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PREPARATION AND SPECTROSCOPIC CHARACTERIZATION OF $[Re(NO)_2X_2L_2]$ ($X = Cl, Br, I$; $L_2 = 2PPh_3$, dppe). APPLICATION OF $[Re(NO)_2Br_2L_2]$ IN OXIDATION OF OLEFINS

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Abstract—A simplified method of synthesis of dinitrosyl complexes $[Re(NO)_2X_2L_2]$, where $X = Cl$, Br, I and $L_2 = 2PPh_3$ or dppe, is described and spectroscopic characterization of the complexes is presented. The application of $[Re(NO)_2Br_2L_2]$ for the oxidation of cyclohexene is also discussed.

Nitrosyl complexes of transition metal ions have been a subject of general interest for many years.[1] NO^- is isoelectronic with the CO and N_2 molecules, while NO is isoelectronic with O_2^+ which makes nitrosyl compounds very important from the practical and theoretical points of view. The NO insertion reactions, however, which are not so common, enable the nitrosyl compounds to be applied in the activation of organic molecules. It is known that olefins can be activated either by coordination to metal ion or, e.g. in the case of nitrosyl or carbonyl compounds, by insertion into CO or NO groups (the insertion reaction follows the initial coordination).[2] Rhenium nitrosyl complexes (coordination number 6) are of special importance since they make available both modes of olefin activation. Some other examples of nitrosyl compounds active as catalysts in olefin oxidation have also been described.[3]

Nitrosyl complexes of rhenium have been known for many years; however, the methods of synthesis are not very effective and usually consist of several steps.[4] Moreover, these compounds have not been fully characterized spectroscopically so far.[5] Thus, the aim of our work was to simplify the method of synthesis of nitrosyl complexes of rhenium, to present their full spectroscopic characterization and to examine their properties in respect of olefin activation.

EXPERIMENTAL

$[ReOX_3(PPh_3)_2]$ and $[ReOBr_3dppe]$ were obtained according to the literature methods.[6] Gaseous NO was purified by washing with a concentrated solution of KOH and treatment with solid NaOH. All the solvents were of the highest purity and were distilled before use.

$[Re(NO)_2Cl_2(PPh_3)_2]$ (1)

NO was passed through a vigorously stirred and refluxing solution of $[ReOCl_3(PPh_3)_2]$ (0.85 g, 1 mmol) in methylene chloride (25 cm^3) under argon. The reaction was carried out for 4–5 h. The colour changed from light green to maroon. Then, the resulting solution was evaporated to half of its volume. The maroon precipitate was formed by adding 15 cm^3 of ethanol to the solution. The crude product was then recrystallized from acetonitrile or methylene chloride. The green or brownish-red crystals were obtained from acetonitrile and methylene chloride, respectively. The elemental analyses and spectral characteristics were, however, identical for both crystals (yields 45%; 0.38 g, 045 mmol). Found: N, 3.3; P, 7.4; Cl, 8.5. Calc.: N, 3.3; P, 7.4; Cl, 8.4%.

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$[Re(NO)_2Br_2(PPh_3)_2]$ (**2**)

An analogous procedure was applied. The colour changed from yellow to reddish-brown. The product was crystallized from acetonitrile. The formed reddish-brown crystals were washed with ether and dried *in vacuo*. Yields 70%. Found: N, 3.0; P, 6.7; Br, 17.1. Calc.: N, 3.0; P, 6.7; Br, 17.2%.

$[Re(NO)_2I_2(PPh_3)_2]$ (**3**)

In an analogous procedure to that above, the colour changed from greenish-brown to maroon. The light brown precipitate was formed by addition of ethanol to the resulting solution. The product was not recrystallized as it decomposes during the recrystallization. Yields 40%. Found: N, 3.4; P, 7.4; I, 24.8. Calc.: N, 2.7; P, 6.1; I, 24.8%.

$[Re(NO)_2Br_2dppe]$ (**4**)

NO was passed through a refluxing solution of green $[ReOBr_3dppe]$ (0.90 g, 1.09 mmol) in tetrahydrofuran (30 cm^3) in the presence of excess of dppe, under an inert atmosphere. After 7 h the solution was evaporated to half its volume and ethanol was added to precipitate the yellow powder. It was washed with ethanol and ether and then dried *in vacuo*. Yields 30%, 0.27 g, 0.34 mmol. Found: N, 3.4; P, 7.4; Br, 19.3. Calc.: N, 3.4; P, 7.5; Br, 19.3%.

Olefin oxidation

In a typical experiment, cyclohexene (5 mmol) and complex **2** or **4** (0.01 mmol) were dissolved in acetonitrile or methylene chloride (100 cm^3). The solution was stirred for 72 h. The reaction flask was maintained at room temperature under an O_2 pressure of 20–30 mm Hg. The colour, initially orange–red, turned yellow and the reaction was finished. The resulting solution was distilled and the products were analysed using GC–MS. The isolated solid residue was analysed, showing IR spectral bands attributed to $\nu(NO)$ and, most likely, to coordinated nitrato groups.

The same procedure was applied to carry out a control oxidation experiment without the complex.

Physical measurements

Absorption bands were recorded using a Beckman 5240 spectrophotometer. IR spectra were obtained in KBr pellets on a Specord IR-75 instrument. Magnetic measurements were done using a Gouy balance and according to Evan's method using a Varian VXR-300 NMR spectrometer. ESR spectra were recorded using a Bruker ST 8945 spectrometer.

The products of cyclohexene oxidation were analysed using a HP-5890 gas chromatograph and a HP-5971A mass spectrometer.

RESULTS AND DISCUSSION

The nitrosyl complexes were obtained by a single step reductive nitrosylation of $[ReOX_3(PPh_3)_2]$ and $[ReOBr_3dppe]$, in contrast to the many-stage methods described in the literature. The yields were good. A potential problem arising from this method is the possible oxidation of phosphine. However, in the IR spectra of the nitrosyl compounds there were no bands typical of phosphine oxide, i.e. from 1130 to 1200 cm^{-1}. Moreover, the ^{31}P NMR spectra of the nitrosyls clearly show that phosphine is not oxidized (chemical shifts of 46.49 and 42.73 ppm for $[Re(NO)_2Cl_2(PPh_3)_2]$ and $[Re(NO)_2Br_2(PPh_3)_2]$, respectively). These shifts differ significantly from that of 29.75 ppm found for $[Re(NO)_2I_2(O{=}PPh_3)_2]$.[7]

The absorption bands and their characteristics are listed in Table 1. The ligand field parameters D_q, D_s and D_τ are presented in Table 2. The synthesized complexes are of low symmetry (see Table 1).

The results presented in Table 2 show that the ligand field parameters depend, as expected,[8] only slightly on the halogen ligand and, on the other hand, are strongly influenced by nitrosyl ligand and phosphine present in the coordination sphere. On the basis of the determined ligand field parameters, the energies of the central metal were calculated, assuming the *cis* configuration of NO groups and halogen ligands in the complexes with PPh_3, and *trans* configuration of NO groups in the complex with dppe. The molecular orbital scheme for the reported complexes is presented in Fig. 1. The bands at *ca.* 37,000 cm^{-1}, assigned as halogen → rhenium, show only slight bathochromic shift for different halogen ligands. For rhenium → halogen transitions, one could expect a hipsochromic shift in the series $Cl^- > Br^- > I^-$. The observed transitions are allowed and this is reflected in their intensities (see Table 1). These transitions can be most likely assigned as π^bRe–halogen (localized on halogen ligand) → π^*Re–halogen (localized on rhenium). The increasing probability of π^b bond formation from chlorine to iodine ligands is reflected in the increase of the extinction coefficients from chlorine to iodine. Two $\nu(NO)$ vibrations for the complexes with PPh_3 and one $\nu(NO)$ vibration for a complex with dppe support the assumed C_{2v} symmetry of the complexes (see Table 3). Thus, on

Table 1. Band positions, molar extinction coefficients and assignments

[Re(NO)$_2$(PPh$_3$)$_2$Cl$_2$]		[Re(NO)$_2$(PPh$_3$)$_2$Br$_2$]		[Re(NO)$_2$(PPh$_3$)$_2$I$_2$]			[Re(NO)$_2$(dppe)Br$_2$]		
Band position (cm^{-1})	Molar extinction coefficient (dm^3 mol^{-1} cm^{-1})	Band position (cm^{-1})	Molar extinction coefficient (dm^3 mol^{-1} cm^{-1})	Band position (cm^{-1})	Molar extinction coefficient (dm^3 mol^{-1} cm^{-1})	Assignments	Band position (cm^{-1})	Molar extinction coefficient (dm^3 mol^{-1} cm^{-1})	Assignments
15,220	49	14,710	94	15,080	63	$d_{xz} \rightarrow \pi^*$NO	15,110	27	$d_{yz} \rightarrow d_{xz}$
18,940	454	18,180	^{a}	19,050	513	$d_{xy} \rightarrow d_{yz}$	21,190	2637^c	$d_{xy} \rightarrow d_{z^2}$
24,550	4080	20,830	4186	24,390	4600	$d_{xy} \rightarrow \pi^*$NO	25,640	3890	$d_{yz} \rightarrow \pi^*$NO
						$d_{yz} \rightarrow d_{x^2-y^2}$			$d_{yz} \rightarrow d_{xy}$
27,780	1627	24,390	1381	27,780	1648	$d_{yz} \rightarrow d_{z^2}$	29,850	1441	$d_{xz} \rightarrow d_{z^2}$
37,740	14,836	37,460	^{b}	37,170	17,465	Hal$^-$ → d Re	37,460	^{d}	Br$^-$ → d Re
41,840	25,861	41,670	20,068	41,990	26,587	$\pi^{\mathrm{b}}_{\mathrm{phen}} \rightarrow 3d$P	41,840	23,971	$\pi^{\mathrm{b}}_{\mathrm{phen}} \rightarrow 3$ P^e

[a] Covered by 20,830 cm^{-1} band.
[b] Covered by 41,840 cm^{-1} band.
[c] Interfering band at 25,640 cm^{-1} increases ε.
[d] Covered by 41,840 cm^{-1} band.
[e] Phosphorus atom.

Table 2. Ligand field parameters D_q, D_s and D_τ for $[Re(NO)_2L_2Hal_2]$ complexes

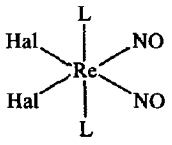
Complex	Ligand field parameter (cm^{-1})		
	D_q	D_s	D_τ
$[Re(NO)_2(PPh_3)_2Cl_2]$	4349	−3142	1885
$[Re(NO)_2(PPh_3)_2Br_2]$	3902	−3115	1772
$[Re(NO)_2(PPh_3)_2I_2]$	4244	−3040	1770
$[Re(NO)_2(dppe)Br_2]$	4704	−7356	714

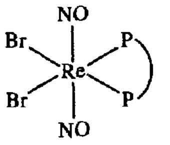
Table 3. The IR vibrations ν(NO) and ν(Re—Hal) for $[Re(NO)_2L_2Hal_2]$

	Vibration band (cm^{-1})	
	ν(NO)	ν(Re—Hal)
$[Re(NO)_2(PPh_3)_2Cl_2]$	1750 vs (B_2)	312 s (B_2)
	1760 vs (A_1)	292 m(A_1)
$[Re(NO)_2(PPh_3)_2Br_2]$	1740 vs (B_2)	302 s (B_2)
	1750 vs (A_1)	299 m (A_1)
$[Re(NO)_2(PPh_3)_2I_2]$	1720 vs (B_2)	292 s (B_2)
	1730 vs (A_1)	285 m (A_1)
$[Re(NO)_2(dppe)Br_2]$	1740 vs (A_{2u})	302 s (B_2)
		299 m (A_1)

[a] vs, very strong; s, strong; m, medium.

the basis of these results, one could suggest that in a complex with PPh_3 the nitrosyl groups are *cis* towards each other, while in a complex with dppe they are *trans* oriented. The suggested compounds were selected from the possible six stereoisomers. The arrangements of the coordinated ligands are presented below:





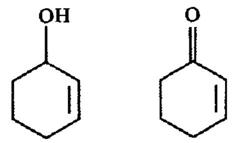
The ν(NO) positions show, as expected, a bathochromic shift from chlorine to iodine in a coordination sphere. The increasing probability of π^bRe-halogen bond formation is followed by the increase in the electron density of the central ion, thus increasing the probability of $d_{xy} \rightarrow \pi^*$ (NO) and $d_{yz} \rightarrow \pi^*$ (NO) transitions in complexes with PPh_3 and dppe, respectively. It is reflected in a decreasing of the ν(NO) vibration frequency. In principle, the mentioned transitions are of *d–d* type, therefore their intensities are not very high. The precise analysis of the electronic spectra is hindered by the interference of the ligand field transitions and charge transfer bands (e.g. $^{\pi}$phenyl → ^{3d}phosphorus). The above mentioned $d \rightarrow \pi^*$ transitions could influence the formal oxidation state of the central ion, which is also affected by polarization of the NO group. It is well known that the NO group can be coordinated as NO^+ or NO^-. In the former case, i.e. for $\{Re(NO)_2\}^7$, the configuration of the central ion should be as follows (assuming the neutrality of the complex): $(xy)^2(xz)^2(yz)^2(x^2-y^2)^1$ and $(yz)^2(xz)^2(xy)^2(z^2)^1$ for complexes with PPh_3 and dppe, respectively. In the latter case, i.e. for $\{Re(NO)_2\}^3$ the configuration is the following: $(xy)^2(xz)^1$ and $(yz)^2(xz)^1$ for complexes as above. The orbitals $d_{x^2-y^2}$ and d_{z^2} (i.e. the highest occupied orbitals) are of a higher energy than the π^*(NO) orbital (see Fig. 1), while the orbitals xz are situated lower than the π^* (NO) orbital. Thus, the observed corresponding electronic transitions are possible in the latter case only. It may be suggested, therefore, that the NO group can be regarded as negatively polarized.

The magnetic measurements show that the nitrosyl complexes are paramagnetic, having magnetic moments equal to 1.79, 1.76 and 1.81 B.M. for chloride, bromide and iodide nitrosyl complexes with PPh_3, respectively, and 1.79 B.M. for a bromide complex with dppe. The half-width of the ^{31}P NMR signal $\nu_{1/2} = 155.8$ Hz also clearly reveals paramagnetism of the examined complexes. It is also reflected in their ESR spectra. The typical signal is presented in Fig. 2. The signal consists of six lines, due to interaction of the unpaired electron with nuclear spins of ^{185}Re and ^{187}Re ($I = 5/2$). The splitting constant $A_{Re} = 300$ G. Two sextet components, situated at the highest frequencies, are distinctly broadened by a triplet arising from interaction of the unpaired electron with the nuclear spins of ^{14}N in the NO groups. The expected narrow doublet signals due to the interaction with ^{31}P nuclear spin are not visible since they are covered by the above mentioned signals, which are, moreover, broadened by the rhenium and nitrogen quadrupole moments. In the solid state, the ESR spectrum reveals a broad, unresolved signal with $g_{av} = 2.19$.

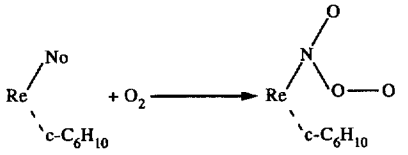
Oxidation experiments

Some nitrosyl complexes, as was mentioned above, can be applied as catalysts for olefin oxidation. Generally the nitrosyl group is involved in such a process, provided that other ligands are oxidation-resistant.[9] The complexes **2** and **4** were applied as precursors for the oxidation of cyclohexene. After the reaction had been completed, the products were analysed using gas chromatography and mass spectroscopy. The products of oxidation without the complexes being present were also analysed. A similar reaction was performed with our initial compounds, i.e. $[ReOBr_3(PPh_3)_2]$ and $[ReOBr_3dppe]$. Such complexes are known to be catalysts for the oxidation of phosphines.[10] However, it is apparent that these complexes have only little ability to coordinate olefins and, therefore, are not catalytically active for the oxidation of olefins. In the case of oxidation without the complexes, no significant amounts of the olefin oxidation products were detected.

The products of oxidation are shown in Table 4. They differ significantly from those usually obtained as the products in a catalytic oxidation of olefins. It should be pointed out, however, that other reported catalysts are able to coordinate both olefin and dioxygen and this is what determines the nature of the products, i.e.



In our case dioxygen is not coordinated by rhenium. Instead, dioxygen can react with the nitrosyl group to form a nitrato compound and then, after rearrangement of the compound formed with the previously coordinated olefin stable products are formed:



(1)

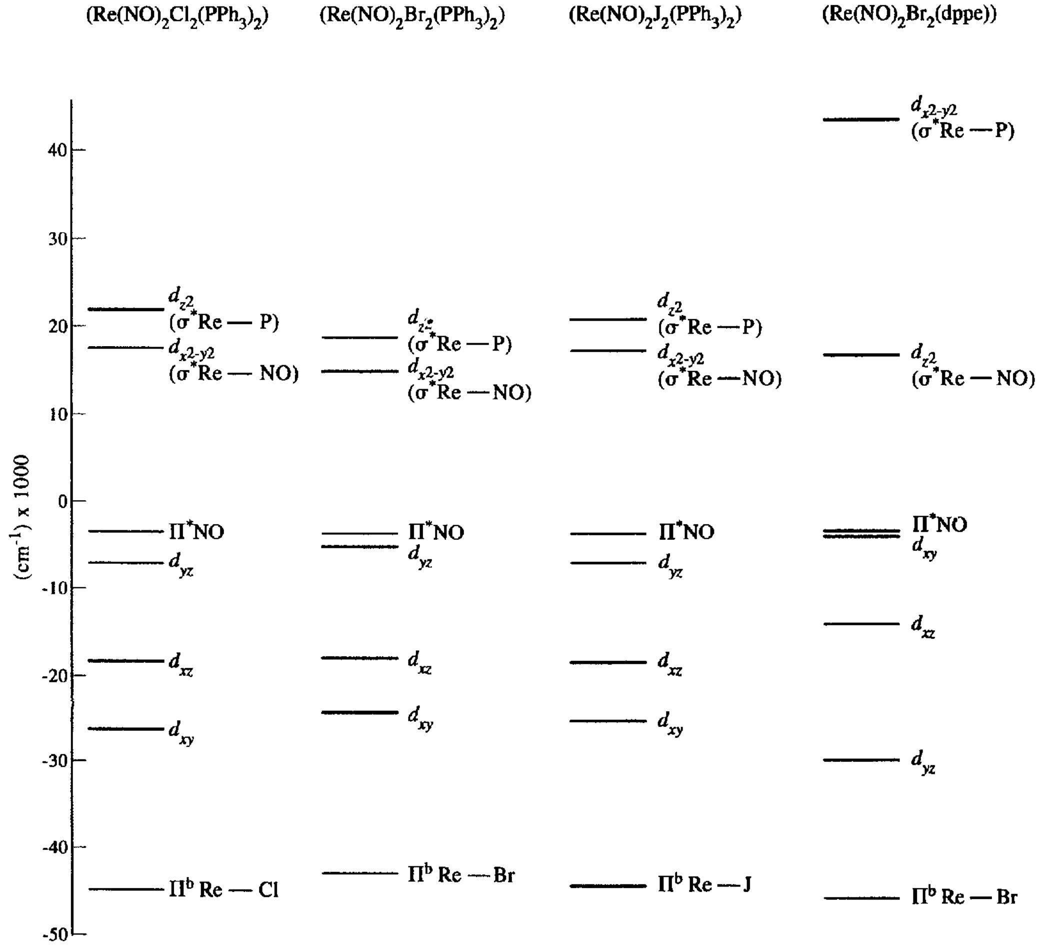


Fig. 1. The molecular orbital diagrams for $[Re(NO)_2L_2X_2]$ complexes.

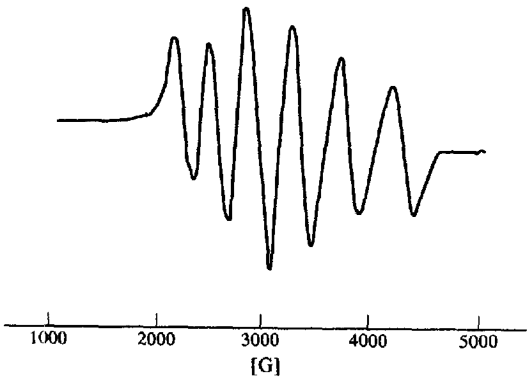
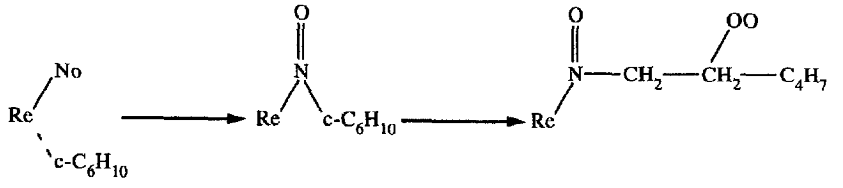


Fig. 2. EPR signals of $[Re(NO)_2Br_2(PPh_3)_2]$ in CS_2 solution at 293 K.

In fact, the IR spectrum of the recovered catalyst, isolated after the reaction, shows vibrations typical for a nitrato compound,[12] i.e. ν_s (A_1) at about 1600 cm^{-1}, ν_{as} (B_2) at 1380 cm^{-1} and $\delta(A_1)$ at about 900 cm^{-1}. The other possibility is the formation of a seven-coordinated compound, its rearrangement by means of insertion of the coordinated olefin into the nitrosyl group, and subsequent addition of dioxygen to form a radical product:



(2)

The transformations of the coordinated peroxo radicals lead to the stable products. The product with molecular mass 59 (see Table 4) seems to confirm possible interaction of the coordinated olefin with the nitrosyl ligand. The presence of low-mass oxidized fragmentation products and the products of olefin dehydrogenation seem to support the suggested radical mechanism of the process. The detailed explanation of the process requires further investigations.

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Table 4. Oxidation of cyclohexene in the presence of $[Re(NO)_2(PPh_3)_2Br_2]$ and $[Re(NO)_2(dppe)Br_2]$

Retention time (min)	Molecular mass	Formula	Yields of reaction products (%), using $[Re(NO)_2(PPh_3)_2Br_2]$	Yields of reaction products (%), using $[Re(NO)_2(dppe)Br_2]$
2.08	58	$H_2C{=}CHCH_2OH$	—	15
2.20	56	$H_2C{=}CHCHO$	50	48
2.32	59	CH_3CH_2NO	5	3
2.70	78	C_6H_6	14	13
4.10	80	C_6H_8	15	13

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