

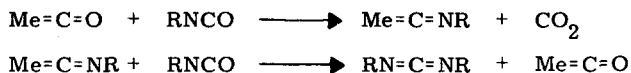
METAL CARBONYLS AS CATALYSTS IN THE CONVERSION  
OF ISOCYANATES TO CARBODIIMIDES

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The bonding in carbon monoxide complexes of d-group transition elements resembles a cumulative double bond system and since back-donation of electrons to the metal is possible, a polarization of the two bonds is indicated.

It was of interest to us to investigate the possibility of a cycloaddition sequence across the polarized bonds in metal carbonyls using isocyanates as the substrate. The first of the anticipated steps would involve the replacement of a carbon monoxide ligand by an isocyanide ligand via a cycloaddition reaction, thereby generating carbon dioxide. A subsequent reaction could result in the reformation of the metal carbonyl compound, and the formation of a carbodiimide. The overall reaction would amount to the catalytic conversion of an isocyanate to a carbodiimide, using the metal carbonyl compound as the catalyst.



The feasibility of occurrence of the first step was indicated by Manuel (1), who isolated carbonyl (phenyl isocyanide) complexes of iron and molybdenum from the reaction of phenyl isocyanate with dodecacarbonyltriiron and hexacarbonylmolybdenum, respectively.

When 1% by weight of iron pentacarbonyl was added to 0.2 mole of o-tolyl isocyanate, a rapid reaction occurred and carbon dioxide was generated. The reaction mixture was heated rapidly to the reflux temperature of o-tolyl isocyanate (approximately 180°C) and the time which was necessary to reach a reflux temperature of 250°C [this temperature was found to be indicative of a high degree of conversion in prior experiments using different catalysts

(2)], was measured. The infrared spectrum of the reaction mixture showed the absence of N=C=O absorption at  $2270\text{ cm}^{-1}$  and a strong N=C=N absorption at  $2125\text{ cm}^{-1}$ . Vacuum distillation afforded an 85.3% yield of di-o-tolylcarbodiimide, b. p.  $130\text{-}132^\circ/0.1\text{ mm}$ .

In Table 1 the metal carbonyls used, as well as the times necessary to convert o-tolyl isocyanate to di-o-tolylcarbodiimide are listed.

TABLE 1

Metal Carbonyl (1% by weight)	Time Required for Conversion (min. )	Yield of Distilled Di- o-Tolylcarbodiimide (%)
$\text{Fe}(\text{CO})_4\text{CNC}_6\text{H}_5$	25	83.0
$\text{Fe}(\text{CO})_5$	36	85.3
$\text{Fe}_2(\text{CO})_9$	43	82.3
$\text{W}(\text{CO})_6$	68	85.6
$\text{Mo}(\text{CO})_6$	200	85.0

The catalytic activity of the readily available metal carbonyls is comparable to that of the cyclic phosphine oxides (2, 3), and the absence of triisocyanurate formation is indicative of a cycloaddition sequence (4).

In order to verify the anticipated mechanism, phenyl isocyanate was added to five equivalents of iron pentacarbonyl in o-dichlorobenzene, and the mixture was heated for one hour at  $120\text{-}125^\circ\text{C}$ . The occurrence of reaction was indicated by the generation of carbon dioxide (5), and by the disappearance of the isocyanate absorption; however, no carbodiimide was detectable by infrared spectroscopy. Evaporation of the solvent and excess iron pentacarbonyl under vacuum afforded a mixture of iron complexes, from which tetracarbonyl-(phenyl isocyanide) iron, m. p.  $55\text{-}58^\circ$ , infrared bands at  $2160, 2058, 1994$  and  $1961\text{ cm}^{-1}$  (6), was isolated by fractional crystallization from ligroin. The less soluble iron complexes also contain isocyanide ligands, as evidenced by the formation of phenyl isocyanide (infrared band at  $2123\text{ cm}^{-1}$ ) upon heating in refluxing o-dichlorobenzene. Phenyl isocyanate-iron complexes, similar to those obtained by Manuel (1), were not present (absence of C=O absorption at  $1751\text{ cm}^{-1}$ ).

The intermediacy of isocyanide complexes in the catalytic scheme was further evidenced by the comparable rate of conversion, using tetracarbonyl (phenyl isocyanide) iron, synthesized according to the literature (7), as the catalyst (see Table 1).

The catalytic activity of metal carbonyls is not limited to aryl isocyanates, because di-cyclohexylcarbodiimide has been obtained when cyclohexyl isocyanate is heated in the presence of a catalytic amount of iron pentacarbonyl.

#### References and Notes

1. T. A. Manuel, J. Inorg. Chem., 3, 1703 (1964).
2. H. Ulrich, B. Tucker and A. A. R. Sayigh, J. Org. Chem., in press.
3. J. J. Monagle and J. V. Mengenhauser, J. Org. Chem., 31, 2321 (1966) and earlier references cited in this publication; see also K. Hunger, Tetrahedron Letters, 47, 5929 (1966).
4. Triisocyanurate formation is a side reaction in the base catalyzed transformation of isocyanates to carbodiimides; see, for example: W. Neumann and P. Fischer, Angew. Chem., 74, 801 (1962).
5. Identified by the precipitation of barium carbonate upon passing the generated gas into barium hydroxide.
6. F. A. Cotton and F. Zingales, J. Am. Chem. Soc., 83, 351 (1961) reported 2165, 2054, 1994 and 1970  $\text{cm}^{-1}$ .
7. W. Hieber and D. v. Pigenot, Chem. Ber., 89, 193 (1956).