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Paramagnetic Rhodium(II) Nitrosyl Compounds. Improved Preparations for $RhNOCl_2(PPh_3)_2$ and $RuNOCl_3(PPh_3)_2$

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Treatment of ethanolic solutions of $RhCl_3 . 3H_2O$ and $RuCl_3 . 3H_2O$ with nitric oxide gives the solvated complexes $RhNOCl_3$ and $RuNOCl_3$. Treatment of the former with triphenylphosphine yields $RhNOCl_3(PPh_3)_2$ and $RhNOCl_2(PPh_3)_2$, while similar treatment of the latter gives $RuNOCl_3(PPh_3)_2$. Esr spectra of the rhodium(II) complexes are also reported.

Introduction

A number of rhodium nitrosyl complexes have been reported recently. Hieber and Heinicke[1] found that dinitrosylrhodium chloride, $Rh(NO)_2Cl$, reacts with triphenylphosphine, arsine and stibine to give compounds of the stoichiometries $RhNOL_3$ and $RhNOCl_2L_2$ ($L = PPh_3, AsPh_3, SbPh_3$), while Collman *et al.*[2] prepared $RhNO(PPh_3)_3$ by treating a tetrahydrofuran solution of $RhCl_3 . 3H_2O$ with nitric oxide and triphenylphosphine in the presence of granulated zinc metal. Two groups of workers[3,4] have reacted *trans*–$RhClCO(PPh_3)_2$ with nitric oxide. Kukushkin and Singh[3] obtained a brown compound which they formulated as $RhCl(NO)_2(PPh_3)_2$ and which decomposed in dimethylformamide to give, apparently, the rhodium(0) compound, $RhClNO(PPh_3)_2$. Hughes,[4] on the other hand, reported that the reaction of $RhClCO(PPh_3)_2$ with NO gives the green nitro compound, $RhCl(NO_2)(NO)(PPh_3)_2$.

We now report that $RhCl_3 . 3H_2O$ reacts with NO in ethanol to give a solution of a paramagnetic rhodium species, probably solvated $RhNOCl_3$. Addition of excess triphenylphosphine gives an orange precipitate which appears to be a mixture of $RhNOCl_3(PPh_3)_2$ and the known $RhNOCl_2(PPh_3)_2$. The former compound is too unstable to purify satisfactorily, but is of particular interest because it is formally a complex of rhodium(II). In comparison, similar reactions with $RuCl_3$ $3H_2O$ give the known ruthenium(II) nitrosyl complex, $RuNOCl_3(PPh_3)_2$, a procedure which is much more convenient than a previously reported method for the preparation of this compound and which is probably general for a number of ligands other than triphenylphosphine.

Experimental Section

Chemical Reagents and Starting Materials. Nitric oxide was prepared by the reaction of sodium nitrite with dilute sulphuric acid as described in Inorganic Syntheses.[5] The hydrated rhodium and ruthenium trichlorides were purchased from Johnson Matthey and Mallory Ltd., the triphenylphosphine from Aldrich Chemical Co.

Reaction of nitric oxide with rhodium trichloride. A stream of NO was passed through a solution of 0.5 g $RhCl_3 . 3H_2O$ in 30 ml of ethanol at room temperature for ten minutes; the solution became lighter in colour. Excess NO was then flushed out by a stream of nitrogen gas. The esr spectrum of the solution at room temperature is shown in Figure 1, and consists of a broadened singlet at $g = 2.17$. Removal of the solvent at room temperature and 0.1 mm Hg pressure yielded a brown residue which did not contain a nitrosyl stretching frequency in the infrared spectrum.

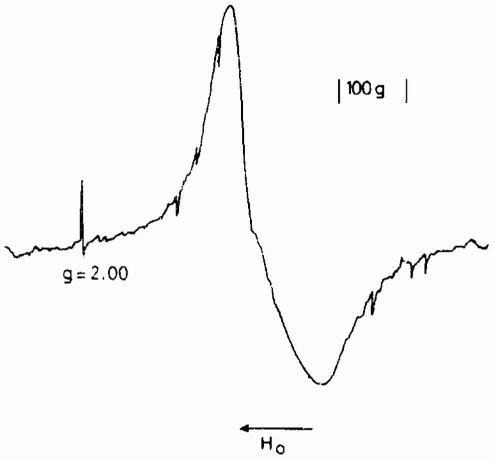

Figure 1. Esr spectrum of « $RhNOCl_3$ » in ethanol.

Preparation of $RhNOCl_3(PPh_3)_2$ and $RhNOCl_2(PPh_3)_2$. Addition of more than two molar equivalents of triphenylphosphine to the above-mentioned

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(1) W. Hieber and K. Heinicke, *Z. anorg. allg. Chem.*, *316*, 321 (1962).
(2) J. P. Collman, N. W. Hoffman, and D. E. Morris, *J. Am. Chem. Soc.*, *91*, 5659 (1969).
(3) Y. N. Kukushkin and M. M. Singh, *Rus. J. Inorg. Chem.*, *14*, 1670 (1969).
(4) W. B. Hughes, *Chem. Comm.*, 1129 (1969).
(5) *Inorganic Syntheses*, VIII, 192 (1966).

solution of « $RhNOCl_3$ » resulted in the rapid formation of an orange precipitate which analyzed as a mixture of $RhNOCl_3(PPh_3)_2$ and $RhNOCl_2(PPh_3)_2$.

Anal. Calcd for $C_{36}H_{30}Cl_2NOP_2Rh$: C, 59.35; H, 4.16; Cl, 9.73. Calcd for $C_{36}H_{30}Cl_3NOP_2Rh$: C, 56.60; H, 3.97; Cl, 13.92. Found: C, 58.16; H, 4.16; Cl, 13.40.

Conversion of the rhodium trichloride to this material is virtually quantitative. The product contains a strong band at 1630 cm^{-1} and a weaker band at 1660 cm^{-1} in the nitrosyl stretching region of its infrared spectrum, and a medium band at 330 cm^{-1} in the rhodium-clorine stretching region (nujol mull). The esr spectrum at room temperature, as shown in Figure 2, can be interpreted in terms of axial symmetry with $g_{\parallel} = 2.03$ and $g_{\perp} = 2.01$.

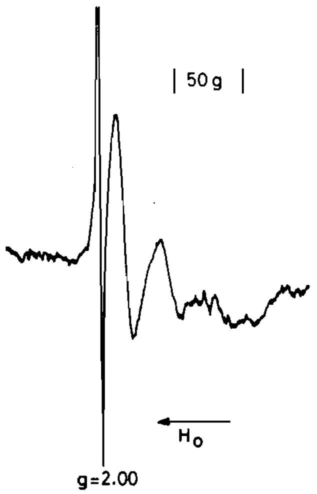

Figure 2. Esr spectrum of $RhNOCl_3(PPh_3)_2$.

Recrystallization of the crude product from chloroform-ethanol solution yielded rust red crystals of $RhNOCl_2(PPh_3)_2$, m.p. 249-252° with decomposition (lit.[1] 210°).

Anal. Calcd for $C_{36}H_{30}Cl_2NOP_2Rh$: C, 59.35; H, 4.16; Cl, 9.73; N, 1.92. Found: C, 58.36; H, 4.87; Cl, 10.64; N, 2.24.

The infrared spectrum of this compound has ν_{NO} at 1630 cm^{-1} and ν_{RhCl} at 330 cm^{-1} (nujol mull). On this basis, the weak band at 1660 cm^{-1} in the infrared spectrum of the crude material may be assigned to ν_{NO} of the compound $RhNOCl_3(PPh_3)_2$.

Reactions of $RhCl_2NO(PPh_3)_2$. Attempts were made to reoxidize $RhCl_2NO(PPh_3)_2$ to the +2 oxidation state with chlorine and iodine. In the former case, chlorine was bubbled through a suspension of $RhNOCl_2(PPh_3)_2$ in chloroform at room temperature for two minutes. The solid dissolved to give a deep orange colour. Addition of ether gave a yellow precipitate which did not contain a nitrosyl stretching band in itsinfrared spectrum, but did contain a broad band in the normal region for rhodium(III)-chlorine stretching modes (300-350 cm^{-1}).

Dropwise treatment of a chloroform solution of $RhNOCl_2(PPh_3)_2$ at 0°C under nitrogen with one equivalent of iodine in chloroform gave a dark solution from which was obtained a dark brown residue when the solvent was removed under vacuum. The material did have a strong nitrosyl stretching band at 1628 cm^{-1}, but no bands in the rhodium-chlorine region. Strong bands at 1180 cm^{-1} and 1115 cm^{-1}, in addition to bands which can be assigned to triphenylphosphine, suggested that the product was a mixture containing triphenylphosphine oxide.

Since the large discrepancy between the experimental and literature[1] values for the melting point of $RhNOCl_2(PPh_3)_2$ left some doubt as to the identity of our product, an attempt was made to reduce it to $RhNO(PPh_3)_3$ with sodium amalgam as described in the literature[1]. Large, violet-red crystals of $RhNO(PPh_3)_3$ were indeed obtained as described.

Preparation of $RuNOCl_3(PPh_3)_2$. Nitric oxide[2] was bubbled through a solution of $RuCl_3 . 3H_2O$ in ethanol for ten minutes. Excess triphenylphosphine was added and the solution was warmed to give a yellow-brown precipitate of $RuNOCl_3(PPh_3)_2$. The compound was recrystallized from $CHCl_3$—EtOH to give orange crystals, m.p. 265-275° (lit.[6] 250°).

Anal. Calcd for $C_{36}H_{30}Cl_3NOP_2Ru$: C, 56.74; H, 3.98; Cl, 13.92. Found: C, 55.74; H, 4.14; Cl, 13.40.

The compound is too insoluble in common organic solvents for molecular weight determinations. The infrared spectrum has ν_{NO} at 1880 cm^{-1}, ν_{RuCl} at 320 cm^{-1} and 310 cm^{-1}.

Reactions of $RhClCO(PPh_3)_2$ with NO. Nitric oxide was bubbled through a refluxing solution of $RhClCO(PPh_3)_2$ in chloroform for fifteen minutes. The solution turned dark brown initially, then lightened to orange-brown. The chloroform was boiled off and ethanol was added to give a tan crystalline compound whose infrared spectrum showed no terminal carbonyl bands, but did have bands in the nitrosyl region at 1628, 1560, 1537 and 1480 cm^{-1}. Other strong bands at 1300 and 812 cm^{-1} may suggest the presence of nitro groups. Recrystallization of the crude product from chloroform-ethanol did not significantly change the infrared spectrum; it still had the appearance of a mixture. Recrystallization of the material from a dimethylformamide-chloroform mixture as per Kukushkin and Singh[3] gave a brown, crystalline compound whose infrared spectrum contained, besides bands attributable to triphenylphosphine, bands at 1630 cm^{-1} (ν_{NO}), 1660 cm^{-1} (ν_{CO}) and 2930 cm^{-1} (ν_{CH}), suggesting the presence of coordinated NO^+ and dimethylformamide. There were no strong bands in the terminal rhodium-chlorine stretching region (300-350 cm^{-1}).

Physical Measurements. Infrared spectra were run on a Beckman IR-10 infrared spectrometer. Esr spectra were run on a Varian V4502 spectrometer with auxiliary equipment. Chemical analyses were done by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y., and Alfred Bernhardt, West Germany.

(6) M. B. Fairy and R. J. Irving, *J. Chem. Soc.* (A), 475 (1966).

Table I. Esr data for rhodium(II) complexes

Complex	g Factors	References
$(Bu_4N)_2RhC_4S_4(CN)_4$	$g_x = 2.447$, $g_y = 2.019$, $g_z = 1.936$	9
$(\pi{-}C_5H_5)_2Rh$	$g_\parallel = 2.033$, $g_\perp = 2.003$	10
$RhCl_2(PPh_3)_n$	$g = 2.19, 2.05$	11
$RhNOCl_3(PPh_3)_2$	$g_\parallel = 2.03$, $g_\perp = 2.01$	This paper
$RhNOCl_3(EtOH)_n$	$g = 2.17$	This paper

Discussion

The compound $RuNOCl_3(PPh_3)_2$ has been prepared previously[6] in a two step reaction involving the isolation of $RuNOCl_3 . 2H_2O$ from hydrochloric acid solution and subsequent reaction of this compound with triphenylphosphine. Our procedure appears to be simpler and more rapid, gives virtually quantitative yields based on the $RuCl_3 . 3H_2O$ used, and should prove to be quite general for other ligands.

Although the crude product initially obtained from the reaction mixture is as previously stated yellow, it is soluble in chloroform and, when recrystallized, is orange in colour. This change in colour is not accompanied by change in the infrared spectrum in the region 300-4000 cm^{-1}.

By analogy, the reaction of $RhCl_3 . 3H_2O$ with nitric oxide was expected to give a derivative of $RhNOCl_3$, formally rhodium(II) and hence paramagnetic. Nitric oxide itself does not show an esr spectrum in solution,[7] and so the generation of a resonance signal on treating $RhCl_3 . 3H_2O$ with NO indicates the presence of a paramagnetic rhodium species. Rhodium(II), which is a d^7 system, would probably form low spin complexes and is expected to show an esr spectrum at room temperature with g factors close to 2.00.[8]

Although the low value of ν_{NO} for this compound is very low compared with that of the analogous ruthenium compound, formulation as a compound of Rh^{IV} with a cordinated NO^- seems unlikely, since esr spectra of low spin d^5 systems are generally not observable at room temperature and do not have g values close to 2.0.[8] Table I lists g values for all the rhodium(II) complexes which we are aware of in the literature. It can be seen that our findings are clearly consistent with the presence of rhodium(II).

Speculation about the reasons for the instability of the rhodium(II) complexes may be in order at this point. The unpaired electron in a low spin octahedral complex is in a relatively high energy σ antibonding orbital. Such a complex could be stabilized by oxidation to a low spin diamagnetic d^6 complex, and it is known that many low spin cobalt(II) complexes are very readily oxidized.[12] By analogy, solvated $RhNOCl_3$ appears to lose the nitric oxide radical on removal of the solvent, the rhodium in effect being oxidized to the +3 oxidation state.

Coordination of triphenylphosphine, however, makes the lower oxidation states more stable, and $RhNOCl_3(PPh_3)_2$ loses a chlorine radical to form $RhNOCl_2(PPh_3)_2$. This complex probably has a trigonal bipyramidal structure; the presence of only one rhodium-chlorine stretching frequency suggests the presence of trans axial chlorine atoms.

The reaction between nitric oxide and $RhClCO(PPh_3)_2$ is clearly very complex. The product obtained from chloroform was not, from its infrared spectrum, the $RhCl(NO)_2(PPh_3)_2$ reported by Kukushkin and Singh[3], nor was it the green $RhNOCl(NO_2)(PPh_3)_2$ reported by Hughes.[4] The existence of the former compound seems unlikely in view of the fact that Hieber[1] found that reaction of $Rh(NO)_2Cl$ with triphenylphosphine yielded $RhNO(PPh_3)_3$ and $RhNOCl_2(PPh_3)_2$, the expected substitution compound, $RhCl(NO)_2(PPh_3)_2$, apparently being unstable. We had expected that the compound $RhClNO(PPh_3)_2$, reported by Kukushkin and Singh,[3] would be identical with $RhNOCl_2(PPh_3)_2$, these two formulations being indistinguishable on the basis of the analyses reported (rhodium and nitrogen only). The material we obtained appeared to be very similar to their compound, but contained dimethylformamide and did not have a recognizable rhodium-chlorine stretching band in its infrared spectrum. Thus its identity remains uncertain also.

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(7) P. W. Atkins and M. C. R. Symons, « The Structure of Inorganic Radicals », Elsevier, New York, 1967, p. 108.

(8) B. R McGarvey, « Transition Metal Chemistry », Vol. 3, R. L. Carlin, Ed., Marcel Dekker, Inc., New York, 1967.

(9) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Amer. Chem. Soc.*, *86*, 4580 (1964).

(10) H. J. Keller and H. Wawersik, *J. Organometal. Chem.*, *8*, 185 (1967).

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

(12) G. N. Schrauzer, *Acc. Chem. Res.*, *1*, 97 (1968).