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Aryl Isocyanate, Carbodiimide, and Isocyanide Prepared from Carbon Dioxide. A Metathetical Group-Transfer Tale Involving a Titanium–Imide Zwitterion

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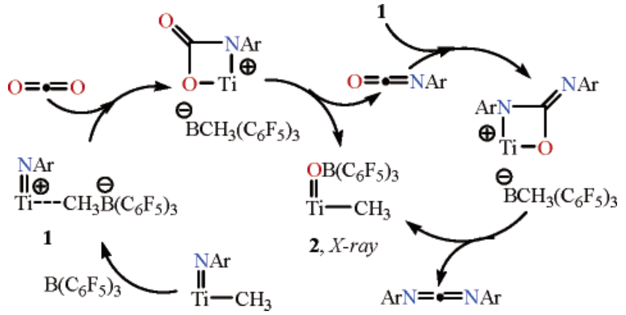
Carbon dioxide can be readily converted quantitatively and under mild conditions into the aryl isocyanate and symmetrical carbodiimide via a metathetical reaction involving a zwitterionic titanium imide (nacnac)Ti═NAr($CH_3B(C_6F_5)_3$) (nacnac$^-$ = [ArNC(^{t}Bu)]$_2$CH, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$). The metathetical process to generate isocyanates allows also for facile formation of sterically demanding aryl isocyanide, by a deoxygenation route. Labeling studies using enriched $^{13}CO_2$ are also described.

Carbon dioxide is often regarded as a nonflammable and thermodynamically inert greenhouse gas.[1] As a result, there has been considerable interest in utilizing carbon dioxide feedstock as a reagent for a wide range of commodity products.[2] Therefore, complexes capable of both activating and functionalizing readily available carbon dioxide into useful chemical building blocks are attractive targets especially if such transformations can be carried out under mild conditions.[3] Employing carbon dioxide as a reagent also is appealing from a spectroscopic standpoint because isotopically enriched forms are both affordable and commercially available. One possible strategy is via atom or group-transfer reactions involving electron-deficient early-transition-metal systems with low-coordination numbers because metal−oxo formation is predicted to be thermodynamically favorable.

Scheme 1. Synthesis of Isocyanate and Carbodiimide from CO_2 Utilizing a Zwitterionic Titanium Imido Complex **1**[a]



[a] The Ti atom represents the cationic (nacnac)Ti scaffold where nacnac$^-$ = [ArNC(^{t}Bu)]$_2$CH and Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$.

We feature in the present paper the quantitative conversion of carbon dioxide into an isocyanate and carbodiimide via ligand metathesis reactions mediated by the imido−zwitterion (nacnac)Ti═NAr($CH_3B(C_6F_5)_3$) (**1**; nacnac$^-$ = [ArNC(^{t}Bu)]$_2$CH, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$).[4] In addition, the aryl isocyanate generated from our metathetical process can be readily converted to an isocyanide, hence unveiling an indirect entry of the isocyano functionality from CO_2. Labeling studies using $^{13}CO_2$ have also been conducted in order to follow the fate of both the CO and C atoms in all of the reactions formerly mentioned.

Treatment of complex **1**, prepared quantitatively from methide abstraction using $B(C_6F_5)_3$ and (nacnac)-Ti═NAr(CH_3) in XC_6H_5 (X = F or Br; Scheme 1),[4] with 1 atm of CO_2 at room temperature elicited a rapid color change from red to pale orange. Examination of the reaction mixture by ^1H and ^{13}C NMR spectroscopy revealed quantitative formation of the isocyanate OCNAr [also determined by electrospray ionization (EIMS) and IR] along with the titanium−oxo complex (nacnac)Ti(OB(C_6F_5)$_3$)(CH_3) (**2**; Scheme 1).[5] Single-crystal X-ray analysis of complex **2** disclosed this species to be a monomer with coordination of

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(5) See the Supporting Information for complete experimental and relevant crystallographic details.

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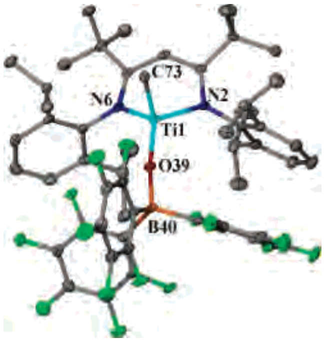

Figure 1. Molecular structure of complex **2** depicting thermal ellipsoids at the 50% probability level. The hydrogen atoms and solvent have been excluded for clarity. Selected metrical parameters: Ti1−N2, 1.969(2) Å; Ti1−N6, 2.004(8) Å; Ti1−O39, 1.732(5) Å; Ti1−C73, 2.091(3) Å; Ti1−O39−B40, 172.3(4)°; N2−Ti1−N6, 98.82(8)°.

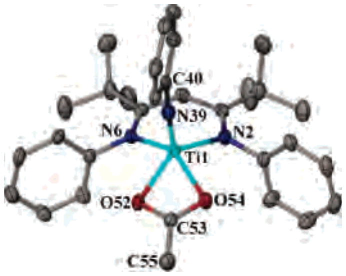

Figure 2. Molecular structure of complex **3** depicting thermal ellipsoids at the 50% probability level. The hydrogen atoms, ^{i}Pr groups on the aryl rings, and solvent molecules have been excluded for clarity. Selected metrical parameters: Ti1−N39, 1.702(2) Å; Ti1−N2, 2.076(2) Å; Ti1−N6, 2.090(2) Å; Ti1−O52, 2.094(7) Å; Ti1−O54, 2.128(7) Å; C53−C55, 1.488(4) Å; Ti1−N39−C40, 175.3(9)°; N2−Ti1−N6, 92.07(8)°; O52−Ti1−O55, 61.88(6)°; O52−C53−O54, 117.0(2)°.

the borane to be on the Ti═O motif (Figure 1).[5] Structure parameters consistent with this formulation for **2** include a short Ti═O bond [1.732(5) Å] confined in a highly distorted tetrahedral geometry. The perfluorinated aryl groups on the boron are twisted in a propellerlike fashion, and the B atom deviates from the plane defined by the three ipso carbons (∼0.545 Å), lending further support for Lewis acid−base adduct formation in **2**.[6,7]

Generation of **2** suggests that ion-paired reorganization processes are occurring in the reaction and that formation of a titanium−oxo dimer is forbidden via blockage by the Lewis acid.[6] We propose that production of OCNAr and **2** proceeds by means of displacement of the labile borate ligand $[CH_3B(C_6F_5)_3]^-$ by CO_2 and subsequent [2 + 2] cycloaddition to afford a hypothetical carbamate complex [(nacnac)Ti(OCONAr)]$^+$,[8] which then undergoes cycloreversion to form the strong Ti═O bond (Scheme 1).[8−11] Unlike other imido systems, excess CO_2 does not appear to insert into the putative carbamate to afford six-membered-ring aryl imidodicarboxylates.[9] The role of the borane is critical because it provides a latent low-coordinate titanium−imide species capable of activating CO_2. Such a charge-separated species also prevents the Ti═O species from dimerizing via Ti−O−Ti linkages.[8−11] More importantly, the ionic nature of complex **2** renders this complex insoluble in C_6H_5X (X = F, Br, Cl), which facilitates separation from the neutral organic product (OCNAr).

Methide abstraction in complex **1** is critical inasmuch as the neutral complex (nacnac)Ti═NAr(CH_3)[4] reacts cleanly with CO_2 to afford the acetate (nacnac)Ti═NAr(η^2-O_2CCH_3) (**3**), a product originating from CO_2 insertion into the Ti−CH_3 bond. Connectivity of **3** was established by a combination in ^{1}H and ^{13}C NMR spectra in addition to the single-crystal solid-state molecular structure. Figure 2 depicts the molecular structure of **3**, clearly revealing insertion of CO_2 into the Ti−CH_3 bond to afford an η^2-acetate ligand.[12]

When the reaction was carried out with a stoichiometric amount of CO_2 ($^1/_2$ equiv at 25 °C, >48 h), we observed the formation of **2** along with carbodiimide ArNCNAr.[5] The occurrence of the carbodiimide is proposed to proceed via a [2 + 2] cycloaddition of OCNAr with **1** and cycloreversion to extrude the organic product and **2** (Scheme 1).[13−15] Such a result indicates that the formation of **2** is slow vis-à-vis

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(7) Crystal data for $2\cdot{}^1/_2Et_2O$: $C_{56}H_{61}BF_{15}N_2O_2Ti$, triclinic, space group $P\bar{1}$, a = 12.7063(18) Å, b = 13.5595(18) Å, c = 16.805(2) Å, α = 105.689(4)°, β = 100.502(4)°, γ = 99.263(4)°, Z = 2, μ(Mo Kα) = 0.256 mm^{-1}, V = 2672.4(6) Å^3, D_c = 1.414 mg/mm^3, GOF on F^2 = 0.911, R1 = 5.12% and wR2 = 12.15% (F^2, all data). Out of a total of 23 577 reflections collected, 12 264 were unique and 8056 were observed (R_{int} = 7.48%) with $I > 2\sigma(I)$ (yellow needle, 0.30 × 0.12 × 0.06 mm, 27.43° ≥ Θ ≥ 3.80°). A disordered diethyl ether is present in the cell.

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(12) Crystal data $3\cdot C_6H_{14}$: $C_{55}H_{87}N_2O_3Ti$, monoclinic, space group $P2(1)/c$, a = 13.1392(16) Å, b = 18.319(2) Å, c = 21.385(3) Å, β = 94.109(3)°, Z = 4, μ(Mo Kσ) = 0.209 mm^{-1}, V = 5133.9(11) Å^3, D_c = 1.128 mg/mm^3, GOF on F^2 = 0.723, R1 = 5.05% and wR2 = 10.05% (F^2, all data). Out of a total of 55 343 reflections collected, 11 890 were unique and 4688 were observed (R_{int} = 15.47%) with $I > 2\sigma(I)$ (yellow prism, 0.25 × 0.05 × 0.05 mm, 27.57° ≥ Θ ≥ 2.04°). In addition to the molecule of interest, there is a region of disordered solvent that could not be resolved. The latter was modeled as a series of partial occupancy carbon atoms. All nonsolvent hydrogen atoms were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement. Solvent hydrogen atoms were ignored.

(13) Complex (nacnac)Ti═NAr(Cl) fails to react with CO_2 under the same conditions.

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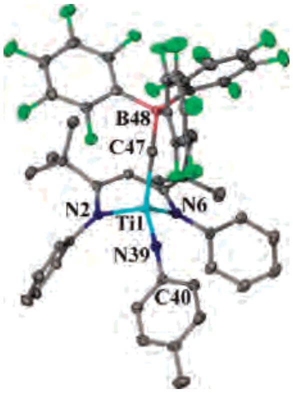
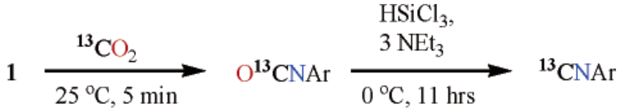


Figure 3. Molecular structure of complex **4** depicting thermal ellipsoids at the 50% probability level. The hydrogen atoms, ^{i}Pr groups on the nacnac aryl rings, and solvent molecules have been excluded for clarity. Selected metrical parameters: Ti1−N39, 1.701(1) Å; Ti1−N2, 1.969(1) Å; Ti1−N6, 2.013(1) Å; Ti1−C47, 2.417(3) Å; C47−B48, 1.665(9) Å; Ti1−N39−C40, 175.33(9)°; N2−Ti1−N6, 97.67(4)°; Ti1−C47−B48, 175.4(1)°.

the consumption of CO_2 by **1**. To test our hypothesis, we treated **1** with OCNAr in C_6H_5Br, which consequently yielded **2** along with the carbodiimide in quantitative yield based on ^{1}H NMR (25 °C, 48 h; Scheme 1). As was observed with the isocyanate formation from **1** (vide supra), separation of the organic product (ArNCNAr) was facilitated by the low solubility of **2** in BrC_6H_5. Interestingly, this result is in a stark contrast to isocyanate cycloaddition reactions with titanium and zirconium imides supported by tetraaza macrocyclic ligands, which takes place at the (N, C) site of the isocyanate to form N,N-disubstituted ureates ($RNCONR'^{2-}$).[10] It is likely that in our system the steric hindrance at the titanium center disfavors the N,N bound isomer from forming. Isotopic labeling studies using $^{13}CO_2$ confirmed exclusive CO and C atom transfer to generate the corresponding isotopomers $O^{13}CNAr$ and $ArN^{13}CNAr$, as supported by ^{13}C NMR, IR, chemical ionization MS (CIMS), and EIMS spectroscopies.[5]

Attempts to prepare asymmetrical carbodiimides of the type ArNCNAr′ via this route were not clean.[14] For instance, treatment of **1** with CO_2, followed by addition of the tolyl imide zwitterion analogue (nacnac)Ti═Ntol($CH_3B(C_6F_5)_3$) (**4**; Figure 3)[5,16] (tol = 4-$CH_3C_6H_4$), resulted in the formation of the asymmetrical carbodiimide ArNCNtol, concomitant with the generation of the oxo **2** and other side products.[5,] Arguably, sterics in **1** appear to play a key role in the clean formation of both OCNAr and ArNCNAr, since C═N carbodiimide metathesis might be a competing reaction in this type of process.

Scheme 2. Formation of the Isotopically Labeled ^{13}CNAr from O^{13}CNAr, Which Is Prepared Easily from **1** and $^{13}CO_2$



Isotopically labeled isocyanate O^{13}CNAr is not only a precursor to the ^{13}C-labeled carbodiimide $ArN^{13}CNAr$ but also a clean source to an isocyanide following the deoxygenation procedure described by Baldwin and co-workers.[17] Based on this precedent, treatment of O^{13}CNAr with $HSiCl_3$ and excess NEt_3 in CH_2Cl_2 under mild conditions affords the isotopically enriched aryl isonitrile ^{13}CNAr in >78% (Scheme 2). The identities of both labeled and unlabeled CNAr were unambiguously confirmed with a combination of ^{1}H and ^{13}C NMR, IR, and CIMS spectroscopies.[5,18]

In conclusion, we have shown that a zwitterion−imido complex of titanium can readily convert CO_2, under mild conditions, into the corresponding aryl isocyanate and symmetrical carbodiimide. The role of the borane is critical in these reactions, and separation of the organic products is facile given the low solubility of the Ti═O material. It has been shown that ^{13}C isotopic labeling of these two heterocumulenes is readily accessible given the availability of $^{13}CO_2$.[19] We have also demonstrated that the isotopically enriched isocyanate can be a precursor to the labeled isocyanide CNAr, a building block in both organic and organometallic chemistry. We are currently exploring ways to convert oxo species such as **2** into reactive systems such as **1** or **3** in order to make the metathetical C and CO transfer process from CO_2 cyclic or catalytic.

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Supporting Information Available: Complete X-ray data for structures (CIF), synthesis and characterization of **2**−**4**, and preparations for all ^{13}C-labeled and unlabeled isocyanates, carbodiimides, and isocyanides. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Crystal data for **4**: $C_{61}H_{63}BF_{15}N_3Ti$, triclinic, space group $P\bar{1}$, $a = 12.0226(7)$ Å, $b = 13.9555(8)$ Å, $c = 18.399(1)$ Å, $\alpha = 89.910(2)°$, $\beta = 83.022(2)°$, $\gamma = 66.659(1)°$, $Z = 2$, μ(Mo Kα) = 0.245 mm^{-1}, $V = 2809.7(3)$ Å^3, $D_c = 1.397$ mg/mm^3, GOF on $F^2 = 0.941$, R1 = 3.76% and wR2 = 8.70% (F^2, all data). Out of a total of 77 094 reflections collected, 16 420 were unique and 11 475 were observed ($R_{int} = 6.06\%$) with $I > 2\sigma(I)$ (orange cleaved fragment, 0.30 × 0.30 × 0.30 mm, 30.04° ≥ Θ ≥ 2.12°).

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