Fixation of Molecular Nitrogen under Mild Conditions

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Summary Molecular nitrogen has been reduced to ammonia by various compounds of niobium, zirconium, and tungsten in a strongly reducing medium.

SOME transition-metal complexes in their reduced states have the ability to fix molecular nitrogen under conditions of essentially atmospheric temperature and pressure.[1] The most extensive study to date has been done with titanium systems. It seemed possible that other transition elements that exhibit two oxidation states two units apart might also be capable of fixing nitrogen. We report our preliminary successes with various compounds of niobium, zirconium, and tungsten.

The experimental method was similar in each case. A solution of the metal compound in tetrahydrofuran was added dropwise to a solution of sodium dihydronaphthylide. A stream of nitrogen was continuously bubbled through the reaction mixture. Ethanol was then added, and the escaping stream of gas was tested qualitatively for ammonia by bubbling it through Nessler's Reagent and quantitatively by passing it into acid.

From the bis-cyclopentadienyl complexes of niobium and zirconium and the alkoxide complexes of tungsten, only modest yields of ammonia have been produced:

$$\text{Reactions: A} + \text{Na}^{+}\text{C}_{10}\text{H}_8^{\cdot-} \xrightarrow{N_2} \text{(B)}$$

$$\text{(B)} + \text{C}_2\text{H}_5\text{OH} \xrightarrow{N_2} \text{NH}_3$$

A	%NH_3[a]
$C_{10}H_{10}NbCl_3$	2·56
$C_{10}H_{10}ZrCl_2$	2·75
$W(OMe)_2Cl_3$	0·28
$W(OEt)_2Cl_2(EtOH)$	0·00[b]

[a] Based on moles of ammonia: moles of transition metal complex.

[b] Although no yield of ammonia could be measured in the acid, the qualitative test for ammonia was positive.

These classes of compounds may form a general means of fixing molecular nitrogen under mild conditions. Of utmost interest is the nature of the intermediate, (B).

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