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FORMATION OF NITROGEN OXIDES FROM THE NITROGEN LIGAND IN CIS-$(Me_2PhP)_4Mo(N_2)_2$ BY THE ACTION OF NITRONIUM SALTS

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We found that the reaction of cis-$(Me_2PhP)_4Mo(N_2)_2$ with nitronium salts in CH_2Cl_2, $CHCl_3$, and sulfolane gives the rapid liberation of gas consisting of molecular nitrogen, N_2O, and NO. A study of this reaction using labelled cis-$(Me_2PhP)_4Mo(^{15}N_2)_2$ and unlabelled nitronium tetrafluoroboride $^{14}NO_2BF_4$ in absolute sulfolane showed that the gaseous products formed under these conditions contain $^{15}N_2$ from the starting complex and ^{14}NO, $^{14}N_2O$, and $^{14}N_2$ obtained as a result of the reduction of $^{14}NO_2BF_4$ due to Mo(0) electrons. Products corresponding to the attack of the nitrogen ligand by the nitronium cation are not found in the gas phase.

We have found, however, that if the reaction of cis-$(Me_2PhP)_4Mo(^{15}M_2)_2$ with $^{14}NO_2BF_4$ is carried out in the presence of small amounts of water, labelled $^{15}N{=}^{14}N{=}O$ and ^{15}NO as well as $^{15}N{\equiv}^{14}N$ appear in the gaseous products in addition to $^{15}N_2$, $^{14}N_2$, $^{14}N_2O$, and ^{14}NO. The yield of these products depends on the amount of added water, reaching about 5 mole % relative to Mo ($^{15}N{=}^{14}N{=}O$:$^{15}N{\equiv}^{14}N$ ~ 20:2:1) when the [Mo]:NO_2BF_4:H_2O mole ratio is 1:6:24. The replacement of NO_2BF_4 by a nitrating mixture ([Mo]:HNO_3:H_2SO_4 = 1:6:12) enhances the yield of $^{15}N{=}^{14}N{=}O$, ^{15}NO, and $^{15}N{\equiv}^{14}N$ to 21 mole % (the mole ratio of these products was 17:1:3). The addition of water is not required in this case. Only trace amounts of $^{15}N{=}^{14}N{=}O$, $^{15}N{=}O$, and $^{15}N{\equiv}^{14}N$ are formed under the same conditions but in the absence of H_2SO_4.

These results indicate the possibility of involving the nitrogen ligand in cis-$(Me_2PhP)_4Mo(N_2)_2$ in a reaction with a nitronium cation to form nitrogen oxides. The protonation of the nitrogen ligand is apparently the first step in this reaction.

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