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The Reaction of Nitric Oxide with Rhodium Complexes

Jitsuo KIJI, Susumu YOSHIKAWA and Junji FURUKAWA

Department of Synthetic Chemistry, Kyoto University, Sakyo-ku, Kyoto

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There has been considerable interest in recent years in the preparation of d^8 complexes because of their significance in oxidative addition and their potentiality in catalysis. The formation and properties of the carbonyl complexes of rhodium have been studied extensively.[1] On the other hand, there have been few reports on the reaction of nitric oxide. Nitric oxide is unique among ligands in that it contains an unpaired electron. The present work stems from our interest in expanding the scope of rhodium complexes by reaction with nitric oxide. Recently Hughes has reported a reaction between nitric oxide and square-planar rhodium complexes of the $RhClL_3$ type to produce nitrosyl-nitro derivatives, $RhCl(NO)(NO_2)L_2$.[2] Both triphenylphosphine and triphenylarsine derivatives exhibit two infrared absorption bands in the N–O stretching region; this splitting is attributed to the presence of isomers.[2] This report prompted us to reveal the results of our own investigation.

This paper deals with the isolation of two nitrosyl complexes. We conclude that the lower band in the N–O stretching region can be assigned to a polymeric nitrosyl complex. Furthermore, we report here about the replacement of the nitrosyl group by carbon monoxide and about the reaction of a diphosphine complex with nitric oxide.

Experimental

Reaction of Nitric Oxide with $RhCl(PPh_3)_3$. Nitric oxide was introduced into 20 m*l* of a benzene solution containing 200 mg of $RhCl(PPh_3)_3$ and 500 mg of triphenylphosphine at room temperature over a 20-min period. The color of the solution thus changed from brown to green. The evaporation of the benzene and subsequent washing with ether gave 123 mg of $RhCl(NO)(NO_2)(PPh_3)_2$. IR: 818, 1310, 1415 (due to NO_2 group), and 1660 cm^{-1} (ν_{NO}).

Found: C, 59.27; H, 4.65; N, 2.95%; mol wt, 718. Calcd for $RhC_{36}H_{30}N_2O_3P_2Cl$: C, 58.52; H, 4.09; N, 3.78%; mol wt, 738.9.

Attempted Isolation of Complex I. A green solution, prepared by the method which has been described above except that triphenylphosphine was added, gradually formed a brown precipitate in a low yield. It was sparingly soluble in organic solvents. IR: 1635 cm^{-1} (ν_{NO}). The average values obtained from two sets of analyses are as follows: C, 56.74; H, 4.48; N, 4.02%.

Reaction of Carbon Monoxide with $RhCl(NO)(NO_2)(PPh_3)_2$. Into 20 m*l* of a benzene solution containing $RhCl(NO)(NO_2)(PPh_3)_2$, prepared from 200 mg of $RhCl(PPh_3)_3$ and 500 mg of triphenylphosphine as has been described above, carbon monoxide was introduced at room temperature over a 60-min period. The addition of ether to the concentrated solution gave 110 mg of a yellow solid, which was identified with $RhCl(CO)(PPh_3)_2$ on the basis of its mp and IR spectrum.

Reaction of Nitric Oxide with $RhCl(CO)(Ph_2PCH_2CH_2PPh_2)$. The treatment of 10 m*l* of a benzene solution containing 77 mg of $Rh_2Cl_2(CO)_4$ with 157 mg of bis(diphenylphosphino)ethane at room temperature for 3 hr gave 195 mg of $RhCl(CO)(Ph_2PCH_2CH_2PPh_2)$,[*1] which had an IR absorption band due to ν_{co} at 2000 cm^{-1}. Nitric oxide was introduced into 5 m*l* of a benzene solution containing 30 mg of the complex at room temperature. Yellow-green $RhCl(NO)(NO_2)(Ph_2PCH_2CH_2PPh_2)$ (25 mg) was thus precipitated from the solution. IR: 825, 1315, 1385 (due to NO_2 group) and 1655 cm^{-1} (ν_{NO}).

Found: C, 50.18; H, 4.49; N, 3.93%. Calcd for $RhC_{26}H_{24}N_2O_3P_2Cl$: C, 50.96; H, 3.94; N, 4.56%.

Results and Discussion

The reaction of $RhCl(PPh_3)_3$ or $RhCl(CO)(PPh_3)_2$ with nitric oxide proceeded smoothly at room temperature. When the benzene solution of $RhCl(PPh_3)_3$ or $RhCl(CO)(PPh_3)_2$ was treated with nitric oxide, a green solution was obtained. The evaporation of the benzene gave a green solid with infrared absorption bands at 1660 and 1635 cm^{-1}[*2] ascribed to ν_{NO}. When the benzene solution was allowed to stand at room temperature under a nitrogen atmosphere, a dark brown complex (1) involving a band at 1635 cm^{-1} due to

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1) J. A. Osborn, F. H. Jardine, J. F. Young and G. Wilkinson, *J. Chem. Soc., A*, **1966**, 1711.

2) W. B. Hughes, *Chem. Commun.*, **1969**, 1126.

[*1] When the diphosphine complex (obtained from 55 mg of $Rh_2Cl_2(CO)_4$ and 110 mg of bis(diphenylphosphino)ethane) was allowed to stand in benzene at room temperature for 2 weeks, a yellow solid (30 mg) was separated out; this was identified with $[Rh(Ph_2PCH_2CH_2PPh_2)_2]Cl$. The evaporation of the benzene from the filtrate gave orange needles, which were identical with $Rh_2Cl_2(CO)_4$. These data suggest that the following reaction occurs:

$$2\,RhCl(CO)(Ph_2PCH_2CH_2PPh_2) \rightarrow [Rh(Ph_2PCH_2CH_2PPh_2)_2]Cl + 1/2Rh_2Cl_2(CO)_4$$

[*2] W. D. Hughes has reported 1666 and 1640 cm^{-1} for ν_{NO}.

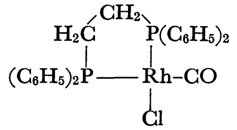
ν_{NO} gradually precipitated. No reliable information could be obtained on this complex because of the difficulty of purifying it. A reasonable formulation for I is, however, as a dimeric or polymeric nitrosyl complex involving bridging chlorine. We base this on the following facts: (1) I is sparingly soluble in organic solvents, (2) its formation is suppressed by the presence of an excess of triphenylphosphine (see below), and (3) there is no band due to the nitro group.

The reaction of nitric oxide with $RhCl(PPh_3)_3$ in the presence of an excess of triphenylphosphine led to a green, air-stable complex (II). The infrared absorption spectrum (KBr) showed a single nitrosyl band at 1660 cm^{-1} and the band assignable to the nitro group. Elemental analysis and molecular-weight measurement support the $RhCl(NO)(NO_2)(PPh_3)_2$ formula. Thus, an excess of triphenylphosphine can be used to prevent the formation of the polymeric nitrosyl complex (I) with the N–O stretching band at 1635 cm^{-1} and a nitrosylnitro complex (II) free from I can be obtained.

On treating a solution of a mixture of I and II with carbon monoxide, the nitrosyl (ν_{NO} at 1660 cm^{-1}) and the nitro groups were replaced by carbon monoxide than that in I. The displacement of the nitrosyl group in I by carbon monoxide was only possible when I was treated under pressure. A carbonyl complex formed from I had, however, an infrared absorption band due to ν_{CO} at 1985 cm^{-1} (KBr).

An attempt to reduce the coordinated nitrosyl group in I or II with molecular hydrogen was unsuccessful.

The reaction of nitric oxide with the diphosphine complex proceeded similarly at room temperature. The following formulation of $RhCl(CO)(Ph_2PCH_2CH_2PPh_2)$ is envisaged:



since the carbonyl group absorbs at 2000 cm^{-1}.3–5) The treatment of the solution of $RhCl(CO)(Ph_2PCH_2CH_2PPh_2)$ in benzene with nitric oxide gave a yellow-green complex. The infrared spectrum showed a band at 1655 due to ν_{NO} and nitro-group bands at 1385, 1315, and 825 cm^{-1}. On the basis of the infrared spectrum and the elemental analysis, the complex may be formulated as $[RhCl(NO)(NO_2)(Ph_2PCH_2CH_2PPh_2)]_n$. The insolubility of this complex supported a dimeric or polymeric formulation involving a bridging diphosphine molecule. In contrast to the triphenylphosphine derivative, the diphosphine derivative exhibits only one band in the N–O stretching region.

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3) W. Hieber and R. Kummer, *Chem. Ber.*, **100**, 148 (1967).

4) A. Sacco and R. Ugo, *J. Chem. Soc.*, **1964**, 3274.

5) J. T. Mague and J. P. Mitchener, *Inorg. Chem.*, **8**, 119 (1969).