In Situ Trapping of NO. A Generalized Method for the Synthesis of Metal Nitrosyls

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Synopsis. Several known nitrosyl complexes of Ru, Rh, Ir, Os, Co, and Mo have been synthesized using a more generalized method, using organic *N*-nitroso compounds. Physical methods such as IR, magnetic measurements, conductance measurements, melting points, and elemental analyses were used for the identification of the products of the reactions.

Although the coupling of gaseous NO with transition metal complexes to yield co-ordinated nitrosyls is a well documented process.[1] Its thermodynamic instability has surged interest in developing new synthetic routes for their synthesis. Our continuing interest in devising a new generalized procedure for introducing NO in metal complexes has suggested to us that the susceptibility of N–N bond cleavage in organic *N*-nitroso amino compounds resulting in the generation of NO in situ under mild experimental conditions could possibly provide a basis for such an attempt. This report suggests that such a goal is indeed realizable for incorporating NO in metal complexes.

Experimental

All the reagents used were of chemically pure grade. Carbon, hydrogen, and nitrogen analyses in the complexes were carried out by the microanalytical laboratory of Indian Institute of Technology.

Halide, cobalt, and rhodium in the complexes were analysed by standard methods. For the phosphorus estimation a weighed amount of the sample was decomposed by heating it for about 15 min with a mixture of sodium peroxide, sugar, and sodium nitrate in the ratio 20:1:3 in a Parr-Bomb crucible. The melt was extracted with water and filtered. After adding a few cm^3 of concentrated sulfuric acid to the filtrate it was evaporated to sulfur trioxide fumes. The resulting mixture was cooled, diluted with water, and filtered, if necessary. Phosphorus was estimated in the filtrate as ammonium molybdophosphate by standard procedure.

The IR spectra were recorded on Shimadzu IR-420 spectrophotometer in the region 4000—400 cm^{-1}. Conductivity measurements were carried out on an Elico Conductivity Bridge type-CM82T. Magnetic measurements were made with a Gouy balance at room temperature (25 °C).

In a typical run 10 cm^3 of a solution containing 0.5 mmol of the metal trihalide in methanol, ethanol, 2-methoxyethanol or benzene (as the ease may be, see Table 1) and 1 mmol of the desired *N*-nitroso amines were added successively to a well stirred, argon purged refluxing solution of about 2 mmol of coligand in the same solvent 15 cm^3. A slow stream of hydrogen chloride gas was also allowed to pass simultaneously through the reaction mixture while using *N*-nitroso alkyl amines, *N*-nitroso diethyl amine as nitrosylating agent (whereas dry chlorine gas was passed during the preparation of the dinitrosyl complex of molybdenum). The resulting reaction mixture was allowed to heat under reflux for about 15 to 20 min, where upon shining crystals of the corresponding nitrosyl in about 60% yield separated in most cases. In the case of molybdenum, a greenish yellow solution was obtained which on concentration to a small volume (5 cm^3), followed by addition of ethanol, gave greenish yellow crystals of the dinitrosyl. These crystals were collected by filtration, washed successively with ethanol, water, ethanol, and ether and dried in vacuo.

Results and Discussion

Table 1 illustrated the application of our procedure to the synthesis of various metal-nitrosyls. Since most of these nitrosyls are known, they have been identified by chemical analyses, and by comparing color, melting point, IR spectra, conductance, and magnetic susceptibility data with those reported.

The analytical data of the diamagnetic, nonconducting, greenish brown complex (mp 168 °C) obtained by the reaction of *N*-nitrosodiethylamine with $RuCl_3 \cdot xH_2O$ and PPh_3 in ethanol medium were in perfect agreement with empirical formula $[Ru\{(C_2H_5)_2N(NO)\}Cl_2(PPh_3)_2]$. Its IR spectrum exhibited bands at 1750(s) and 880(mw) cm^{-1}, assigned to ν(NO) and ν(C–N), respectively, in addition to all the characteristic bands of PPh_3 and the ligand.

In order to facilitate the release of NO by protonating the nitrogen atom N–NO, hydrogen chloride gas was passed through the reaction mixture while using *N*-nitrosodiethylamine as nitrosylating agent. The latter failed to nitrosylate without hydrogen chloride, probably because of its inability to acquire hydrogen ion from the reaction medium.

The purpose of passing dry chlorine gas in the reaction medium while preparing $[Mo(NO)_2Cl_2(PPh_3)_2]$, was two fold: (a) to oxidize molybdenum from zero to a higher oxidation state, and (b) to provide a source of chloride ions in the reaction after reduction.

Rapid perusal of Table 1 shows that the *N*-nitroso amino compounds having electron attracting substituents (R), ($\overset{R}{\underset{R}{}}\!\!>$N–NO) effect the formation of nitrosyls with ease while the ones with electron-donating groups do not, but for the ruthenium case. The variations in the nitrosylating properties of *N*-nitroso amines may presumably be caused by the variation of electron density on nitrogen which will effect the N–N bond strength. The negative inductive effect (−I) resulting in the decrease of electron density at nitrogen might facilitate the scission of the N–N bond and vice versa. Thus, we expect that the presence of even one of the two substituents like C_6H_5, CN, CO, C_5H_5N, etc., on the nitrogen atom NO substituted will lead to nitrosylating reaction while the *N*-nitroso amines with both electron-donating groups like CH_3, C_2H_5,

Table 1. Preparation of Metal Nitrosyls

Reaction product	*N*-Nitroso derivative used	Metal used	Coligand	Reaction medium	Special conditions (if any)	ν(NO(cm^{-1}) for metal No synthesized
$[Ru(NO)Cl_3(PPh_3)_2]$[10] $[Rh(NO)Cl_2(PPh_3)_2]$[11] $[Ir(NO)Cl_2(PPh^3)_2]$[11]	Diphenyl *N*-Nitrosoamine *N*-Nitroso-*N*-methylaniline[4] *N*-Nitrosodibenzylamine[5] *N*-Nitrosomethylurethane[6] *N*-Nitroso-*N*-phenylbenzylamine[4] *N*-Nitroso ethylcynamide[7] *N*-Nitroso-*N*-methylurea[8] *N*-Nitrosomethylamminopyridine[9]	$MCl_3 \cdot xH_2O$ (M=Ru, Rh, Ir)	$(C_6H_5)_3P$	Ethanol (for M=Ru) or 2-methoxyethanol (for M=Rh, Ir)	—	1875(M=Ru) 1630(M=Rh) 1560(M=Ir)
$[Ru(NO)_2(PPh_3)_2]$[12]	*N*-Nitrosodiphenylamine	$RuCl_3 \cdot xH_2O$	$(C_6H_5)_3P$	Ethanol	In presence of $(C_2H_5)_3N$ in the reaction medium	1655, 1610
$[Ru(NO)Cl_3(PPh_3)_2]$[10]	*N*-Nitrosodiethylamine	$RuCl_3 \cdot xH_2O$	$(C_6H_5)_3P$	Ethanol	In presence of HCl gas in the reaction medium	1875
$[Ru(C_2H_5)_2N(NO)Cl_2(PPh_3)_2]$[14]	*N*-Nitrosodiethylamine	$RuCl_3 \cdot xH_2O$	$(C_6H_5)_3P$	Ethanol	—	1750
$[Os(NO)Cl_3(PPh_3)_2]$[12]	*N*-Nitrosodiphenylamine	$Na_2OsCl_6 \cdot 6H_2O$	$(C_6H_5)_3P$	2-Methoxyethanol	—	1850
$[Co(NO)(en)_2Cl]Cl$[15]	*N*-Nitrosodiphenylamine	$CoCl_2 \cdot 6H_2O$	Ethylenediamine (en)	Methanol	—	1630
$[Mo(NO)_2Cl_2(PPh_3)_2]$[13]		$Mo(CO)_6$	$(C_6H_5)_3P$	Benzene	In presence of Cl_2 gas in the reaction medium	1679, 1790

etc., on nitrogen atom, will not be effective nitrosylating agents but for ruthenium case. In the latter case the increased basicity of nitrogen (attached to NO group) because of the presence of alkyl groups, may cause *N*-nitroso amines preferentially coordinated to Ru through N atom attached to NO (i. e. $\text{-Ru-N}\langle{}^{R^1}_{R}$). Ruthenium being acid may withdraw electron density from nitrogen effecting the release of NO from the nitroso amines which subsequently attack on ruthenium with the formation of its nitrosyl. Thus, in case the metal ion is of low σ acidity (low oxidation states), the nitrosylation reaction may not take place.

Although the application of this new procedure has not yet been extensively extended, our present evidence indicates that the nitrosylation reactions will take place with *N*-nitroso amino compounds having at least one electron withdrawing group linked to NO substituted nitrogen atom. We believe that extension of the in situ, trapping of NO has an enormous potential for the effecient synthesis of metal nitrosyls which are rather difficult to synthesize under normal reaction conditions.

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