FORMATION OF NITROGEN OXIDES FROM THE NITROGEN LIGAND IN cis-(Me₂PhP)₄Mo(N₂)₂ AND trans-(Ph₂PCH₂CH₂PPh₂)₂W(N₂)₂ BY THE ACTION OF NITROSONIUM SALTS

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UDC 542.91:546.172.7:541.49:547.1'13:546.77/78

In recent work [1], we have shown that the reaction of cis- $(Me_2PhP)_4Mo({}^{15}N_2)_2$ (I) with unlabelled nitrosonium tetrafluoroborate ${}^{14}NO_2BF_4$ in sulfolane in the presence of water or acids gives significant amounts of labelled nitrous oxide (${}^{15}N={}^{14}N=0$) and nitric oxide (${}^{15}NO$) as well as ${}^{15}N={}^{14}N$, which may be seen as the products of the attack of the nitrogen ligand by the nitronium cation. In the present communication, we report that an analogous reaction is observed upon the reaction of the nitrosonium cation with (I) and trans- $(dppe)_2W({}^{15}N_2)_2$ (II, dppe = $Ph_2PCH_2CH_2PPh_2$) in the presence of acids.

In a typical experiment, 0.1 mmole complex (I) was mixed with 0.6 mmole ${}^{14}\text{NOBF}_4$ and 0.12 mmole concentrated $H_2\text{SO}_4$ in 2 ml sulfolane at 25°C in vacuum. Vigorous gas evolution was noted. Mass spectral analysis indicated that this gas consisted of a 68:3:29 mixture of ${}^{15}\text{N}={}^{14}\text{N}=0$, ${}^{15}\text{NO}$, and ${}^{15}\text{N}={}^{14}\text{N}$ (the total yield was 19 mole % relative to Mo). The same products are formed in 53:4:43 ratio upon the reaction of (II) with ${}^{14}\text{NOBF}_4$ in the presence of $H_2\text{SO}_4$. In this case, the total yield was 17 mole %. Also, the same products are formed in 50:9:41 ratio upon the reaction of (II) with ${}^{14}\text{NO}_2\text{BF}_4$ in the presence of $H_2\text{SO}_4$; the total yield was 7 mole %. If the reaction is carried out in the absence of acid, only traces of these products are obtained in all cases.

We may assume that the formation of the labelled nitrogen oxides and $^{15}=^{14}N$ in the reactions of (I) and (II) with either $^{14}NOBF_4$ or $^{14}NO_2BF_4$ proceeds, at least partially, through the initial protonation of the nitrogen ligand with the formation of the corresponding hydrazido(2-) complexes [2], which are then attacked by nitrosonium or nitronium cations. Indeed, we found that independently synthesized (Me_2PhP)_3Mo($^{15}N_2H_2$)Cl₂ and (dppe)_2W($^{15}N_2H_2$)Cl₂ [2] react with $^{14}NOBF_4$ or $^{14}NO_2BF_4$ in sulfolane at 25°C in the absence of acid to give $^{15}N=^{14}N=0$, ^{15}NO , and $^{15}N=^{14}N$; the overall yield was 10-20 mole %.

The reactions of (I) and (II) with $NOBF_4$ and NO_2BF_4 may be considered a proton-catalyzed attack of a nitrogen ligand in these complexes by nitrosonium and nitronium cations.

LITERATURE CITED

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