

## Organometallic Chemistry

### Acid-catalyzed attack of the dinitrogen ligand in the *cis*-(Me<sub>2</sub>PhP)<sub>4</sub>Mo(N<sub>2</sub>)<sub>2</sub> and *trans*-(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>W(N<sub>2</sub>)<sub>2</sub> complexes by nitronium and nitrosonium cations with the formation of nitrogen oxides

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The interaction of labeled dinitrogen complexes *cis*-(Me<sub>2</sub>PhP)<sub>4</sub>Mo(<sup>15</sup>N<sub>2</sub>)<sub>2</sub> and *trans*-(dppe)<sub>2</sub>W(<sup>15</sup>N<sub>2</sub>)<sub>2</sub> with non-labeled nitronium and nitrosonium fluoroborates, <sup>14</sup>NO<sub>2</sub>BF<sub>4</sub> and <sup>14</sup>NOBF<sub>4</sub>, in sulfolane at room temperature in the presence of H<sub>2</sub>SO<sub>4</sub> results in rapid formation of labeled nitrous and nitric oxides (<sup>15</sup>N<sup>14</sup>NO, <sup>15</sup>NO), as well as <sup>15</sup>N<sup>14</sup>N. The yield of the products depends on the reagent ratio and reaches 10–20 mol. % per mole of a complex under optimum conditions. The mechanism of the reactions found is proposed. It involves the step of protonation of the dinitrogen ligand to form the corresponding hydrazido(2-) derivatives, which are then attacked by nitronium or nitrosonium cations. In accordance with the mechanism proposed, it was established that the hydrazido(2-) complexes, (Me<sub>2</sub>PhP)<sub>3</sub>Mo(<sup>15</sup>N<sub>2</sub>H<sub>2</sub>)Cl<sub>2</sub> and (dppe)<sub>2</sub>W(<sup>15</sup>N<sub>2</sub>H<sub>2</sub>)Cl<sub>2</sub>, are capable of forming <sup>15</sup>N<sup>14</sup>NO, <sup>15</sup>NO, and <sup>15</sup>N<sup>14</sup>N under the action of <sup>14</sup>NO<sub>2</sub>BF<sub>4</sub> and <sup>14</sup>NOBF<sub>4</sub> in the absence of an acid.

**Key words:** complexes of molecular nitrogen, hydrazido(2-) complexes, molybdenum, tungsten, nitrogen oxides, nitronium and nitrosonium salts, catalysis by acids.

It is known that in a number of dinitrogen complexes of transition metals, the coordinated dinitrogen molecule can undergo electrophilic attack by protic and Lewis acids. It has been demonstrated for the rhenium complex, (Me<sub>2</sub>PhP)<sub>4</sub>Re(N<sub>2</sub>)<sub>2</sub>, that the attack of the dinitrogen ligand by Lewis acids (BF<sub>3</sub>, R<sub>3</sub>Al, etc.) occurs through the formation of adducts at the terminal nitrogen atom (e.g., (Me<sub>2</sub>PhP)<sub>4</sub>Re(Cl)N=N·AlEt<sub>3</sub>).<sup>1</sup> The composition of the products of the interaction of the

dinitrogen ligand with protons depends on the nature of the transition metal and the ligands surrounding it. In the case of bis-dinitrogen complexes of molybdenum and tungsten, (dppe)<sub>2</sub>M(N<sub>2</sub>)<sub>2</sub> (M = Mo, W; dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>), the reaction stops at the step of the formation of hydrazido(2-) derivatives, (dppe)<sub>2</sub>M(N<sub>2</sub>H<sub>2</sub>)X<sub>2</sub>, which can be isolated in pure form.<sup>2</sup> If L<sub>4</sub>M(N<sub>2</sub>)<sub>2</sub> (M = Mo, W; L = Me<sub>2</sub>PhP, MePh<sub>2</sub>P) complexes, as well as (Ph<sub>3</sub>P)<sub>3</sub>Co(N<sub>2</sub>)Mg(THF)<sub>2</sub> and

**Table 1.** Ratio of the products of the dinitrogen ligand transformation and overall yield of the products in the reaction of complex **1** with  $^{14}\text{NO}_2\text{BF}_4$  in sulfolane in the presence of water

$\text{NO}_2^+:\text{H}_2\text{O}:\mathbf{1}$ molar ratio	Amount of gas liberated  mol/mol <b>1</b>	Products of dinitrogen ligand transformation and ratio of the products (%)			Overall yield of the products per mol of <b>1</b> (mol. %)
		$^{15}\text{NO}$	$^{15}\text{N}^{14}\text{NO}$	$^{15}\text{N}^{14}\text{N}$	
6 : 0 : 1	3.3	47	53	0	0.3
6 : 3 : 1	3.6	39	61	0	0.5
6 : 6 : 1	3.9	28	72	0	0.9
6 : 12 : 1	3.7	42	58	0	2.5
6 : 24 : 1	4.1	8	90	2	4.9

( $\text{Cp}_2\text{ZrN}_2$ ) $_2\text{N}_2$  complexes, are used, the reaction proceeds further to form ammonia and/or hydrazine.<sup>3–5</sup>

The purpose of the present work was to study the possibility of the attack of the dinitrogen ligand in the *cis*-( $\text{Me}_2\text{PhP}$ ) $_4\text{Mo}(\text{N}_2)_2$  and *trans*-( $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ) $_2\text{W}(\text{N}_2)_2$  complexes by strong electrophilic agents, such as nitronium and nitrosonium cations.\*

### Results and Discussion

The interaction of dinitrogen complexes with nitronium and nitrosonium cations can follow three main pathways. The first pathway is an attack of the dinitrogen ligand by the positively charged nitrogen atom of  $\text{NO}_2^+$  or  $\text{NO}^+$  cations. The second pathway is oxidation of the dinitrogen ligand due to transfer of oxygen from the nitronium or nitrosonium cation. Finally, the third pathway is an attack of the  $\text{NO}_2^+$  or  $\text{NO}^+$  cations on the metal atom with displacement of the dinitrogen ligand.

It is possible to discriminate these pathways and to understand the origin of the reaction products by using  $^{15}\text{N}$ -labeled compounds. To achieve this goal, we studied the interaction of labeled (97 at. %  $^{15}\text{N}$ ) dinitrogen complexes, *cis*-( $\text{Me}_2\text{PhP}$ ) $_4\text{Mo}(^{15}\text{N}_2)_2$  (**1**) and *trans*-( $\text{dppe}$ ) $_2\text{W}(^{15}\text{N}_2)_2$  (**2**), with non-labeled nitronium and nitrosonium fluoroborates,  $^{14}\text{NO}_2\text{BF}_4$  and  $^{14}\text{NOBF}_4$ .

The experiments were carried out in various solvents (sulfolane,  $\text{CH}_2\text{Cl}_2$ , THF, *etc.*) at room temperature by mixing the reagents *in vacuo*. Vigorous liberation of a gas in 10–15 min in the course of the reaction was observed. The analysis of gaseous products by high resolution mass spectrometry ( $M/\Delta M = 15000$ ) showed that they were composed of  $^{15}\text{N}_2$ , as well as  $^{14}\text{NO}$ ,  $^{14}\text{N}_2\text{O}$ , and  $^{14}\text{N}_2$ . Absorption bands in the region of 1800–2200  $\text{cm}^{-1}$ , which are typical of the coordinated dinitrogen molecule, were absent in the IR spectra of the solid products isolated after the reaction was completed. This indicates total destruction of the starting complex during the reaction.

The overall amount of gas liberated increases with increasing excess of nitronium or nitrosonium cations with respect to complexes **1** and **2**, but no more than 6–8 mols of the gas per mol of the complex is formed even with a reagent ratio of 18 : 1. In most cases, the amount of  $^{15}\text{N}_2$  liberated is close to 2 mol per mol of complex **1** or **2**. The rest of the gas consists of  $^{14}\text{NO}$ ,  $^{14}\text{N}_2\text{O}$ , and  $^{14}\text{N}_2$ . The data obtained suggest that the main direction of the reaction is attack of the metal atom in complexes **1** and **2** by nitronium and nitrosonium cations resulting in displacement of the dinitrogen ligand from the coordination sphere and reduction of  $\text{NO}_2^+$  and  $\text{NO}^+$  cations into nitrogen oxides and molecular nitrogen by electrons from Mo(0) or W(0).

Nevertheless, in some experiments we found that, along with the above gaseous products ( $^{15}\text{N}_2$ ,  $^{14}\text{NO}$ ,  $^{14}\text{N}_2\text{O}$ , and  $^{14}\text{N}_2$ ), small amounts of labeled nitrous and nitric oxides ( $^{15}\text{N}^{14}\text{NO}$ ,\*  $^{15}\text{NO}$ ), as well as  $^{15}\text{N}^{14}\text{N}$ , which may be considered the products of the attack of the dinitrogen ligand in the complexes by the nitronium and nitrosonium cations, are formed in the reaction. However, the yields of  $^{15}\text{N}^{14}\text{NO}$ ,  $^{15}\text{NO}$ , and  $^{15}\text{N}^{14}\text{N}$  differed from one experiment to another and sometimes were equal to zero. Since nitronium and nitrosonium salts are very hygroscopic and rapidly undergo hydrolysis, the instability of the results can be explained by the different degree of hydrolysis of the starting nitronium and nitrosonium fluoroborates.

In fact, it turned out (Table 1) that the overall yield of  $^{15}\text{N}^{14}\text{NO}$  and  $^{15}\text{NO}$  does not exceed 0.3 mol. % with respect to Mo, and  $^{15}\text{N}^{14}\text{N}$  is absent,\*\* when the

\* Although the peak of the labeled nitrous oxide with a mass of 45.012 a.u. may correspond to two isotopomers,  $^{15}\text{N}^{14}\text{NO}$  and  $^{14}\text{N}^{15}\text{NO}$ , quantitative treatment of the mass-spectrometry data taking into account fragmentation processes indicates that not less than 80–85 % of the peak with  $m/z$  45.012 belongs to the  $^{15}\text{N}^{14}\text{NO}$  isotopomer both in this series of experiments and in all subsequent experiments.

\*\* To be more accurate, the amount of  $^{15}\text{N}^{14}\text{N}$  does not exceed its starting amount in the labeled dinitrogen complex. All data given in this work are corrected with respect to isotopic composition of the starting products and fragmentation processes.

\* For the preliminary communications, see Refs. 6 and 7.

**Table 2.** Ratio of the products of dinitrogen ligand transformation and overall yield of the products in the reactions of complexes **1** and **2** with  $^{14}\text{NO}_2\text{BF}_4$  in sulfolane in the presence of acids

Complex	Reagents	Reagents complex molar ratio	Amount of gas liberated (mol/mol of complex)	Products of dinitrogen ligand transformation and ratio of the products (%)			Overall yield of the products per mol of complex (mol. %)
				$^{15}\text{NO}$	$^{15}\text{N}^{14}\text{NO}$	$^{15}\text{N}^{14}\text{N}$	
<b>1</b>	$^{14}\text{NO}_2\text{BF}_4 + \text{H}^{14}\text{NO}_3 + \text{HBF}_4$	3:3:6:1	4.0	7	93	0	9
	$^{14}\text{NO}_2\text{BF}_4 + \text{H}_2\text{SO}_4$	6:12:1	4.6	3	77	20	23
	$\text{H}^{14}\text{NO}_3 + \text{H}_2\text{SO}_4$	6:12:1	4.2	5	79	16	21
	$\text{H}^{14}\text{NO}_3$	6:1	3.7	38	62	0	0.4
<b>2</b>	$^{14}\text{NO}_2\text{BF}_4 + \text{H}_2\text{SO}_4$	3:12:1	2.7	6	51	43	7
		6:12:1	4.5	9	50	41	7
		18:12:1	5.7	19	49	32	4

reaction of complex **1** with dry  $\text{NO}_2\text{BF}_4$  (the reagent purchased from the Alpha company) is carried out in dry sulfolane. However, if the sulfolane is moistened, the yield of the labeled nitrogen oxides is increased with increasing the amount of water added and reaches ~5 mol. % (with respect to Mo) at the ratio  $\text{NO}_2\text{BF}_4 : \text{H}_2\text{O} : 1 = 6 : 24 : 1$ , in this case  $^{15}\text{N}^{14}\text{N}$  also appears.

Since  $\text{HNO}_3$  and  $\text{HBF}_4$  are formed upon hydrolysis of  $\text{NO}_2\text{BF}_4$ , one may assume that the presence of an acid in the reaction medium is necessary for the interaction of the dinitrogen ligand with the nitronium cation. To check this assumption, we studied the interaction of complex **1** with  $\text{NO}_2\text{BF}_4$  in the absence of water but in the presence of acids in the reaction mixture (Table 2). It turned out that the reaction of complex **1** with a mixture of  $\text{NO}_2\text{BF}_4$ ,  $\text{HNO}_3$ , and  $\text{HBF}_4$ , which simulates partial hydrolysis of  $\text{NO}_2\text{BF}_4$ , leads to products similar to those obtained when water was added. If the reaction of complex **1** with  $\text{NO}_2\text{BF}_4$  is carried out in the presence of conc.  $\text{H}_2\text{SO}_4$ , the yield of  $^{15}\text{N}^{14}\text{NO}$ ,  $^{15}\text{NO}$ , and  $^{15}\text{N}^{14}\text{N}$  is increased to 23 mol. % with respect to Mo. Similar results are obtained when nitration mixture ( $\text{HNO}_3 + \text{H}_2\text{SO}_4$ ), which is known to generate nitronium cations, is used instead of  $\text{NO}_2\text{BF}_4$ . However, fuming nitric acid in the absence of  $\text{H}_2\text{SO}_4$  and  $\text{NO}_2\text{BF}_4$  gives only traces of  $^{15}\text{N}^{14}\text{NO}$  and  $^{15}\text{NO}$ , and  $^{15}\text{N}^{14}\text{N}$  is not formed at all under these conditions. Such a dramatic decrease in the yield of labeled nitrogen oxides and  $^{15}\text{N}^{14}\text{N}$  is evidently due to negligible  $\text{NO}_2^+$  concentration (no more than 1 %) in 100%  $\text{HNO}_3$  (as compared with the nitration mixture).<sup>8</sup> Hence, simultaneous presence of nitronium cations and protons in the reaction medium is necessary for the formation of  $^{15}\text{N}^{14}\text{NO}$ ,  $^{15}\text{NO}$ , and  $^{15}\text{N}^{14}\text{N}$  from the coordinated labeled dinitrogen in complex **1**.

In order to prove the validity of this conclusion for the tungsten dinitrogen complex **2**, we studied the interaction of **2** with  $\text{NO}_2\text{BF}_4$  in the presence of  $\text{H}_2\text{SO}_4$ . As

can be seen from Table 2, the same labeled products ( $^{15}\text{N}^{14}\text{NO}$ ,  $^{15}\text{NO}$ , and  $^{15}\text{N}^{14}\text{N}$ ) as with complex **1** are formed in this case, although their overall yield is lower. In addition, the change in the ratio of these products, namely, the significant increase in the fraction of  $^{15}\text{N}^{14}\text{N}$ , is observed, but  $^{15}\text{N}^{14}\text{NO}$  is still the main component. The increase in the excess of  $\text{NO}_2\text{BF}_4$ , with respect to complex **2**, from 3 : 1 to 6 : 1 does not result in an increase in the overall yield of  $^{15}\text{N}^{14}\text{NO}$ ,  $^{15}\text{NO}$ , and  $^{15}\text{N}^{14}\text{N}$ , as well as in a change in their ratio. At the same time, the overall yield of gas liberated is increased due to the rise of the amount of products formed as a result of the reduction of the nitronium cation ( $^{14}\text{NO}$ ,  $^{14}\text{N}_2\text{O}$ , and  $^{14}\text{N}_2$ ). The main compound among these non-labeled substances is  $^{14}\text{NO}$ ,  $^{14}\text{N}_2\text{O}$  (the product of reductive dimerization of  $^{14}\text{NO}$ ) is formed in smaller amounts, and  $^{14}\text{N}_2$  is formed in an even lower amount, *i.e.*, the yields are decreased with increasing degree of reduction of  $^{14}\text{NO}_2^+$ . The same picture is observed during the interaction of  $\text{NO}_2^+$  with molybdenum complex **1** in the presence of acids or water.

It is important that, in all experiments with  $\text{NO}_2^+$ , the ratios of  $^{14}\text{NO} : ^{14}\text{N}_2\text{O}$  differ strongly from those of the corresponding labeled products,  $^{15}\text{NO} : ^{15}\text{N}^{14}\text{NO}$  (Table 3). This fact, as well as the above-mentioned observation that the peak of the labeled nitrous oxide is composed of no less than 80–85 %  $^{15}\text{N}^{14}\text{NO}$ , indicates that the predominant part of  $^{15}\text{N}^{14}\text{NO}$  is formed not in the reaction of reductive codimerization of  $^{15}\text{NO}$  and  $^{14}\text{NO}$  (which should give equal amounts of  $^{15}\text{N}^{14}\text{NO}$  and  $^{14}\text{N}^{15}\text{NO}$ ) but according to another route of the reaction. The similar conclusion can also be made concerning the ways of the formation of  $^{15}\text{N}^{14}\text{N}$  (*cf.* the  $^{14}\text{N}_2\text{O} : ^{14}\text{N}_2$  and  $^{15}\text{N}^{14}\text{NO} : ^{15}\text{N}^{14}\text{N}$  ratios in Table 3). In this case at least a fraction of  $^{15}\text{N}^{14}\text{N}$  is formed by an independent mechanism rather than by reduction of  $^{15}\text{N}^{14}\text{NO}$ .

Along with nitronium salts, nitrosonium salts (for example,  $\text{NOBF}_4$ ) also react with complexes **1** and **2** to give the same products (Tables 3 and 4) and with

**Table 3.** Ratio of  $^{15}\text{NO} : ^{15}\text{N}^{14}\text{NO} : ^{15}\text{N}^{14}\text{N}$  and  $^{14}\text{NO} : ^{14}\text{N}_2\text{O} : ^{14}\text{N}_2$  in reactions of complexes **1–4** with  $^{14}\text{NO}_2\text{BF}_4$  and  $^{14}\text{NOBF}_4$  in sulfolane

Complex	Reagents	Reagents	Molar ratio	
		complex molar ratio	$^{15}\text{NO} : ^{15}\text{N}^{14}\text{NO} : ^{15}\text{N}^{14}\text{N}$	$^{14}\text{NO} : ^{14}\text{N}_2\text{O} : ^{14}\text{N}_2$
<b>1</b>	$^{14}\text{NO}_2\text{BF}_4 + \text{H}_2\text{SO}_4$	6:12:1	1:22:5.6	7.5:1.5:1
	$^{14}\text{NOBF}_4 + \text{H}_2\text{SO}_4$	6:12:1	1:22:9.3	6:2:1
<b>2</b>	$^{14}\text{NO}_2\text{BF}_4 + \text{H}_2\text{SO}_4$	6:12:1	1:5.8:4.8	7.3:5.8:1
	$^{14}\text{NOBF}_4 + \text{H}_2\text{SO}_4$	6:12:1	1:13:11	10:11:1
<b>3</b>	$^{14}\text{NO}_2\text{BF}_4$	6:1	1:11:4.5	0.8:2:1
	$^{14}\text{NOBF}_4$	6:1	0:1.4:1	14:4.7:1
<b>4</b>	$^{14}\text{NO}_2\text{BF}_4$	6:1	1:11:20	5.6:2.8:1
	$^{14}\text{NOBF}_4$	6:1	0:1:2.2	15:12:1

**Table 4.** Ratio of the products of the dinitrogen ligand transformation and overall yield of the products in the reactions of complexes **1** and **2** with  $^{14}\text{NO}_2\text{BF}_4$  in sulfolane in the presence of acids

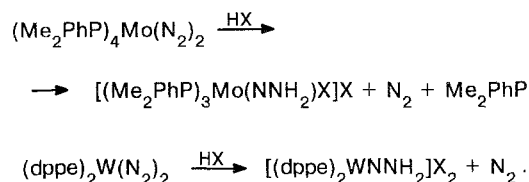
Complex	Reagents	Reagents	Amount of gas liberated (mol/mol of complex)	Products of dinitrogen ligand transformation and ratio of the products (%)			Overall yield of the products per mol of complex (mol. %)
		complex molar ratio		$^{15}\text{NO}$	$^{15}\text{N}^{14}\text{NO}$	$^{15}\text{N}^{14}\text{N}$	
<b>1</b>	$^{14}\text{NOBF}_4 + \text{H}_2\text{SO}_4$	3:12:1	3.0	2	79	19	23
		6:12:1	5.1	3	68	29	19
		18:12:1	7.8	4	73	23	18
	$\text{Na}^{14}\text{NO}_2 + \text{H}_2\text{SO}_4$	6:30:1	5.7	8	54	38	7
<b>2</b>	$^{14}\text{NOBF}_4 + \text{H}_2\text{SO}_4$	3:12:1	2.9	3	53	44	9
		6:12:1	4.7	4	53	43	17
		18:12:1	6.4	5	83	12	15
	$\text{Na}^{14}\text{NO}_2 + \text{H}_2\text{SO}_4$	6:30:1	6.5	47	47	6	2

retention of the same regularities, as in the above reaction of compounds **1** and **2** with  $\text{NO}_2\text{BF}_4$ .

Thus, in the case of complex **1**, the overall yield of labeled products ( $^{15}\text{NO}$ ,  $^{15}\text{N}^{14}\text{NO}$ , and  $^{15}\text{N}^{14}\text{N}$ ) remains practically unchanged (18–23 mol. % with respect to Mo) when the ratio  $\text{NO}^+ : \text{H}_2\text{SO}_4 : \mathbf{1}$  is changed from 3 : 12 : 1 to 18 : 12 : 1, the ratio of the products also changes insignificantly, like the ratio of the products of the reduction of  $\text{NO}^+$  ( $^{14}\text{NO}$ ,  $^{14}\text{N}_2\text{O}$ , and  $^{14}\text{N}_2$ ). In the case of complex **2**, with the ratio  $\text{NO}^+ : \text{H}_2\text{SO}_4 : \mathbf{2} = 3 : 12 : 1$ , the overall yield of  $^{15}\text{NO}$ ,  $^{15}\text{N}^{14}\text{NO}$  and  $^{15}\text{N}^{14}\text{N}$  is as low as 9 mol. %. At higher ratios, the yield is increased to 15–17 mol. %. The relative composition of both labeled and non-labeled reaction products is changed simultaneously.  $\text{NaNO}_2$  (in the presence of  $\text{H}_2\text{SO}_4$ ) can be used instead of  $\text{NOBF}_4$ . However, in this case the yields of  $^{15}\text{NO}$ ,  $^{15}\text{N}^{14}\text{NO}$ , and  $^{15}\text{N}^{14}\text{N}$  decrease. If the interaction of complexes **1** and **2** with  $^{14}\text{NOBF}_4$  is carried out in the absence of an acid,  $^{15}\text{NO}$ ,  $^{15}\text{N}^{14}\text{NO}$ , and  $^{15}\text{N}^{14}\text{N}$  are not formed.

Previously Chatt and his colleagues<sup>2</sup> have shown that the dinitrogen ligand in complexes **1** and **2** is readily

protonated by acids to give the corresponding hydrazido(2–) derivatives:



Taking this fact into account, one may suppose that the revealed reactions of complexes **1** and **2** with  $\text{NO}_2^+$  and  $\text{NO}^+$  proceed in the presence of acids (at least, partially) through the intermediate formation of such hydrazide derivatives which are then attacked by nitronium or nitrosonium cations.

In fact, we showed that the complexes  $(\text{Me}_2\text{PhP})_3\text{Mo}(^{15}\text{N}_2\text{H}_2)\text{Cl}_2$  (**3**) and  $(\text{dppe})_2\text{W}(^{15}\text{N}_2\text{H}_2)\text{Cl}_2$  (**4**) react with  $^{14}\text{NO}_2\text{BF}_4$  (Table 5) and  $^{14}\text{NOBF}_4$  (Table 6) in sulfolane at 25 °C in the absence of an acid to form  $^{15}\text{NO}$ ,  $^{15}\text{N}^{14}\text{NO}$ , and  $^{15}\text{N}^{14}\text{N}$  in approximately the

**Table 5.** Ratio of the products of hydrazido ligand transformation and overall yield of the products in the reactions of complexes **3** and **4** with  $^{14}\text{NO}_2\text{BF}_4$  in sulfolane in the presence of acids

Complex	Reagents	Reagents complex molar ratio	Amount of gas liberated (mol/mol of complex)	Products of dinitrogen ligand transformation and ratio of the products (%)			Overall yield of the products per mol of complex (mol. %)
				$^{15}\text{NO}$	$^{15}\text{N}^{14}\text{NO}$	$^{15}\text{N}^{14}\text{N}$	
<b>3</b>	$^{14}\text{NO}_2\text{BF}_4$	3:1	2.3	6	67	27	11
		6:1	2.2	6	67	27	13
		18:1	2.3	7	64	29	14
	$^{14}\text{NO}_2\text{BF}_4 + \text{H}_2\text{SO}_4$	6:12:1	3.4	9	77	14	25
<b>4</b>	$^{14}\text{NO}_2\text{BF}_4$	3:1	1.6	4	34	62	15
		6:1	3.2	3	36	61	19
		18:1	3.6	3	46	51	11
	$^{14}\text{NO}_2\text{BF}_4 + \text{H}_2\text{SO}_4$	6:12:1	3.1	5	53	42	24

**Table 6.** Ratio of the products of hydrazido ligand transformation and overall yield of the products in the reactions of complexes **3** and **4** with  $^{14}\text{NOBF}_4$  in sulfolane in the presence of acids

Complex	Reagents	Reagents complex molar ratio	Amount of gas liberated (mol/mol of complex)	Products of dinitrogen ligand transformation and ratio of the products (%)			Overall yield of the products per mol of complex (mol. %)
				$^{15}\text{NO}$	$^{15}\text{N}^{14}\text{NO}$	$^{15}\text{N}^{14}\text{N}$	
<b>3</b>	$^{14}\text{NOBF}_4$	3:1	1.8	0	53	47	3
		6:1	3.8	0	59	41	10
		18:1	4.8	0	60	40	5
	$^{14}\text{NOBF}_4 + \text{H}_2\text{SO}_4$	6:12:1	3.6	5	56	39	13
<b>4</b>	$^{14}\text{NOBF}_4$	3:1	2.5	0	17	83	13
		6:1	3.8	0	31	69	15
		18:1	5.7	0	54	46	16
	$^{14}\text{NOBF}_4 + \text{H}_2\text{SO}_4$	6:12:1	4.4	5	40	55	9

same overall yield (10–20 mol. %) as in the case of dinitrogen complexes **1** and **2**. An increase in the yield in the presence of  $\text{H}_2\text{SO}_4$  is observed only in the reaction of complexes **3** and **4** with  $\text{NO}_2\text{BF}_4$ . It should be noted that labeled gaseous nitrogen  $^{15}\text{N}_2$  is also liberated in all reactions (80–90 mol. % per mol of the complex), *i.e.*, the reverse oxidation of the hydrazido ligand into the dinitrogen ligand followed by its displacement from the coordination sphere of the metal occurs in parallel. This is the reason for the fact that the overall yield of  $^{15}\text{NO}$ ,  $^{15}\text{N}^{14}\text{NO}$ , and  $^{15}\text{N}^{14}\text{N}$  is much lower than quantitative.

Hence, the data obtained show that two processes occur simultaneously upon interaction of the nitronium and nitrosonium salts with dinitrogen complexes **1** and **2**. One of them is stepwise reduction of the nitronium and nitrosonium cations into  $\text{NO}$ ,  $\text{N}_2\text{O}$  and  $\text{N}_2$  due to electrons of the metal,  $\text{N}_2\text{O}$  being formed as a result of reductive dimerization of  $\text{NO}$ . The second process is attack of nitronium and nitrosonium cations on the

protonated dinitrogen ligand with the formation of labeled nitrogen oxides ( $^{15}\text{NO}$  and  $^{15}\text{N}^{14}\text{NO}$ ) along with  $^{15}\text{N}^{14}\text{N}$ .

Scheme 1 shows one of the possible mechanisms for the formation of labeled products in the reaction of complexes **1** and **2** with the  $\text{NO}^+$  cation ( $\text{M} = \text{Mo}, \text{W}$ ;  $\text{N}^*$  is  $^{15}\text{N}$ ; the phosphine ligands are not shown in Scheme 1 because they can be partially lost).

According to Scheme 1, protonation of the dinitrogen ligand followed by attack of the hydrazido complex by the nitrosonium cation results in the formation of *N*-nitroso-derivative (**A**), which can be decomposed according to two parallel pathways. The first pathway is deprotonation of **A** followed by fragmentation of the product obtained into labeled nitrous oxide  $^{15}\text{N}^{14}\text{NO}$  and a nitride complex. According to the second pathway, the process occurs similarly to diazotization of primary aliphatic amines and hydrazones and should result in the formation of labelled dinitrogen  $^{15}\text{N}^{14}\text{N}$  and a complex with a protonated nitroso ligand ( $\text{M}=\text{N}^{15}\text{N}-\text{OH}$ ). This complex may be regarded as an



0.013 mol). The complex obtained was recrystallized from a  $C_6H_6$ /MeOH mixture to give 4.6 g (34 %) of compound **2** as bright orange crystals. Found (%): C, 59.73; H, 4.77; N, 4.92.  $C_{52}H_{48}N_4P_4W$ . Calculated (%): C, 60.24; H, 4.67; N, 5.4. IR,  $\nu/cm^{-1}$ : 1872, 1955 ( $^{15}N=^{15}N$ ).

**(Me<sub>2</sub>PhP)<sub>3</sub>Mo(<sup>15</sup>N<sub>2</sub>H<sub>2</sub>)Cl<sub>2</sub> (3).** A solution of conc. HCl (3.5 mL, 30 mmol) in 30 mL of MeOH was added to a suspension of compound **1** (2.1 g, 3 mmol) in 170 mL of MeOH. The reaction mixture was stirred for 3–4 h at 20 °C. The reaction was accompanied by a slow liberation of gas with gradual dissolution of the starting complex and formation of a brown precipitate of compound **3**. The amount of gas liberated corresponded to one mol per mol of compound **1**. The precipitate formed was filtered off, washed with methanol and ether, and dried *in vacuo* to give 1.3 g (71 %) of compound **3** as a cream-colored powder. Found (%): C, 46.94; H, 5.57; Cl, 10.98; N, 4.79; P, 14.80.  $C_{24}H_{35}Cl_2MoN_2P_3$ . Found (%): C, 47.01; H, 5.75; Cl, 11.56; N, 4.88; P, 15.15.

**(dppe)<sub>2</sub>W(<sup>15</sup>N<sub>2</sub>H<sub>2</sub>)Cl<sub>2</sub> (4).** The synthesis was carried out similarly to the previous one. A 5 N solution of HCl in MeOH (3 mL) previously prepared by saturation of methanol with gaseous HCl was added to a suspension of compound **2** (0.93 g, 0.9 mmol) in 10 mL of MeOH. After stirring for 6–7 h at 20 °C, liberation of gas stopped. The precipitate formed was treated as described above to give 0.6 g (61.6 %) of **4**. Found (%): C, 54.36; H, 4.78; Cl, 6.75; N, 1.87; P, 10.47.  $C_{52}H_{50}Cl_2N_2P_4W$ . Calculated (%): C, 57.74; H, 4.66; Cl, 6.55; N, 2.59; P, 11.45.

#### Reactions of complexes **1–4** with NOBF<sub>4</sub> and NO<sub>2</sub>BF<sub>4</sub>.

All experiments described in this work were carried out according to the standard procedure in three-horned all-glass vessel connected with a high-vacuum setup and a Toepler pump. One knee of the reaction vessel was charged with dinitrogen or a hydrazido complex (~0.1 mol), the second knee was charged with the corresponding amount of NOBF<sub>4</sub> or NO<sub>2</sub>BF<sub>4</sub>, and sulfolane (2 mL) and, if needed, a definite amount of water or acid was placed into the third knee. The vessel was evacuated *in vacuo* and the components were mixed. In all cases the reaction proceeded very vigorously with foaming and completed in 5–15 min. After 0.5–1 h, the gas that liberated was transferred into a gas burette by the Toepler

pump. After measuring the volume, a portion of the gas was withdrawn into previously evacuated glass tubes for mass spectrometric analysis, and the tubes were sealed.

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