Phenyl-Isocyanate as a Source of Phenylimido-ligand

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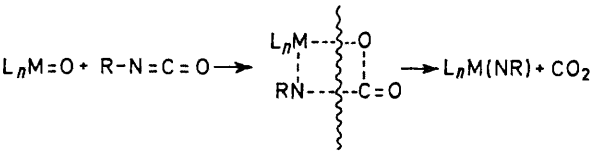
Summary Organic isocyanates react with transition-metal oxo-complexes to give imido-complexes plus carbon dioxide.

WE were interested to find out whether organic isocyanates RNCO can react with oxo-complexes of transition metals to yield carbon dioxide, the remaining imido (nitrene) fragment RN becoming co-ordinated to the transition-metal atom. The reaction might be envisaged as a kind of dismutation:



To test this possibility, the reaction of phenyl isocyanate with known[1] rhenium oxo-complexes *cis*- and *trans*-L_2ReOCl_3, where $L = Et_2PhP$, was chosen. In this case, identification of the expected reaction product, the phenylimido-complex of rhenium, $L_2Re(NPh)Cl_3$, was straightforward since the compound has been described by Chatt and Rowe.[1]

Heating (4 h) the blue *cis*-L_2ReOCl_3 (0·64 g, 0·1 mmole) with phenyl isocyanate (0·55 ml, 0·5 mmole) under reflux in xylene (6 ml) in an argon atmosphere resulted in rapid evolution of carbon dioxide (0·07 mmole). After evaporation of solvent, the residue was recrystallized several times from toluene–hexane to remove the *trans*-L_2ReOCl_3 impurity,[†] giving the complex $L_2Re(NPh)Cl_3$, m.p. 196—199°. The same complex has been isolated from the reaction of *trans*-L_2ReOCl_3 with phenyl isocyanate under similar conditions. Comparison of i.r. spectra and mixed m.p. determinations showed the products to be identical with the phenylimido-complex $L_2Re(NPh)Cl_3$ obtained earlier by Chatt and Rowe[1] in the reaction of blue *cis*-L_2ReOCl_3 with aniline. The *trans*-L_2ReOCl_3 complex also reacted with aniline in boiling xylene, affording the phenylimido-complex $L_2Re(NPh)(Cl_3$ in quantitative yield.

We have observed similar reactions in the case of $(Ph_3P)_2ReOCl_3$.[1] The complex reacted both with phenyl isocyanate (in boiling xylene) and with aniline (in boiling benzene) to yield the same solid, m.p. $>$ 150° (slow decomposition). On the basis of elemental analysis and the i.r. spectrum of the compound (absence of Re–O and N–H absorptions), the structure is tentatively assigned as $(Ph_3P)_2Re(NPh)Cl_3$.

This reaction of transition-metal oxo-complexes with phenyl isocyanate seems to be fairly general. Carbon dioxide evolution has also been observed as a result of the reaction of phenyl isocyanate with other oxo-complexes such as $(\pi\text{-}C_5H_5)_2TiO_2$, $(Ph_3P)_2PtO_2$, $(acac)_2VO$, $(\pi\text{-}C_5H_5)\text{-}MoOCl_2$ *etc.*

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[†] On heating the blue *cis*-L_2ReOCl_3 with phenyl isocyanate under reflux in benzene instead of in xylene, only *cis–trans*-isomerization occurred.

[1] J. Chatt and G. A. Rowe, *J. Chem. Soc.*, 1962, 4028.