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Novel double substrate insertion *versus* isocyanate extrusion in reactions of imidotitanium complexes with CO_2: critical dependence on imido N-substituents†

Aldo E. Guiducci, Andrew R. Cowley, Michael E. G. Skinner and Philip Mountford *

Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR.
E-mail: philip.mountford@chemistry.oxford.ac.uk;

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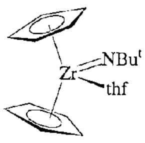
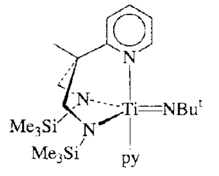
Reaction of the cyclopentadienyl–amidinate supported imidotitanium complexes [Ti(η-C_5Me_5){MeC(N^iPr)$_2$}(NR)] (R = ^{t}Bu 1a or Ar 1b where Ar = 2,6-$C_6H_3Me_2$) with CO_2 proceed *via* initial cycloaddition reactions, but depending on the imido N-substituent go on to yield products of either isocyanate extrusion or double CO_2 insertion, the latter forming [Ti(η-C_5Me_5){MeC(N^iPr)$_2$}{O(CO)N(Ar)(CO)O}] 4; the double CO_2 insertion reaction leading to 4 is the first example for any transition metal imide.

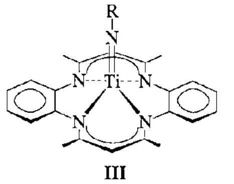
Group 4 organoimido complexes were only first reported just over ten years ago[1] and continue to be the focus of considerable attention.[2] The main point of interest in these systems is the reactivity of the M=NR imido linkage itself. A variety of [2 + 2] cycloaddition, insertion and NR group transfer reactions of this moiety with a range of saturated and unsaturated organic and organometallic substrates have been described. Of the various classes of Group 4 imido complex reported to date, the most intensively and systematically studied are the bis(cyclopentadienyl), diamido–amine and macrocyclic systems. Specific derivatives are shown by way of example in **I**–**III** respectively.[2a–c] We were interested to continue our studies of the influence of the supporting ligand set(s) on the reactivity of the Ti=NR linkage. We report here preliminary results on the synthesis of new cyclopentadienyl–amidinate supported imidotitanium complexes that show novel and interesting chemistry in their reactions with CO_2, and the outcomes of these depend critically on the imido N-substituent.



I

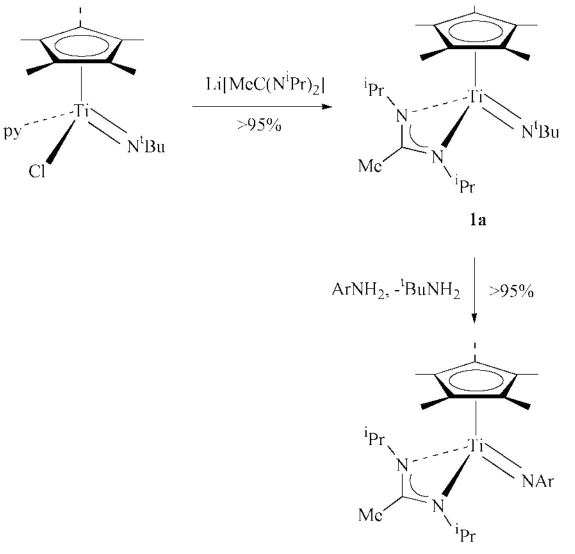


II



III

Titanium imido complexes with certain amidinate ligands have been reported previously by us and others[3] but chemistry at the Ti=NR linkage has never been explored in these systems. One attraction of the combined cyclopentadienyl–amidinate supporting group is the potential for widely varying the electronic and steric properties of this system as demonstrated in the context of olefin polymerisation catalysts containing these ligands.[4] We have found that the C_5Me_5 and MeC(N^iPr)$_2$ supporting ligands in combination provide a good balance of steric protection and electron donation conducive with promoting reactivity at the Ti=NR bond. The extremely high-yielding syntheses of the new imidotitanium compounds [Ti(η-C_5Me_5){MeC(N^iPr)$_2$}(NR)] (R = ^{t}Bu **1a** or Ar **1b**, where Ar = 2,6-$C_6H_3Me_2$) ‡ are summarised in eqn. (1) starting from the readily-available [Ti(η-C_5Me_5)(NBu^t)Cl(py)].[5]



1a

1b

The new compounds **1a**,**b** are the first structurally characterised cyclopentadienyl–amidinate supported Group 4 imido complexes. The solid state structure§ of [Ti(η-C_5Me_5){MeC(N^iPr)$_2$}(NAr)] **1b** is shown in Fig. 1 and reveals an approximately linear Ti=N–Ar linkage with a Ti-N$_{\text{imide}}$ distance consistent with a formal metal–nitrogen triple bond ($\sigma^2\pi^4$).[1] The monomeric pseudo-tetrahedral geometry at Ti(1) is reminiscent of that in the bis(cyclopentadienyl) Group 4 imido systems of the type **I**, except that the formal valence electron count in **1a**,**b** is only 16. Initial studies have shown that the compounds **1a**,**b** undergo productive reactions with a range of unsaturated substrates including alkynes and the heteroallenes RCNO, CS_2, RCNS, COS and CO_2 thus demonstrating the viability of this supporting ligand set in developing metal imido chemistry. It is the reactions with CO_2 that are especially interesting and novel, and we therefore focus on these here.

Cycloaddition reactions of metal imides with CO_2 are very uncommon[1] and only two structurally authenticated metallacyclic products of this type of reaction have been reported.[2b,6] Reaction of **1a**,**b** with CO_2 (1 atm) for 10 or less min followed by immediate isolation gave the cherry red N,O-bound carbamate complexes [Ti(η-C_5Me_5){MeC(N^iPr)$_2$}{O(CO)NR}] (R = ^{t}Bu **2a** or Ar **2b**) in good isolated yield (Scheme 1). The

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† Electronic supplementary information (ESI) available: characterising data for compounds **1**–**4**. See http://www.rsc.org/suppdata/dt/b1/b102704m/

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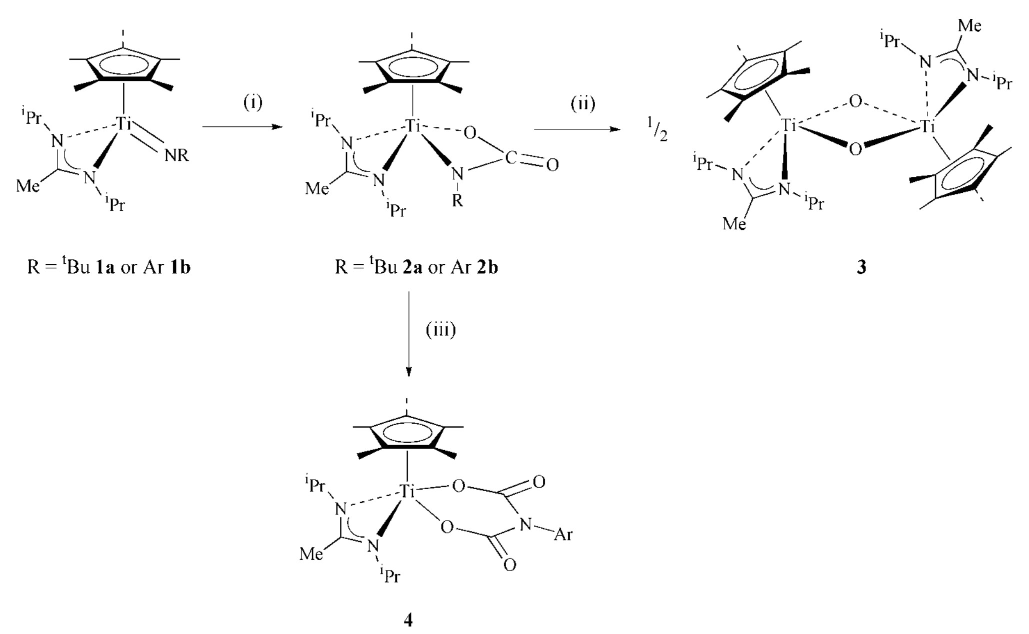

Scheme 1 *Reagents and conditions:* (i) CO_2 (1 atm), 10 min (for **2a**) or 3 min (for **2b**), 60% (for **2a**) or 66% (for **2b**); (ii) 12 h, >95%; (iii) CO_2 (1 atm), 24 h, 82%.

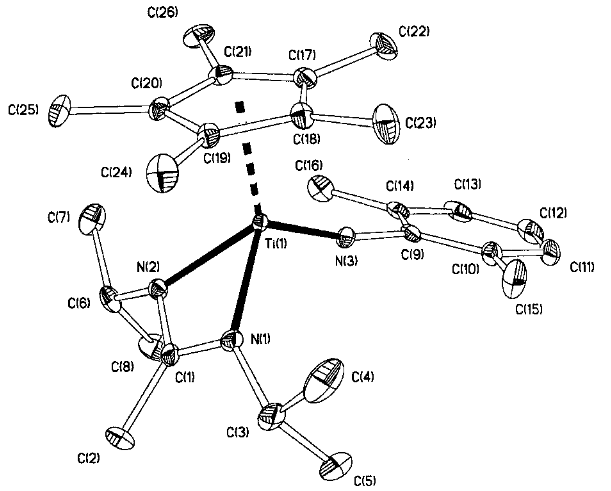

Fig. 1 Displacement ellipsoid (30%) plot of [Ti(η-C_5Me_5){MeC-(N^iPr)$_2$}(NAr)] **1b**. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles: Ti(1)–Cp*$_{cent}$ 2.085, Ti(1)–N(1) 2.094(2), Ti(1)–N(2) 2.099(2), Ti(1)–N(3) 1.738(2) Å; Ti(1)–N(3)–C(9) 168.9(2), Cp*$_{cent}$–Ti(1)–N(1) 119.1, Cp*$_{cent}$–Ti(1)–N(2) 119.5, Cp*$_{cent}$–Ti(1)–N(3) 121.4°, where Cp*cent is the C_5Me_5 ring carbon centroid.

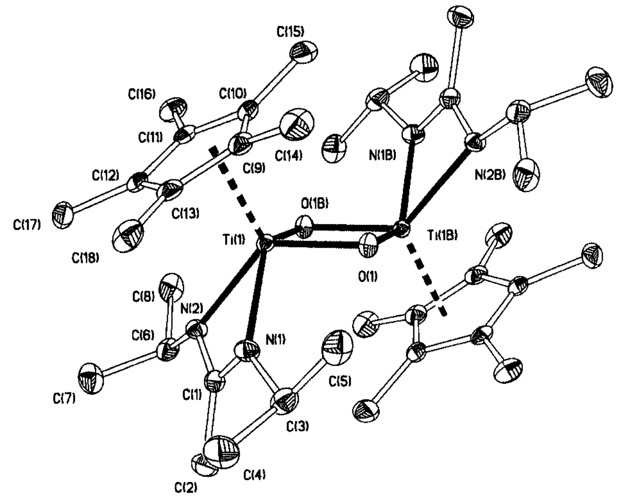

Fig. 2 Displacement ellipsoid (40%) plot of [Ti_2(η-C_5Me_5)$_2$-{MeC(N^iPr)$_2$}$_2$(μ-O)$_2$] **3**. Hydrogen atoms are omitted for clarity; atoms carrying the suffix 'B' are related to their counterparts by the operator [−*x*, −*y*, 1 − *z*]. Selected bond lengths: Ti(1)–Cp*$_{cent}$ 2.130, Ti(1)–N(1) 2.188(3), Ti(1)–N(2) 2.168(3), Ti(1)–O(1) 1.855(2), Ti(1)–O(1B) 1.869(2) Å where Cp*$_{cent}$ is the C_5Me_5 ring carbon centroid.

N,O-coordination for the O(CO)NR ligand is implied by the presence of two inequivalent ^{i}Pr groups for the MeC(N^iPr)$_2$ ligand in the ^{1}H and ^{13}C NMR spectra, and by strong ν(C=O) bands between 1646 and 1669 cm^{-1} in the IR spectra.[2b]

The *tert*-butyl derivative **2a** does not react further with CO_2 in solution (1–2 atm) and under these conditions (or in the absence of CO_2) quantitatively undergoes a retrocyclisation process over 12 hours to yield the isocyanate ^{t}BuNCO and the dimeric μ-oxo complex [Ti_2(η-C_5Me_5)$_2${MeC(N^iPr)$_2$}$_2${μ-O)$_2$] **3**, the dimeric nature of which has been confirmed by X-ray crystallography (Fig. 2). Under otherwise *identical* conditions the aryl derivative [Ti(η-C_5Me_5){MeC(N^iPr)$_2$}{O(CO)NAr}] **2b** reacts smoothly with further CO_2 to give a product **4** that has equivalent ^{i}Pr groups in its ^{1}H and ^{13}C NMR spectra and features *two* strong bands attributable to ν(C=O) at 1651 and 1694 cm^{-1} in its IR spectrum. The structure proposed for [Ti(η-C_5Me_5){MeC(N^iPr)$_2$}{O(CO)N(Ar)(CO)O}] **4** in Scheme 1 is supported by the solid state structure determined by X-ray diffraction (Fig. 3).

Fig. 3 clearly confirms that **4** contains two CO_2 molecules that have been activated and inserted into the original triple Ti–NAr bond of [Ti(η-C_5Me_5){MeC(N^iPr)$_2$}(NAr)] **1b**. The geometry at Ti(1) is typical of a four-legged piano stool complex; distances within and between the ligands are as expected. The two ν(C=O) bands in the IR spectrum of **4** are attributed to symmetric and antisymmetric combinations. The type of double substrate insertion with complete cleavage of the metal–imide bond is highly unusual and has not been authenticated before for any allenes or their hetero-analogues. The only related example is for the reaction of the late transition metal imide [Ir(η-C_5Me_5)(N^tBu)] with certain alkynes.[6] The O(CO)N(Ar)(CO)O fragment in **4** (derived formally from the dianionic conjugate base of azamalonic acid) has not been structurally characterised previously and represents a new type of ligand.[7]

The reasons why compound **2a** does not insert a second CO_2 into the Ti–N_{imide} bond while **2b** does are as yet unclear, but may reflect the electron-withdrawing ability of the aryl group in comparison to the electron-releasing nature of *tert*-butyl. Insertion of the second CO_2 presumably causes polarisation of the Ti–NR (R = ^{t}Bu or Ar) of **2a,b** in the transition state with concomitant build-up of partial positive and negative charge on

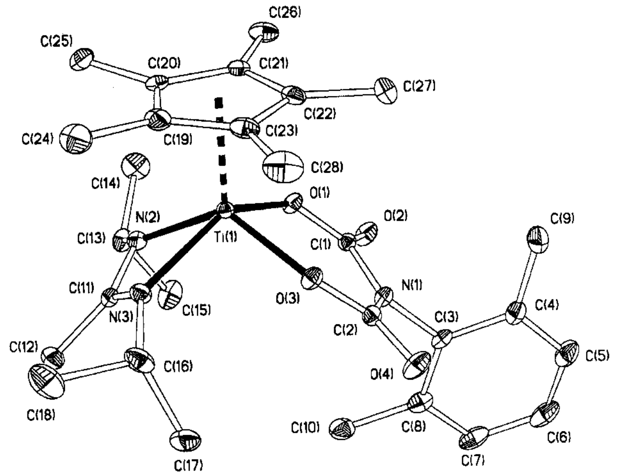

Fig. 3 Displacement ellipsoid (30%) plot of [Ti(η-C_5Me_5){MeC($N^iPr)_2$}{O(CO)N(2,6-$C_6H_3Me_2$)(CO)O}] **4**. Hydrogen atoms are omitted for clarity. Selected bond lengths: Ti(1)–Cp^*_{cent} 2.046. Ti(1)–N(2) 2.064(3), Ti(1)–N(3) 2.071(3), Ti(1)–O(1) 1.932(2), Ti(1)–O(3), N(1)–C(1) 1.410(3), N(1)–C(2) 1.417(3), C(1)–O(2) 1.213(3), C(2)–O(4) 1.210(3) Å where Cp^*_{cent} is the C_5Me_5 ring carbon centroid.

Ti and N, respectively. Therefore an aryl-substituted carbamate nitrogen would be better stabilised during this process. In this regard we have recently found in preliminary studies that fluoraryl analogues of **2b** undergo the second CO_2 insertion reaction at faster relative rates compared to those of the non-fluorinated homologues, consistent with the view that electron-withdrawing groups can accelerate the novel double insertion reaction. Further studies of the role of the imide N-substituent on the pathway of these and related reactions are underway, along with a survey of the chemistry of **1a**,**b** and their homologues in general. Moreover, it is clear that a better understanding of the role and influence of the imido N-substituent on the reactions of imido complexes will progress the rational design of useful imido group transfer reagents.

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Notes and references

‡ Satisfactory characterising data have been obtained for all the new compounds (see ESI).

§ Crystal data for **1b**: $C_{26}H_{41}N_3Ti$, $M = 443.53$, tetragonal, $I4_1cd$, $a = b = 20.5223(4)$, $c = 24.3873(6)$ Å, $U = 10271.1$ Å^3, $Z = 16$, $T = 150$ K, $\mu = 0.35$ mm^{-1}, 5910 independent reflections ($R_{merge} = 0.060$), 4139 $I > 3\sigma(I)$ used in refinement, final R indices: $R = 0.0396$, $R_w = 0.0418$. For **3**: $C_{36}H_{64}N_4O_2Ti_2$, $M = 680.71$, monoclinic, $P2_1/n$, $a = 9.7810(4)$, $b = 15.4630(4)$, $c = 12.0930(5)$ Å, $\beta = 92.625(2)°$, $U = 1827.1$ Å^3, $Z = 2$, $T = 150$ K, $\mu = 0.47$ mm^{-1}, 3890 independent reflections ($R_{merge} = 0.07$), 2403 $I > 3\sigma(I)$ used in refinement, final R indices: $R = 0.0523$, $R_w = 0.0395$. For **4**: $C_{28}H_{41}N_3O_4Ti{\cdot}0.5(C_6H_6)$, $M = 570.61$, orthorhombic, $Pbca$, $a = 14.4250(2)$, $b = 17.2619(3)$, $c = 24.3318(4)$ Å, $U = 6058.7$ Å^3, $Z = 8$, $T = 150$ K, $\mu = 0.32$ mm^{-1}, 6916 independent reflections ($R_{merge} = 0.055$), 4551 $I > 3\sigma(I)$ used in refinement, final R indices: $R = 0.0463$, $R_w = 0.0534$. CCDC reference numbers 160966–160968. See http://www.rsc.org/suppdata/dt/b1/b102704m/ for crystallographic data in CIF or other electronic format.

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7 The X-ray structure of the homologous N,O-bound carbamate complex [Ti(η-C_5Me_5){κ^2-$Me_3SiNC(Ph)NCH_2CH_2NMe_2$}{O(CO)$N^tBu$}] has been determined: C. L. Boyd, A. E. Guiducci and P. Mountford, unpublished results.