)Cl_2Py_3$ (**10a**) and $Ti(NPh(2,6-^iPr)_2)Cl_2Py_3$ (**10b**) underwent the same reaction (Equation 3). As these were also the only two complexes that we could form the analogous 12-electron complexes **2a, b** by removal of a pyridine ligand under vacuum (Scheme 3), we propose that this particular cumulene metathesis reaction with CO_2 requires a coordinatively unsaturated 12-electron complex. Further studies with $Ti(NPh(2,6-^iPr)_2)Cl_2Py_3$ (**10b**) that tried to intercept reaction intermediates after treatment with CO_2 by the addition of H_2O or EtOH gave no identifiable products. Treatment instead with NaOEt led to symmetrical urea and addition of $BnNH_2$ led to the unsymmetrical urea (Scheme 4). The formation of symmetrical urea from treatment with CO_2 and acid workup suggests hydrolysis of the corresponding carbodiimide **9** or hydrolysis of an intermediate complex **7** or **8**, of which the existence of the latter is supported by some NMR data from our previous work.[7b] Formation of symmetrical urea from treatment with NaOEt and unsymmetrical urea from treatment with $BnNH_2$ are both consistent with displacement of the urea like ligand from **7/8** by ethoxide ion and an acyl substitution type mechanism by the amine at the central urea carbon of the bidentate ligand in **7/8**. No products derived from direct reaction with isocyanate

Table 2 Synthesis of ureas with CO_2[a]

3	R	Yield urea% 3 equiv RNH_2	Yield urea% 1 equiv RNH_2	Yield urea% 6 equiv RNH_2	Yield urea[b]% 300 equiv RNH_2
a	*t*-Bu	7	2	26	99
c	Bn	48	16	34	99
d	$Ph(CH_2)_2$	56	17	42	99
e	Cy	36	14	19	99

[a] Isolated yields. [b] 230 equiv of pyridine used.

5 were detected. We generated the same intermediate **7/8** from our previous work by the treatment of Ti(N^{t}Bu)Cl$_2$Py$_2$ (**2a**) with t-BuNCO and treated this mixture with aqueous acid, ethoxide ion and BnNH$_2$ to repeat the results above (Scheme 5). This is strong evidence for the pathway of this reaction proceeding through intermediate **7** or **8** or some equilibrating mixture of the two. NMR experiments showed the t-Bu imido 14-electron complexes **10a** to be more reactive towards CO$_2$ than the analagous 2,6-(i-Pr)$_2$Ph complex **10b** (Table 1). The formation of symmetrical urea from **2a** upon treatment with CO$_2$ could be made nearly quantitative by the addition of bis-silylated amines (eqn (6)). The exact role of the silylated amines is unknown at present, but could be due to some Lewis acid effect by the silicon groups and we are investigating this further. This could represent a very efficient synthetic method for preparing ureas from an easy to make complex and CO$_2$. However, at present the generality of this process was restricted by our inability to prepare pure alkyl (aside from t-Bu) analogues of the complexes **2** and **10**. Using an *in situ* preparation from TiCl$_4$ and amines we were able to isolate symmetrical ureas of alkyl amines (eqn (7), Table 2). Interestingly the yields were moderate with an optimised 3 equivalents, but near quantitative with a vast excess of amine. This again is a curious result we are investigating further. Initial attempts to make the process catalytic in titanium by converting the presumed titanium oxo complex back to an imido complex have proven unsuccessful, but is the subject of our current and future endeavours.

Acknowledgements

Notes and references

1 (a) H. Arakawa, M. Aresta, J. N. Armour, M. A. Barteau, E. J. Beckman, A. T. Bell, J. E. Bercaw, C. Creutz, E. Dinjus, D. A. Dixon, K. Domen, D. L. DuBois, C. A. Eckert, E. Fujita, D. 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; (b) M. Aresta and A. Dibenedetto, *Dalton Trans.*, 2007, 2975; (c) T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365; (d) *Carbon Dioxide as Chemical Feedstock*, ed. M. Aresta, Wiley-VCH, Weinheim, 2010.
2 N. MacDowell, N. Florin, A. Buchard, J. Hallett, A. Galindo, G. Jackson, C. S. Adjiman, C. K. Williams, N. Shah and P. Fennell, *Energy Environ. Sci.*, 2010, **3**, 1645.
3 (a) M. R. Kember, A. Buchard and C. K. Williams, *Chem. Commun.*, 2011, **47**, 141; (b) D. J. Darensbourg, *Chem. Rev.*, 2007, **107**, 2388; (c) G. W. Coates and D. R. Moore, *Angew. Chem., Int. Ed.*, 2004, **43**, 6618; (d) H. Sugimoto and S. Inoue, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 5561; (e) K. Nozaki, *Pure Appl. Chem.*, 2004, **76**, 541; (f) C. Koning, J. Wildeson, R. Parton, B. Plum, P. Steemna and D. J. Darensbourg, *Polymer*, 2001, **42**, 3995.
4 (a) N. Yamazaki, F. Higashi and T. Iguchi, *Tetrahedron Lett.*, 1974, **13**, 1191; (b) A. Lorenzo, E. Aller and P. Molina, *Tetrahedron*, 2009, **65**, 1397; (c) R. Nomura, M. Yamamoto and H. Matsuda, *Ind. Eng. Chem. Res.*, 1987, **26**, 1056.
5 (a) D. C. Bradley, M. B. Hursthouse, K. M. A. Malik, A. J. Nielson and R. L. Shirt, *J. Chem. Soc., Dalton Trans.*, 1983, 2651; (b) L. K. Johnson, S. C. Virgil and R. H. Grubbs, *J. Am. Chem. Soc.*, 1990, **112**, 5384; (c) A. Antiñolo, S. Garcí-Lledó, J. M. Ilarduya and A. Otero, *J. Organomet. Chem.*, 1987, **335**, 85; (d) W. A. Hermann, G. Welchselbaumer, R. A. Paciello, R. A. Fischer, E. Herdtweck, J. Okuda and D. W. Marz, *Organometallics*, 1990, **9**, 489; (e) D. D. Devore, J. D. Lichtenhan, F. Takusagawa and E. A. Maata, *J. Am. Chem. Soc.*, 1987, **109**, 7408; (f) A. J. Nielson, M. W. Glenny, C. E. F. Rickard and J. M. Waters, *J. Chem. Soc., Dalton Trans.*, 2000, 4569; (g) W. B. Cross, J. C. Anderson, C. Wilson and A. J. Blake, *Inorg. Chem.*, 2006, **45**, 4556.
6 (a) R. E. Blake Jr, D. M. Antonelli, L. Henling, W. P. Schaefer, K. I. Hardcastle and J. E. Bercaw, *Organometallics*, 1998, **17**, 718; (b) R. Royo and J. Sánchez-Nieves, *J. Organomet. Chem.*, 2000, **597**, 61; (c) S. C. Bart, C. Anthon, F. W. Heinmann, E. Bill, N. M. Edelstein and K. Meyer, *J. Am. Chem. Soc.*, 2008, **130**, 12536.
7 (a) D. Swallow, J. M. McInnes and P. Mountford, *J. Chem. Soc., Dalton Trans.*, 1998, 2253; (b) A. J. Blake, J. M. McInnes, P. Mountford, G. I. Nikonov, D. Swallow and D. J. Watkin, *J. Chem. Soc., Dalton Trans.*, 1999, 379; (c) A. E. Guiducci, A. R. Cowley, M. E. G. Skinner and P. Mountford, *J. Chem. Soc., Dalton Trans.*, 2001, 1392; (d) S. R. Dubberley, A. Friedrich, D. A. Willman, P. Mountford and U. Radius, *Chem.–Eur. J.*, 2003, **9**, 3634; (e) C. L. Boyd, T. Toupance, B. R. Tyrrell, B. J. Ward, C. R. Wilson, A. R. Cowley and P. Mountford, *Organometallics*, 2005, **24**, 309; (f) C. L. Boyd, E. Clot, A. E. Guiducci and P. Mountford, *Organometallics*, 2005, **24**, 2347; (g) A. E. Guiducci, C. L. Boyd and P. Mountford, *Organometallics*, 2006, **25**, 1167; (h) S. C. Dunn, N. Hazari, A. R. Cowley, J. C. Green and P. Mountford, *Organometallics*, 2006, **25**, 1755.
8 (a) F. Basuli, B. C. Bailey, J. Tomaszewski, J. C. Huffman and D. J. Mindiola, *J. Am. Chem. Soc.*, 2003, **125**, 6052; (b) F. Basuli, B. C. Bailey, L. A. Watson, J. Tomaszewski, J. C. Huffman and D. J. Mindiola, *Organometallics*, 2005, **24**, 1886; (c) U. J. Kilgore, F. Basuli, J. C. Huffman and D. J. Mindiola, *Inorg. Chem.*, 2006, **45**, 487.
9 (a) D. S. Glueck, J. Wu, F. J. Hollander and R. G. Bergman, *J. Am. Chem. Soc.*, 1991, **113**, 2041; (b) S.-H. Hsu, Jr.-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.
10 (a) P. J. Walsh, F. J. Hollander and R. G. Bergman, *Organometallics*, 1993, **12**, 3705; (b) J. C. Anderson and R. B. Moreno, *Tetrahedron*, 2010, **66**, 9182 and references therein.
11 Some examples are: (a) M. B. Dinger and W. Henderson, *Chem. Commun.*, 1996, 211; (b) P. Mountford, *Chem. Commun.*, 1997, 2127.
12 A. J. Blake, P. E. Collier, S. C. Dunn, W.-S. Li, P. Mountford and O. V. Shishkin, *J. Chem. Soc., Dalton Trans.*, 1997, 1549 and references therein.
13 Retrospectively we think that the increased yield of **3a** in this experiment compared to that in eqn (3) can be explained by the extended reaction time of 16 h *versus* 5 h .
14 J. B. Alexander, R. R. Schrock, W. M. Davis, K. C. Hultzsch, A. H. Hoveyda and J. H. Houser, *Organometallics*, 2000, **19**, 3700.

1338 | *Org. Biomol. Chem.*, 2012, **10**, 1334–1338

This journal is © The Royal Society of Chemistry 2012