Catalysis of Phenyl Isocyanate Condensation to *N,N'*-Diphenylcarbodiimide via Vanadium Oxo and Imido Complexes

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Summary: The following complexes catalyze the condensation of phenyl isocyanate to N,N'-diphenylcarbodiimide: V(O)(OR)$_3$ (R = tBu, iPr), V(NC$_6$H$_4$Me)(O-tBu)$_3$, and V(O)(acac)$_2$ (acac = acetylacetonate). GC yields of N,N'-diphenylcarbodiimide ranged from 67 to 96%. Spectroscopic results implicate an interconversion of an oxo complex to an imido complex followed by an imido group transfer to an isocyanate to complete the catalytic cycle.

Reactions involving imido complexes[1] and imido group transfer[2] are of great current interest. We have been interested in studying the imido group transfer reactivity of group V imido complexes by using reactions which are well-established in isoelectronic phosphorus complexes. It is well-known that trialkylphosphine oxides are catalysts for the condensation of isocyanates to carbodiimides (eq 1).[3] The catalytic cycle proposed for the reaction in eq 1

$$2RNCO \overset{R_3PO}{\rightleftharpoons} RNCNR + CO_2 \qquad (1)$$

is shown in Figure 1.[3a] The two key intermediates in the catalytic cycle are the phosphine oxide **10** and the phosphinimine (imido) compound **12**.

We report here the first use of vanadium oxo and imido complexes as catalysts for the condensation of aryl isocyanates to *N,N'*-diarylcarbodiimides (eq 1). We have been studying vanadium oxo and imido complexes that are isoelectronic and isostructural with the phosphorus intermediates in the above catalytic cycle (Figure 1) in the hope of finding active vanadium catalysts for the isocyanate condensation reaction (eq 1). The following complexes were found to catalyze the condensation of phenyl isocyanate to *N,N'*-diphenylcarbodiimide (DPC) (eq 1): V(O)(OtBu)$_3$ (**1a**), V(O)(O-iPr)$_3$ (**1b**), V(NC$_6$H$_4$Me)(O-tBu)$_3$ (**2a**), and V(O)(acac)$_2$ (**3**; acac = acetylacetonate).[4] The catalytic activity of complexes **1**–**3** for the PhNCO condensation reaction (eq 1) was assessed by determining yields of DPC by GC and/or isolation. A representative procedure for the catalytic condensation of phenyl isocyanate is given in ref 7. The results for all catalysts tried are compiled in Table I.

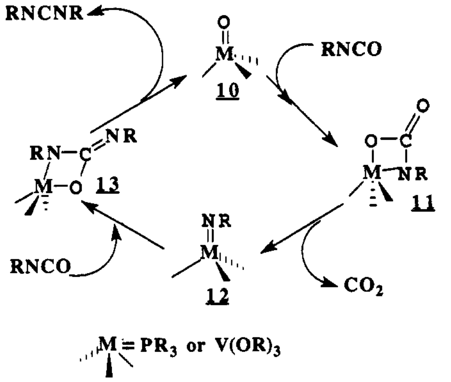
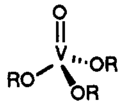
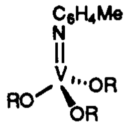


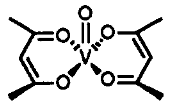
Figure 1. Proposed cycle for the condensation of isocyanates to carbodiimides catalyzed by trialkylphosphine oxides or vanadium oxide and imido complexes.



1a, R = tBu
b, R = iPr



2a, R = tBu



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Reaction of Vanadium Imido Complexes (2a, 4). The reaction of V(NC$_6$H$_4$Me)(O-tBu)$_3$ (**2a**) with excess PhNCO in *p*-xylene at 140 °C proceeds to completion, and a GC/MS of the distilled product revealed two compounds with relative areas of 96% and 4%. The two compounds were assigned to DPC and *N-p*-tolyl-*N'*-phenylcarbodiimide,

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(1) (a) Nugent, W. A.; Mayer, J. M. *Metal Ligand Multiple Bonds*; Wiley: New York, 1988, and references therein. (b) Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Kruger, C.; Betz, P. *Organometallics* **1990**, *9*, 2262. (c) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.

(2) (a) Atagi, L. M.; Over, D. E.; McAlister, D. R.; Mayer, J. M. *J. Am. Chem. Soc.* **1991**, *113*, 870. (b) Meisel, I.; Hertel, G.; Weiss, K. *J. Mol. Catal.* **1986**, *36*, 159. (c) Harlan, E. W.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 186. (d) Pilato, R. S.; Williams, G. D.; Geoffroy, G. L.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 3665. (e) Arndtisen, B. A.; Sleiman, H. F.; Chang, A. K.; McElwee-White, L. *J. Am. Chem. Soc.* **1991**, *113*, 4871. (f) Chan, D. M. T.; Nugent, W. A. *Inorg. Chem.* **1985**, *24*, 1422.

(3) (a) Monagle, J. J.; Campbell, T. W.; McShane, H. F. *J. Am. Chem. Soc.* **1962**, *84*, 4288. (b) Campbell, T. W.; Monagle, J. J.; Foldi, V. S. *J. Am. Chem. Soc.* **1962**, *84*, 3673. (c) Williams, A.; Ibrahim, I. T. *Chem. Rev.* **1981**, *81*, 589.

(4) Compounds **3** and **1b** were obtained from Strem Chemical Co. and Johnson/Mathey Alfa products, respectively. Compounds **1a**,[5] **2a**,[6] and **4**[6] were prepared by literature methods.

(5) Fuchs, J.; Jahr, K. F. *Chem. Ber.* **1963**, *96*, 2460.

(6) Devore, D. D.; Lichtenhan, J. D.; Takusagawa, F.; Maatta, E. A. *J. Am. Chem. Soc.* **1987**, *109*, 7408.

(7) A Schlenk flask was charged with complex **1b** (2.6 mmol), PhNCO (57.8 mmol), and 10 mL of dry *p*-xylene.[8] The mixture was refluxed under nitrogen for 20 h, and the solvent was removed in vacuo. Reduced-pressure distillation of the remaining oil at 110–120 °C (ca. 0.5 mmHg) (lit.[9] bp 110–112 °C/0.5 mmHg)[9] yielded 2.62 g (47% yield) of *N,N'*-diphenylcarbodiimide as a colorless oil.[10] Details on the preparation of the GC calibration graph for *N,N'*-diphenylcarbodiimide and an example of a determination of the yield by GC of a catalytic procedure are in the supplementary material. Reaction of excess tBuNCO with precatalysts **1a**, **1b**, **3**, and **4** produced no carbodiimide after 15 h in refluxing *p*-xylene. Cyclohexyl isocyanate is converted to *N,N'*-dicyclohexylcarbodiimide using **3** as a catalyst over several days in refluxing *p*-xylene.

(8) Some reactions were run in neat PhNCO for ease of isolation. The temperature was held between 160 and 170 °C for approximately 6 h in these reactions.

(9) Campbell, T. W.; Monagle, J. J. *Org. Synth.* **1963**, *43*, 31.

(10) *N,N'*-Diphenylcarbodiimide was characterized by GC/MS, IR, and comparison to an authentic sample prepared by literature methods.[11]

(11) Hunig, V. S.; Lehmann, H.; Grimmer, G. *Ann. Chem.* **1953**, *579*, 77. A modification of this procedure is described in: Hessell, E. T.; Jones, W. D. *Organometallics* **1992**, *11*, 1496.

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respectively (eq 2).[12] The small amount of *N*-*p*-tolyl-*N′*-phenylcarbodiimide formed is consistent with the initiation step of the reaction being transfer of the *p*-tolylimido ligand of V(NC$_6$H$_4$Me)(O-tBu)$_3$ to PhNCO, nicely establishing imido group transfer as a key component of the reaction.

$$\mathrm{PhNCO\ (excess)} + \underset{\textbf{2a}}{\mathrm{(MeC_6H_4N)V(O\text{-}tBu)_3}} \rightleftharpoons \underset{96\%}{\mathrm{PhNCNPh}} + \underset{<4\%}{\mathrm{PhNCNC_6H_4Me}} + \mathrm{CO_2} \quad (2)$$

In contrast to V(NC$_6$H$_4$Me)(O-tBu)$_3$ (**2a**), V(NC$_6$H$_4$Me)Cl$_3$ (**4**) displays no catalytic activity toward the condensation of PhNCO. The lack of reactivity may be due to the poor π-donating ability of the chloride ligands of **4** relative to the alkoxide ligands of **2a**, which may result in a much stronger, less reactive V=N double bond in **4** versus **2a**.

Reactions of Vanadium(IV) and -(V) Oxo Compounds. The vanadyl esters V(O)(O-tBu)$_3$ (**1a**) and V(O)(O-iPr)$_3$ (**1b**) are also active catalysts for PhNCO condensation and produce the highest yields of isolated DPC (see Table I). A solution IR in xylene of a mixture of MeC$_6$H$_4$NCO and **1a** after 20 h at 140 °C reveals *N*,*N′*-di-*p*-tolylcarbodiimide (DTC) and no *p*-MeC$_6$H$_4$NCO, confirming complete reaction.

While the V(IV) oxo species V(O)(acac)$_2$ (**3**) also catalyzes the condensation of phenyl isocyanate, isolated yields using **3** are much lower than for the other catalysts (see Table I). Following the reaction of **3** and PhNCO by GC shows steady production of DPC for 5 h and decomposition of product upon further heating. It is likely that isolated yields of the product are low in this system due to DPC decomposition during distillation.

Mechanistic Comments. The proposed catalytic cycle for the vanadium oxo catalyzed phenyl isocyanate condensation is completely analogous to the mechanism proposed for the trialkylphosphine oxide catalyzed reaction[3a] (Figure 1), except R$_3$P is replaced by V(OR)$_3$. Conversion of **10** to **12** in Figure 1 is a common preparative method for imido complexes from metal oxo complexes.[13] High-valent complexes of Ir, Re, and Mo similar to intermediate **11** (Figure 1) have recently been characterized.[14] Furthermore, consistent with Figure 1, carbon dioxide is evolved from all the catalytic reactions in Table I. The final step, imido transfer from **12** (Figure 1) to an isocyanate resulting in product and re-formation of the oxo compound, was implicated by the formation of a small amount of *N*-*p*-tolyl-*N′*-phenylcarbodiimide in eq 2.

Table I. Condensation of Phenyl Isocyanate to Diphenylcarbodiimide Catalyzed by Vanadium Oxo and Imido Complexes (Eq 1)

precatalyst	amt of catalyst (mol %)	solvent	time (h)	% yield[a] (GC % yield)[7]
V(O)(O-tBu)$_3$ (**1a**)	4.4	*p*-xylene	20	41 (80)[b]
V(O)(O-iPr)$_3$ (**1b**)	4.3	*p*-xylene	20	47 (96)
V(NC$_6$H$_4$Me)(O-tBu)$_3$ (**2a**)	3.3	PhNCO[c]	6	33 (67)
V(O)(acac)$_2$ (**3**)	4.2	PhNCO[c]	6	10 (88)
V(NC$_6$H$_4$Me)Cl$_3$ (**4**)	3.9	*p*-xylene	24	no reacn[d]
V$_2$O$_5$	4.0	*p*-xylene	125	*e*
control (no catalyst)	0	*p*-xylene	28	none

[a] Isolated yield from reduced-pressure distillation of product mixture. [b] This is the average of two runs. [c] PhNCO was used as the solvent, and the temperature of the reaction mixture was held between 160 and 170 °C. [d] *p*-Tolyl isocyanate was used instead of PhNCO, and no carbodiimide was detected by IR after 24 h. [e] After 125 h approximately equal amounts of PhNCO and PhNCNPh were observed in IR.

Information supporting the proposed catalytic cycle was obtained by a series of NMR and IR experiments. Addition of excess *p*-MeC$_6$H$_4$NCO to V(NC$_6$H$_4$Me)(O-tBu)$_3$ (**2a**) in *p*-xylene results in an immediate color change and a new IR absorption at 1718 cm^{-1}, which is reasonable for a CO or CN stretch of some form of complexed isocyanate.[15] An IR after this solution was heated at 140 °C for 8 h reveals complete conversion to DTC. A complementary NMR experiment combining an excess of *p*-MeC$_6$H$_4$NCO and **2a** in benzene-*d*$_6$ displays signals for DTC immediately in the room-temperature ^{1}H NMR.[16] Integration reveals the ratio of relative concentrations of **2a**:*p*-MeC$_6$H$_4$NCO:DTC to be 10:280:1, indicating a small amount of DTC formation. *Apparently tolylimido transfer from **2a** to tolyl isocyanates is facile at room temperature with excess isocyanate.* Heating this mixture for 1 h at 140 °C results in extensive reaction with relative concentrations of **2a**:*p*-MeC$_6$H$_4$NCO:DTC of 0.25:0.9:1. After 6 h the reaction is essentially complete.

Upon addition of excess *p*-MeC$_6$H$_4$NCO to V(O)(O-tBu)$_3$ (**1a**) an immediate color change and a new IR absorption at 1730 cm^{-1} appears, indicating isocyanate complexation.[15] In contrast to the reactivity of **2a** with excess *p*-MeC$_6$H$_4$NCO, the ^{1}H NMR of *p*-MeC$_6$H$_4$NCO and **1a** (4:1) in benzene after 1 day at room temperature shows *p*-MeC$_6$H$_4$NCO and **1a**, but *no **2a** or DTC is observed.*[17] After 1 h at 165 °C, the NMR sample reveals **1a**, **2a**, *p*-MeC$_6$H$_4$NCO, and DTC, indicating that conversion of the metal oxo **1a** to the metal imido **2a** is slow at room temperature but occurs rapidly at 165 °C.

The above NMR and IR experiments suggest that transfer of tolylimido from **2a** to *p*-MeC$_6$H$_4$NCO (**12** to **10** in Figure 1) is fast relative to conversion of **1a** (oxo complex) to **2a** (imido complex) (**10** to **12** in Figure 1). This implies that imido formation is the rate-determining step in the catalytic cycle. Consistent with this picture are preliminary kinetic studies which show a first-order dependence on [**2a**] and [PhNCO].[18]

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(12) The two compounds were identified by GC/MS. GC/MS (70 eV; *m/z* (%)): 194 (100) [M$^+$] for PhNCNPh, 208 (100) [M$^+$] for MeC$_6$H$_4$NCNPh. More details are in the supplementary material.

(13) (a) Kolomnikov, I. S.; Koreshkov, Yu. D.; Lobeeva, T. S.; Volpin, M. E. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1971**, 2065. (b) Pedersen, S. F.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 7483. (c) Nielson, A. J. *Inorg. Synth.* **1986**, *24*, 194.

(14) (a) Jernakoff, P.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1610. (b) Kusthardt, U.; Herrmann, W. A.; Zeigler, M. L.; Zahn, T.; Nuber, B. *J. Organomet. Chem.* **1986**, *311*, 163. (c) Glueck, D. S.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2719. (d) Glueck, D. S.; Wu, J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 2041. As pointed out by a reviewer, structures **11** and **13** in Figure 1 may simply represent transition states instead of true intermediates.

(15) (a) Antinolo, A.; Garcia-Lledo, S.; Martinez de Ilarduya, J.; Otero, A. *J. Organomet. Chem.* **1987**, *335*, 85. (b) IR (ν(NCN) or ν(NCO) in xylene, cm^{-1}): PhNCO (2260); PhNCNPh (2135, 2110); Cp$_2$NbCl(η^2-PhNCO) (1720).[15a]

(16) Several minor components are also observed in the aromatic and C$_6$H$_4$*Me* region; of these, the greatest components has signals at δ 7.02 (AB q, J_{AB} = 8 Hz, C$_6$*H*$_4$Me) and 1.99 (s, C$_6$H$_4$*Me*), which is consistent with a complexed isocyanate. Separation and isolation of this complex from **2a** by chromatography are not likely due to the extreme sensitivity of these complexes to hydrolysis.

(17) Also observed are several weak multiplets in the aromatic region at δ 7.57, 7.20, and 6.99 as well as several singlets in the C$_6$H$_4$*Me* region at δ 2.09, 2.05, and 2.03, which are in the correct region for a complexed tolyl isocyanate, consistent with the observed IR absorption at 1730 cm^{-1}.

(18) Kinetics of diphenylcarbodiimide formation catalyzed by **2a** or **3** were monitored by the rate of evolution of CO$_2$ in a closed system: Ensminger, M.; Johnson, M., Unpublished data.

Studies are continuing to determine the relative efficacy of these catalysts. Kinetic studies to quantify the details of the imido transfer reaction and to ascertain the determining factors in imido transfer in this system are planned. Finally, we have observed that all the complexes in Table I with the exception of V_2O_5 are catalysts for the metathesis of *N,N′*-diarylcarbodiimides and *N,N′*-dialkylcarbodiimides[19] (eq 3).

$$\mathrm{RNCNR} + \mathrm{R'NCNR'} \overset{\text{[V cat.]}}{\rightleftharpoons} 2\mathrm{RNCNR'} \qquad (3)$$

$$\mathrm{R} = \mathrm{C_6H_4Me};\ \mathrm{R'} = \text{cyclohexyl, iPr}$$

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Supplementary Material Available: Text giving the procedure for determining the GC yield for the condensation of phenyl isocyanate to diphenylcarbodiimide and spectroscopic data on relevant complexes (3 pages). Ordering information is given on any current masthead page.

OM920728R

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(19) Birdwhistell, K. R.; Mahoney, D. *Abstracts of Papers*, 203rd National Meeting of the American Chemical Society, San Francisco, CA; American Chemical Society: Washington, DC, 1992; INOR 124.