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# Carbodiimide metathesis catalyzed by vanadium oxo and imido complexes via imido transfer

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**Abstract**

Vanadium oxo and imido complexes: $V(NC_6H_4Me)(O^tBu)_3$ (**1**), $V(NC_6H_4Me)Cl_3$ (**2**), $V(O)(O^tBu)_3$ (**3**), $V(O)(O^iPr)_3$ (**4**), $V(O)(acac)_2$ (**5**), are catalysts for the metathesis of symmetrical carbodiimides (RNCNR, where R = cyclohexyl, isopropyl, and *p*-tolyl). At 138°C in *p*-xylene using 5 mol% of complexes **1**–**5**, the above carbodiimides are metathesized to the asymmetrical carbodiimides: *N*-cyclohexyl,*N*′-*p*-tolylcarbodiimide (**6**), *N*-isopropyl,*N*′-*p*-tolylcarbodiimide (**7**), *N*-cyclohexyl,*N*′-isopropylcarbodiimide (**8**). An equilibrium mixture of carbodiimides is reached within minutes to hours depending on the catalyst employed. Yields obtained from gas chromatography range from 32 to 70%. Complex **2** is the most efficient catalyst with a turnover frequency greater than 100 $h^{-1}$. The oxo complexes (**3**–**5**) appear to be precatalysts. A mechanism is proposed for initiation with oxo complexes and a subsequent catalytic cycle involving imido complexes. 

*Keywords:* Vanadium imido; Vanadium oxo; Carbodiimide metathesis; Unsymmetrical carbodiimide; Catalysis; Imido transfer

## 1. Introduction

Reactions involving imido complexes and imido transfer are of great current interest due to the use of these complexes as catalysts in alkene metathesis and their proposed intermediacy in catalytic ammoxidation of arenes and alkenes [1]. We reported that several high valent vanadium oxo and imido complexes are catalysts for the condensation of phenyl isocyanate to *N*,*N*′-diphenylcarbodiimide (Eq. (1)) [2]. Imido transfer appears to be a key step in this catalytic process.

$$2PhNCO \overset{[V(E)OR_3]}{\rightleftharpoons} PhNCNPh + CO_2 \quad (1)$$

where E = O, NR.

Weiss proposes an imido transfer in the catalytic metathesis of carbodiimides by $W(NPh)Cl_4$ (Eq. (2)) [3].

$$R-N{=}C{=}N-R + R'-N{=}C{=}N-R' \overset{PhNWCl_4}{\rightleftharpoons} 2R-N{=}C{=}N\text{-}R' \quad (2)$$

Imido transfer in Eq. (2) purportedly occurs via a diazametallacyclobutane intermediate. Carbodiimide metathesis has also been catalyzed by $Cr(II)/SiO_2$ [4] and $W(CO)_5(CN^iPr)$ [5]. Both catalytic and stoichiometric imine metathesis has been observed using imido complexes [6]. Sita has developed a stoichiometric metathesis to unsymmetrical carbodiimides mediated by Group 14 amide complexes [7].

Condensation of phenyl isocyanates (Eq. (1)) and metathesis of carbodiimides (Eq. (2)) are both examples of heterocumulene metatheses. The similarities in these reactions led us to investigate the use of vanadium oxo and imido complexes as carbodiimide metathesis catalysts. We now report the use of the following vanadium complexes: $V(NC_6H_4Me)(O^tBu)_3$ (**1**), $V(NC_6H_4Me)Cl_3$ (**2**), $V(O)(O^tBu)_3$ (**3**), $V(O)(O^iPr)_3$ (**4**), $V(O)(acac)_2$ (**5**) as precatalysts or catalysts for the metathesis of *N*,*N*′-dialkylcarbodiimides and *N*,*N*′-diarylcarbodiimides (Eq. (3)).

$$R-N{=}C{=}N-R + R'-N{=}C{=}N-R' \overset{[V\ cat.]}{\rightleftharpoons} 2R-N{=}C{=}N\text{-}R' \quad (3)$$

## 2. Results and discussion

We studied the use of complexes **1**–**5** as catalysts or precatalysts for the metathesis of *N*,*N*′-dialkyl- and *N*,*N*′-diarylcarbodimiides (Eq. (4)).

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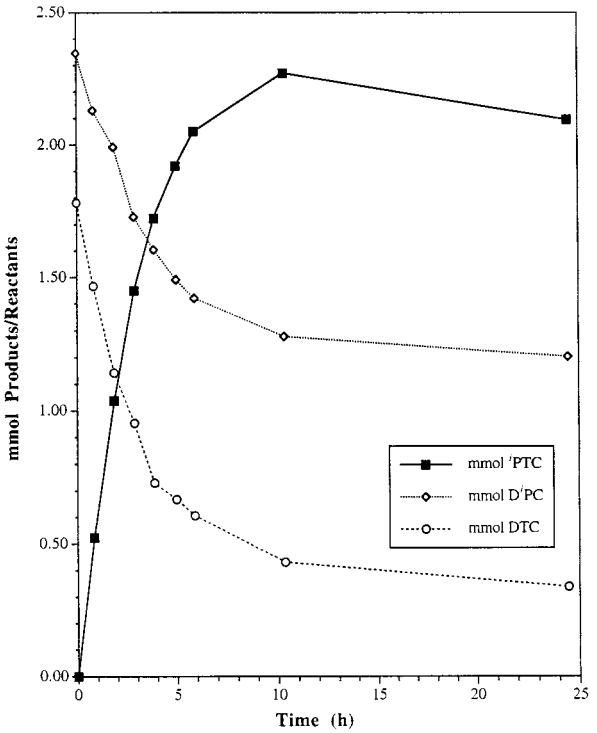



Fig. 1. Reaction profile of the metathesis of D$^i$PC and DTC catalyzed by V(O)(O$^t$Bu)$_3$, **3**.

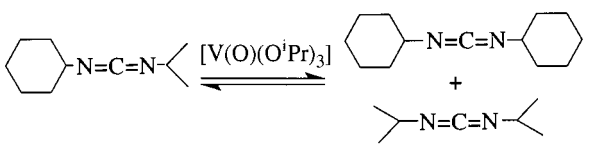
$$R-N{=}C{=}N-R + R'-N{=}C{=}N-R' \overset{[V(E)Xn]}{\rightleftharpoons} 2R-N{=}C{=}N{-}R' \quad (4)$$

where E = NR, O; X = OR, Cl, acac.

| R–N=C=N–R | R | R–N=C=N–R′ | R | R′ |
|---|---|---|---|---|
| DTC | *p*-$C_6H_4Me$ | CTC, **6** | $C_6H_{11}$ | *p*-$C_6H_4Me$ |
| D$^i$PC | $^i$Pr | $^i$PTC, **7** | $^i$Pr | *p*-$C_6H_4Me$ |
| DCC | $C_6H_{11}$ | C$^i$PC, **8** | $C_6H_{11}$ | $^i$Pr |

The above metatheses were performed in *p*-xylene at 138°C with millimolar concentrations of reagents and catalyst. Typically 3–7 mol% of catalyst is used. Product concentrations are monitored by GC as a function of time using the internal standard method. Reactions are followed until equilibrium is established as indicated by little change in concentration over several hours. A typical reaction profile for a metathesis is shown in Fig. 1.

Equilibrium in these metatheses results in an approximate 2:1 mixture of products and reagents. The equilibrium nature of these reactions was confirmed by the metathesis of one of the products (C$^i$PC) using V(O)(O$^i$Pr)$_3$ to make DCC and D$^i$PC under the same reaction conditions as the standard metathesis (Eq. (5)).




(5)

Table 1
Results from the catalytic metathesis of *N*,*N*′-diaryl and *N*,*N*′-dialkylcarbodiimides (RNCNR where R = $C_6H_{11}$, $^i$Pr, *p*-$C_6H_4Me$ with vanadium oxo and imido complexes (Eq. (4))

| Catalyst | Metathesis products | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $C_6H_{11}NCN^iPr$, **8** | | | $C_6H_{11}NCNC_6H_4Me$, **6** | | | $^iPrNCNC_6H_4Me$, **7** | | |
| | Cat. (mol%) | % Yield[a] | TOF[b] ($h^{-1}$) | Cat. (mol%) | % Yield[a] | TOF[b] ($h^{-1}$) | Cat. (mol%) | % Yield[a] | TOF[b] ($h^{-1}$) |
| V(NPhMe)(O$^t$Bu)$_3$, **1**[f] | 5 | 32 | 0.5 | 4 | 70 | 3 | 3 | 61 | 8 |
| V(NPhMe)Cl$_3$, **2** | 4 | 63[d] | 40[c] | 5 | 65[d] | 60[c] | 5 | 50[d] | 60[c] |
| V(O)(O$^t$Bu)$_3$, **3** | 5 | 44[d] | 2 | 4 | 60[d] | 2 | 6 | 41[d] | 2 |
| V(O)(O$^i$Pr)$_3$, **4** | 7 | 61[d] | 2 | 5 | 60[d] | 4 | 5 | 41[d] | 4 |
| V(O)(acac)$_2$ **5** | 5 | 69[d] | 3 | 6 | 50[d] | 4 | 4 | 49[d] | 3 |
| Control | | | | 0[e] | 0 | | | | |

[a] Yields were determined by gas chromatography. Percent yield based on 100% conversion of limiting carbodiimide. These yields represent 10–20 catalyst turnovers.

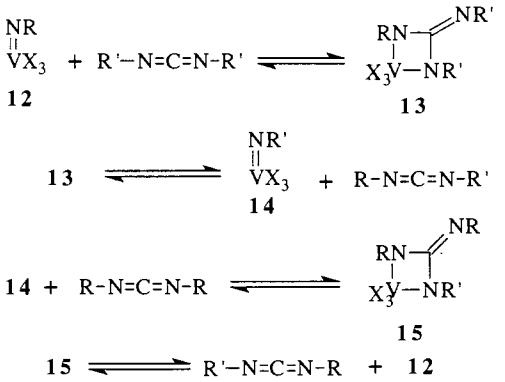
[b] The turnover frequency (TOF) was determined by finding the maximum in the following ratio: {[Δ[Prod]/Δ*t*]/[Cat.]}. TOF was determined from a plot of mmol of product versus time constructed from GC data.

[c] These values represent a lower limit to TOF due to limitations of the sampling procedure.

[d] Average of two runs.

[e] After 9 h at 138° C

[f] Complex **1** has one run for each reaction due to the difficulty using this catalyst.



Scheme 1. Proposed catalytic cycle for metathesis with imido complexes.

The results for all metatheses are summarized in Table 1. The time required to reach equilibrium for the metatheses in Table 1 varied from 20 min to several hours depending on catalyst and carbodiimides employed.

### 2.1. Yields

The yields were determined by GC using 1,2,3,4-tetramethylbenzene as an internal standard. Table 1 shows a large amount of variability in the yield of the various carbodiimides depending on which catalyst was used. Some of the yield variability can be attributed to side reactions which decompose the asymmetrical carbodiimides to unknown products. The reported yields are not optimized.

### 2.2. Catalyst efficiency

The turnover frequency (TOF) for each catalyst was determined by finding the slope maximum in the plot of mmols of product versus time. We report maximum turnover frequency in Table 1 because the oxo complexes **3**–**5** have variable initiation periods before propagation proceeds smoothly. Except for imido **2**, all catalysts showed similar turnover frequencies. Imido **2** was by far the most efficient catalyst. Using a lower catalyst concentration (0.4 mol% of imido **2**) than the standard metathesis conditions with DCC and D$^i$PC as reagents, the TOF of imido **2** was 90 $h^{-1}$.

The catalytic lifetime of imido **2** was also investigated. A mixture of DCC and D$^i$PC with 0.4 mol% imido **2** was metathesized to C$^i$PC within 30 min in *p*-xylene at 138°C. After establishing equilibrium, another aliquot of DCC and D$^i$PC was added. Equilibrium was reestablished within 20 min after addition, producing over 100 catalyst turnovers without loss of catalytic activity. The yields reported in Table 1 represent 10–20 catalyst turnovers.

### 2.3. Catalytic metathesis

Eqs. (6) and (7) display proposed initiation steps and Scheme 1 shows the catalytic cycle for the metathesis of carbodiimides using oxo and imido complexes. Scheme 1 is essentially the mechanism proposed by Weiss [3] using tungsten imido complexes. Imido **12** reacts with another carbodiimide (R′N=C=NR′) to form one asymmetrical carbodiimide (R′N=C=NR) and imido **14**. The cycle is completed by the reaction of RN=C=NR and **14** to form another asymmetrical carbodiimide (R′NCNR) and reform **12**. The diazametallacycles **13** and **15** represent possible transition states.

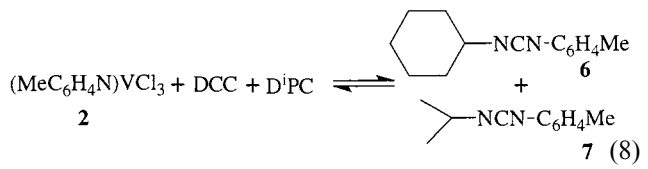
$$\underset{\mathbf{10}}{V(O)X_3} + R - N{=}C{=}N - R \rightleftharpoons RNCO + \underset{\mathbf{12}}{V(NR)X_3} \quad (6)$$

$$\underset{\mathbf{10}}{V(O)X_3} + RNCO \rightleftharpoons CO_2(g) + \underset{\mathbf{12}}{V(NR)X_3} \quad (7)$$

Eqs. (6) and (7) are proposed initiation pathways for the metal oxo complexes. Oxo **10** reacts with RN=C=NR to form one equivalent of imido **12** and RNCO (Eq. (6)). A possible intermediate is the oxometallacyle formed by addition of the carbodiimide C=N bond across the V=O bond with the nitrogen ligating the vanadium. Related oxometallacycles of this type formed by addition of an isocyanate C=N bond across the M=O bond have been isolated for Mo, Re, and Ir [8]. Another pathway for formation of imido **12** is reaction of the isocyanate formed in Eq. (6) with oxo **10** (Eq. (7)). Reaction of isocyanates with metal oxo complexes is a common synthetic route to metal imido complexes [9]. Moreover oxos **3**–**5** catalyze the condensation of PhNCO to PhNCNPh via an imido intermediate (Eq. (1)) [2]. Several experiments support these proposed initiation pathways.

The initiation step of the metathesis using oxo **5** combined with DCC and D$^i$PC in refluxing *p*-xylene is observed as a blue–yellow color change over 2 h followed by initial product formation (C$^i$PC). An IR experiment with oxo **5** further substantiates the oxo initiation paths of Eqs. (6) and (7). The same color change is observed upon heating a mixture of oxo **5** and a three fold excess of D$^i$PC in *p*-xylene. An infrared spectrum following the color change shows the intense NCN absorption for D$^i$PC and a weak absorption at 2255 $cm^{-1}$ attributed to the NCO absorption of isopropyl isocyanate [10]. The 2255 $cm^{-1}$ absorption disappears upon continued heating, consistent with Eqs. (6) and (7). A complementary experiment heating oxo **5** and a three fold excess of DCC in *p*-xylene resulted in immediate formation of cyclohexyl isocyanate (CyNCO) as observed by GC. The CyNCO was quantified by using an internal standard. The CyNCO concentration increased for 5 h where it maximized at 17 mol% of oxo **5**. Wholly consistent with the reactions in Eqs. (6) and (7), the continued heating of the reaction mixture results in the disappearance of the CyNCO.

In Scheme 1, the carbodiimides are metathesized by imido exchange or imido transfer via a diazametallacycle. The metathesis of DCC and D$^i$PC with tolylimido **2** provides supporting evidence for the imido transfer step in Scheme 1. In the initial 20 min of the metathesis, GC evidence shows carbodiimides **6** and **7** are formed (Eq.(8)). These carbodiimides (**6** and **7**) are produced by transfer of the tolyl imido group of imido **2** to DCC and D$^i$PC, respectively (Eq.(8))



(8)

Quantitative GC results indicate greater than 50% of the tolyl group of imido **2** is found in carbodiimides **6** and **7**.

## 3. Conclusions

The above data show that complexes **1**–**5** catalyze the metathesis of both *N*,*N*′-dialkyl- and *N*,*N*′-diarylcarbodiimides to equilibrium mixtures. The oxo complexes **3**–**5** are precatalysts which are converted to imido complexes by the reactions indicated in Eqs. (6) and (7). The turnover frequency (TOF) data indicate imido **2** is by far the most active metathesis catalyst.

It is not clear whether the rate difference between imido **2** and catalysts (**1**, **3**–**5**) is purely a consequence of steric factors or results from some electronic contribution. Interestingly, while imido **2** is the most efficient carbodiimide metathesis catalyst, **2** is the only one of the complexes **1**–**5** which shows no catalytic activity for isocyanate condensation (Eq. (1)). Both of these catalytic reactions are heterocumulene metatheses which appear to involve imido transfer. In a continuing effort to understand imido transfer in these systems we are attempting to determine what factors effectively shut off imido transfer from V(NC$_6$H$_4$Me)Cl$_3$ (**2**) to aryl isocyanates, but allow **2** to be an efficient imido transfer agent for carbodiimide metatheses.

## 4. Experimental

### 4.1. General

The reagents *N*,*N*′-di-*p*-tolylcarbodiimide (DTC), *N*,*N*′-di-isopropylcarbodiimide (D$^i$PC), *N*,*N*′-dicyclohexylcarbodiimide (DCC), isopropylamine, *p*-tolyl isothiocyanate, cyclohexyl iso-thiocyanate, 1,2,3,4-tetramethylbenzene, mercuric oxide, V(O)(O$^i$Pr)$_3$, and V(O)(acac)$_2$ were used as obtained from commercial suppliers. V(NC$_6$H$_4$Me)(O$^t$Bu)$_3$ [11], V(NC$_6$H$_4$Me)Cl$_3$ [11], and V(O)(O$^t$Bu)$_3$ [12] were prepared by literature methods. The asymmetrical carbodiimides (*N*-cyclohexyl,*N*′-isopropylcarbodiimide (C$^i$PC), *N*-isopropyl,*N*′-*p*-tolylcarbodiimide ($^i$PTC), *N*-cyclohexyl, *N*′-*p*-tolylcarbodiimdide (CTC)) used for GC references were prepared according to a modified literature method [13]. All syntheses were done under dry nitrogen with dry solvents. The solvents were distilled from potassium or sodium under dry nitrogen. Acetone was dried over activated 4 Å mole sieves.

#### 4.1.1. Equipment

The GC analyses were performed on a Hewlett–Packard 5890 chromatograph fitted with a 12 m × 0.2 mm × 0.33 μm HP-1 capillary column and a flame ionization detector. The infrared spectra were obtained on a Mattson Cygnus 100 series FTIR or a Perkin–Elmer model 1430 spectrometer. The high-resolution mass spectra were obtained on a Kratos Concept $^1$H Spectrometer in positive ion mode at 30°C at 70 eV. The elemental analysis was done by Desert Analytics of Tucson, AZ. The $^1$H-NMR were recorded on an IBM AMX 200 MHz or a General Electric QE 400 MHz spectrometer. The $^{13}$C-NMR were recorded on a General Electric QE 400 MHz spectrometer.

### 4.2. Representative metathesis reaction

#### 4.2.1. Metathesis of DTC and D$^i$PC catalyzed by V(O)(O$^t$Bu)$_3$, **3** to prepare $^i$PTC, **7**

A 100 ml Schlenk flask is charged with V(O)(O$^t$Bu)$_3$ (0.063 g, 0.22 mmol), D$^i$PC (0.349 g, 1.55 mmol), DTC (0.449 g, 1.94 mmol), 1,2,3,4-tetramethylbenzene (TMB, internal standard) (0.068 g, 0.51 mmol), and 30 ml of *p*-xylene resulting in a light yellow mixture. The initial concentrations of reagents are as follows: [V(O)(O$^t$Bu)$_3$] = 0.0074 M, [D$^i$PC] = 0.052 M, [DTC] = 0.065 M. The mixture is heated to reflux under nitrogen. The reaction mixture is periodically sampled by removing a 1–2 ml aliquot of the reaction mixture via cannula and transferring it to a sealed test tube containing an equivalent amount of dry (0°C) THF. These samples are analyzed immediately upon cooling by gas chromatography. An initial sample is taken upon reaching reflux temperature and other samples are taken at least every hour for a minimum of 5 h. Reaction is allowed to continue overnight and a final sample is taken after 25 h. Final reaction mixture is spiked with (independently prepared, see below) $^i$PTC, **7** to confirm GC assignment. The yield of $^i$PTC determined by GC using the internal standard method is 58%.

### 4.3. Preparation of *N*-cyclohexyl-*N*′-*p*-tolylcarbodiimide, ($C_6H_{11}NCNC_6H_4Me$) (CTC) **6**

A Schlenk flask is charged with cyclohexyl isothiocyanate (6.89 g, 48.8 mmol) and 40 ml of THF. To this solution a solution of *p*-toluidine (6.04 g, 56.4 mmol) in 40 ml of THF, at 0°C, is added dropwise over 10 min. The resulting solution is stirred overnight at room temperature. The THF is removed in vacuo resulting in the white crystalline *N*-cyclohexyl-*N*′-tolylthiourea (m.p. 94–97).

The thiourea (48 mmol) is dissolved in 80 ml of dry acetone under nitrogen. To this mixture is added HgO (15 g, 69 mmol) and 1 g of anhydrous calcium chloride. This suspension is stirred overnight under nitrogen resulting in a black solid suspended in solution. The mixture is filtered and the solvent removed in vacuo producing a light yellow oil. The *N*-cyclohexyl-*N*′-tolylcarbodiimide (CTC) is formed essentially quantitatively as determined by GC/MS.

$^1$H-NMR(200 MHz) ($CDCl_3$) $\delta$: 7.03 (ABq, $J$(HA–HB) = 8 Hz, N$\underline{Ph}$CH$_3$, 4H) 3.44 (tt, $J(^1H-^1H) = 9$, 4 Hz, N$\underline{CH}$(CH$_2$)$_5$ 1H) 2.30 (s, Ph$\underline{CH_3}$, 3H), 2.00 (m, NCH(C$\underline{H_2}$)$_5$,2H), 1.76 (m, NCH(C$\underline{H_2}$)$_5$,2H) 1.41 (m, NCH(C$\underline{H_2}$)$_5$, 6H); $^{13}$C-NMR (100 MHz) ($CDCl_3$) 138.02 (s, *ipso* Ph or NCN), 134.20 (s, *ipso* Ph or NCN), 130.59 (s, *ipso* Ph or NCN), 129.95 (s, Ph C–H), 123.14 (s, Ph C–H), 56.64 (s, $\underline{C}$H$_3$–Ph), 34.99 (s, $C_6H_{11}$), 25.38 (s, $C_6H_{11}$), 24.43 (s, $C_6H_{11}$), 20.93 (s, $C_6H_{11}$); IR (neat, $\nu$, cm$^{-1}$) 3010 w, 2928 s, 2850 s, 2125 vs (NCN), 1605 m, 1510 vs, 815 vs, 610 vs; HRMS. Anal. Calc. for $C_{14}H_{18}N_2$: 214.146998; Found: 214.14706 (0.29 ppm deviation); GC/MS (70 eV) $m/z$ (% relative intensity) 214 (29) [M$^+$], 132 (100) [M–$C_6H_{10}^+$], 91 (22) [M–NCNC$_6$H$_{11}^+$].

### 4.4. Preparation of *N*-isopropyl-*N*′-*p*-tolylcarbodiimide (*p*-Me$C_6H_4NCN^iPr$), ($^i$PTC) **7**

Compound **7** is synthesized similarly to compound **6**. A solution of isopropylamine (2.21 g, 37 mmol) in THF is added dropwise to a solution of *p*-tolyl isothiocyanate (4.66 g, 31.2 mmol) at 0°C over 15 min. The mixture is stirred overnight at room temperature. The solvent is removed in vacuo resulting in *N*-isopropyl-*N*′-tolylthiourea as a white solid (m.p. 106–111).

To a solution of thiourea (31 mmol) in acetone an excess of mercuric oxide (15 g, 69 mmol) and $CaCl_2$ (1 g) is added. The heterogeneous reaction is stirred overnight at room temperature. The black HgS is filtered away and the solvent removed from the filtrate in vacuo resulting in a quantitative yield of a yellow oil of *N*-isopropyl-*N*′-*p*-tolylcarbodiimide.

$^1$H-NMR (200 MHz) ($CDCl_3$) $\delta$: 7.03 (ABq, $J$(HA–HB) = 8 Hz, N–$\underline{Ph}$–Me, 4H), 3.76 (sep, $J(^1H-^1H) = 6$ Hz, NC$\underline{H}$(CH$_3$)$_2$, 1H); 2.30 (s, Ph$\underline{CH_3}$, 3H) 1.32 (d, $J(^1H-^1H) = 6$ Hz, NCH(C$\underline{H_3}$)$_2$, 6H) IR (neat, $\nu$, cm$^{-1}$) 3020 w, 2970 m, 2920 w, 2120 vs(NCN), 1605 m, 1505 s, 812 m, 610 m; $^{13}$C-NMR (100 MHz)($CDCl_3$) $\delta$: 137.7 (s, *ipso* Ph or NCN) 136.9 (s, *ipso* Ph or N$\underline{C}$N) 134.0 (s, *ipso* Ph or NCN), 129.7 (s, $\underline{C}$H of Ph), 122.9 (s, $\underline{C}$H of Ph), 49.95 (s, N$\underline{C}$H(CH$_3$)$_2$), 24.66 (s, NCH(C$\underline{H_3}$)$_2$), 20.69 (s, Ph$\underline{C}$H$_3$); Anal. Calc. for $C_{11}H_{14}N_2$: C, 75.82; H, 8.10; N, 16.08; Found: C, 75.38; H, 8.04; N, 15.57; GC/MS (70 eV) $m/z$ (% relative intensity): 174 (56) [M$^+$], 132 (100) [M–$C_3H_6^+$], 131 (64) [M–$C_3H_7^+$]; HRMS Calc. for $C_{11}H_{14}N_2$: 174.115698; Found: 174.1157(0.06 ppm deviation).

### 4.5. Preparation of *N*-cyclohexyl-*N*′-isopropylcarbodiimide ($C_6H_{11}NCN^iPr$) ($C^iPC$) **8**

Compound **8** is prepared in a similar fashion to complex **6**. A solution of isopropylamine (4.2 g, 71 mmol) in THF is added dropwise at 0°C to a THF solution of cyclohexyl isothiocyanate (6.9 g, 49.0 mmol) over a 10 min period. The mixture is allowed to react overnight at room temperature. The solvent is removed in vacuo resulting in *N*-cyclohexyl-*N*′-isopropylthiourea as a white solid (m.p. 138).

To a solution of the thiourea (48 mmol) in 80 ml of acetone, an excess of mercuric oxide (15.0 g, 69 mmol) and $CaCl_2$ (1.0 g) is added. The heterogenous mixture is stirred overnight. The mixture is filtered and more mercuric oxide (8.0 g, 37 mmol) is added. After another 8 h the reaction appears complete by GC/MS. The reaction mixture is filtered and the solvent removed from the filtrate in vacuo resulting in an essentially quantitative yield of pure *N*-cyclohexyl-*N*′-isopropylcarbodiimide as a yellow oil.

$^1$H-NMR (200 MHz) (benzene-$d_6$) $\delta$: 3.37 [sept, $J$(HH) = 6 Hz, 1H, NC$\underline{H}$(CH$_3$)$_2$)]; 3.07(triplet of triplets, $J(^1H-^1H) = 10$, 4 Hz, 1H, NC$\underline{H}$(CH$_2$)$_5$), 1.78 (m, 2H, NCH(C$\underline{H_2}$)$_5$), 1.54 (m, 2H, NCH(C$\underline{H_2}$)$_5$), 1.28 (m, 2H, NCH(C$\underline{H_2}$)$_5$), 1.06(d, $J(^1H-^1H) = 6$ Hz, 6H, NCH(C$\underline{H_3}$)$_2$); $^{13}$C-NMR (100 MHz) ($CDCl_3$) $\delta$: 139.8 (s, NCN), 55.5 (s, N–$\underline{C}$H), 48.7 (s, N–$\underline{C}$H), 34.7(s, $\underline{C}$H$_2$), 25.2(s, $\underline{C}$H$_2$), 24.5(s, $\underline{C}$H$_2$), 24.2(s, CH(C$\underline{H_3}$)$_2$), assignments were aided by a DEPT experiment. IR (neat, $\nu$, cm$^{-1}$) 2968 m, 2923 s, 2855 m, 2120 vs (NCN), 1448 m, 1360 m, 1300 m, 1205 m, 943 m, 879 m; GC/MS (70eV) $m/z$ (% relative intensity): 166 (2.3) [M$^+$], 151 (100) [M–$CH_3^+$]; HRMS. Anal. Calc. for $C_{10}H_{18}N_2$: 166.146998, Found: 166.14708 (0.51 ppm deviation).

### 4.6. GC calibration graphs for asymmetrical carbodiimides and cyclohexyl isocyanate

#### 4.6.1. GC calibration curve for **7** ($^i$PTC)

Five standard samples of $^i$PTC are made with concentrations ranging from 0.00520 to 0.105 M in a 50:50

(V/V) mixture of tetrahydrofuran:*p*-xylene. Each standard contained 0.0203 M 1,2,3,4-tetramethylbenzene (TMB). For the five samples the ratio of $Area_{iPTC}/Area_{TMB}$ was plotted versus ratio of mmol $^{i}$PTC/mmolTMB resulting in a linear plot. The data is fit to the equation below by a least-squares analysis:

$$\text{Area}(^{i}\text{PTC})/\text{Area(TMB)} = 1.138\ \{\text{mmol } ^{i}\text{PTC/mmol TMB}\} - 0.0614 \text{ with a correlation coefficient of } 0.99.$$

The calibration graphs for **8**, **6**, and cyclohexyl isocyanate are prepared similarly and display correlation coefficients of $\geq 0.99$.

*4.6.2. Metathesis plots of time versus mmol of product*

Using response factors obtained from the calibration curves, plots of mmols of metathesis product versus time were constructed. These curves are used to determine percent yield of product, the stability of product under reaction conditions, and turnover frequency (TOF) of the catalyst.

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