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Catalytic conversion of isocyanates to carbodiimides by cyclopentadienyl manganese tricarbonyl and cyclopentadienyl iron dicarbonyl dimer

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Abstract—Isocyanates are catalytically converted to the corresponding carbodiimides in the presence of low valent transition metal complexes. The best conversions and yields were accomplished using $[(C_5R_5)Fe(CO)_2]_2$ (R = H or Me) or $MeCpMn(CO)_3$ as catalysts.

Carbodiimides are reactive compounds with wide utility as synthetic intermediates and in several industrial applications.[1–3] These compounds have been prepared by a variety of methods, including the thermolysis–decarboxylation of isocyanates,[4a] the dehydration of ureas,[5] and the dehydrosulfurization of thioureas.[6] A number of catalysts have been reported for the conversion of isocyanates to carbodiimides, including phospholine oxides,[4b] phosphine and arsine oxides,[4c] and vanadium oxo and imido complexes.[4d] The conversion of isocyanates to carbodimides, catalyzed by binary Fe-, M- and W-metal carbonyls at 250 °C, was also briefly noted:[7]

$$2RNCO \overset{(cat)}{\Rightarrow} R{-}N{=}C{=}N{-}R + CO_2 \qquad (1)$$

Decarbonylations of organic isocyanates by low-valent metal complexes have been observed and suggested to generate nitrene derivatives. For example, $Ni(PPh_3)_2(PhNCO)$ decarbonylates to produce $Ni(CO)_2(Ph_3P)_2$ and possibly [Ph–N].[8] Similarly, $WCl_2(PMe_2Ph)_4$ reacts with isocyanates to afford the imido carbonyl complex $WCl_2(NR)(CO)(PMe_2Ph)_2$.[9] Decarbonylation of isocyanate has also been observed in the isolation of the structurally characterized titanium, ruthenium and iron complexes.[10] Nitrene (imido) complexes may also be intermediates in the transition metal-catalyzed preparation of isocyanates from nitro compounds.[11] We earlier employed $[(C_5H_5)Fe(CO)_2]_2$ as a catalyst in the reaction of olefins with nitroaromatic compounds/carbon monoxide to form allyl amines regioselectively (and CO_2).[12] In the $[(C_5Me_5)Fe(CO)_2]_2$-catalyzed reactions a novel carbamato complex was isolated, suggesting the intervention of a reactive imido complex.[13] We therefore postulated that organic isocyanates could act both as nitrenoid precursors and hence could be a suitable nitrogen source for the amination of olefins.

When phenyl isocyanate and α-methyl styrene were refluxed together in xylene in the presence of the allylic amination catalyst $[CpFe(CO)_2]_2$,[12] the major product was found to be diphenyl carbodimide based on its spectroscopic properties (MS, NMR), rather than the corresponding *N*-phenyl 2-phenylallyl amine. A survey of the thermal reaction of phenyl isocyanate alone under the same conditions in the presence of other representative low valent metal complexes was conducted, including $(PPh_3)_2PdCl_2$, $[Cu(CH_3CN)_4]BF_4$, $[(C_5Me_5)RuCl_2]_n$, $[(C_5Me_5)IrCl_2]_2$, $[(C_5Me_5)RhCl(PMe_3)]_2$, $[(C_5H_5)Fe(CO)_2]_2$, $[(C_5Me_5)Fe(CO)_2]_2$ and $MeCpMn(CO)_3$. The progress of the PhNCO conversion into the carbodiimide was monitored by infrared spectroscopy and gas chromatography; the results are given in Table 1. Two rhodium phosphine complexes, $(Ph_3P)_3RhCl$ and $[(C_5Me_5)RhCl(PMe_3)]_2$, and the inexpensive metal carbonyl derivatives, $[(C_5R_5)Fe(CO)_2]_2$ (R = H, Me) and

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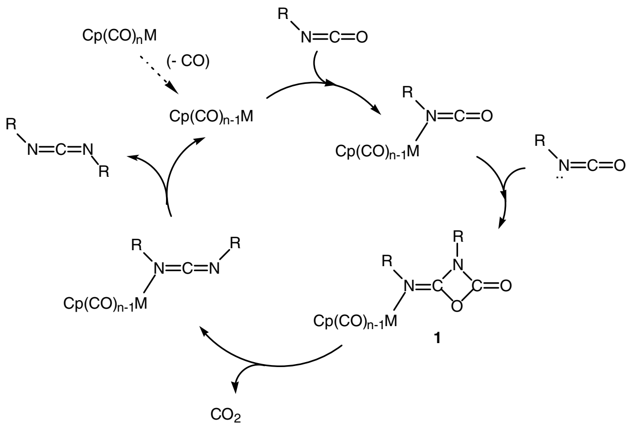
Table 1. Conversion of phenyl isocyanate to diphenyl carbodiimide with various catalysts

Complex	Time (h)	GC conversion (%)
$(PPh_3)_2PdCl_2$	48	25
$[Cu(CH_3CN)_4]BF_4$	60	None
$[(C_5Me_5)RuCl_2]_n$	60	Trace
$[(C_5Me_5)RhCl(PMe_3)]_2$	36	95
$[(C_5Me_5)IrCl_2]_2$	60	Trace
$(PPh_3)_3RhCl$	36	90
$MeCpMn(CO)_3$	24	87
$[(C_5H_5)Fe(CO)_2]_2$	24	88
$[(C_5Me_5)Fe(CO)_2]_2$	36	90

$(MeC_5H_4)Mn(CO)_3$, were found to be the most active; $[Cu(CH_3CN)_4]$, $[(C_5Me_5RuCl)]_2$, and $[(C_5Me_5)IrCl]_2$ gave poor or no yields.

To establish the generality of the catalytic processes with the CpFe- and CpMn-catalysts we used a series of isocyanates, including phenyl, *p*-chlorophenyl, *p*-methoxyphenyl, cyclohexyl and trimethylsilyl isocyanates. In a typical reaction approximately 25 mg of catalyst and 2 g of isocyanate in 20 mL of xylene were heated at reflux for 2–3 days. Conversions were determined by monitoring the infrared absorptions and the GC peaks of the residual isocyanate and the carbodiimide products. The isocyanates absorb at 2260–2265 cm^{-1} and the carbodiimides at 2120–2160 cm^{-1}; the isocyanourate (trimer) C=O appears at ~1675 cm^{-1} and the uretidione (dimer) at ~1756 cm^{-1}. Dimerization and trimerization of isocyanates were observed to a limited extent (less than 15%).

The results obtained from the reactions of the various isocyanates using the catalysts $[CpFe(CO)_2]_2$ and $MeCpMn(CO)_3$ are summarized in Table 2. With the same series of isocyanates the iron complex gave about 15% better conversion compared to the manganese compound. The electronic character of the isocyanate did not have a significant effect on reactivity or yield of the carbodiimide. For example, the conversions of phenyl isocyanate (94%) and cyclohexyl isocyanate (92%) using the iron catalyst are comparable. The carbodiimides were isolated as white solids in 15–40% yield upon cooling the reaction mixtures and filtration.[14]



Scheme 1.

A possible mechanism for the catalytic conversion of the isocyanate to carbodiimide is suggested in Scheme 1. Coordination of the isocyanate (after dissociation of a ligated CO) could enhance its susceptibility to nucleophilic attack by a second isocyanate to produce the heterocyclic complex **1**. This species could readily fragment with loss of CO_2 to generate the coordinated carbodiimide. Dissociation of the latter with association of another isocyanate would complete the catalytic cycle.

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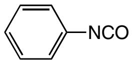
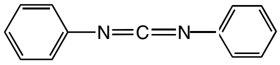
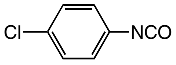
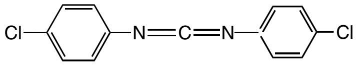
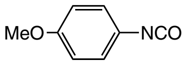
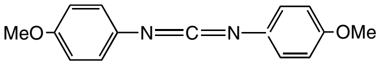
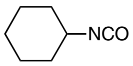
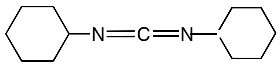
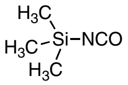
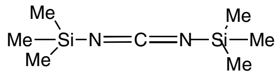
Table 2. Conversion of isocyantes to carbodiimides catalyzed by $CpMn(CO)_3$ and $[CpFe(CO)_2]_2$

Isocyanate	ν N=C=O (cm^{-1})	Carbodiimide	M^+	ν N=C=N (cm^{-1})	Conversion (%)[A]	Isolated yield (%)
	2260		*m/e* 194	2153	(a) 84[B] (b) 94[C]	(a) 43 (b) 41
	2264		*m/e* 263	2138	(a) 79 (b) 93	(a) 34 (b) 24
	2253		*m/e* 254	2143	(a) 88 (b) 96	(a) 22 (b) 28
	2259		*m/e* 206	2115	(a) 76 (b) 92	(a) 28 (b) 27
	2263		*m/e* 186	2127	(a) 68 (b) 93	(a) 12 —

[A] Determined by GC detection of RNCO versus internal naphthalene reference.

[B] $CpMn(Co)_3$ catalyst.

[C] $[CpFe(CO)_2]_2$ catalyst.

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14. *Representative procedure:* Cyclohexyl isocyanate (2.94 g, 0.0235 mol) in 25 mL of dry xylene was refluxed under nitrogen with 44 mg (0.125 mmol) of $[C_5H_5Fe(CO)_2]_2$ for 24 h. Upon cooling in an ice water bath, white crystalline dicyclohexyl carbodiimide precipitated, was collected by filtration and washed with cold diethyl ether; 0.29 g (27%), mp 30–35 °C. Its IR, NMR and mass spectra were identical to a commercial sample. IR and GC analysis of the reaction filtrates indicated an additional 30–40% of carbodiimide remaining in solution. All the carbodiimides have been reported previously and were characterized by IR, NMR and MS and compared with commercial samples (R = cyclohexyl and Me_3Si) or literature data (Ref. 15).
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