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SYNTHESIS AND REACTIONS OF DIHYDRIDONITROSYLTRIS-(TRIPHENYLPHOSPHINE)RHENIUM

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Summary

The synthesis of the novel rhenium hydridonitrosyl complex $ReH_2(NO)(PPh_3)_3$ and its reactions with X_2, HX (X = Cl, Br, I) and carbon monoxide are described.

Introduction

The pentahalogenonitrosylrhenate complexes $[Re(NO)X_5]^{2-}$ (X = Cl, Br [1] and I [2]) have proved to be very useful starting materials for the syntheses of a variety of rhenium nitrosyl compounds. We have described the preparation of complexes containing solvents such as alcohols, acetonitrile and dimethylsulphoxide with formula $[Re(NO)X_4L]^-$ (X = Cl, Br [3], I [2]; L = solvent molecule). The reactions with phosphines, diphosphines, amines, pyridine and picolines give a number of products which will be reported later. Since in all the above derivatives the rhenium atoms exhibit formal oxidation numbers of +2 or +1, attempts were made to prepare compounds with the metal atom in a lower oxidation state, using strong reducing agents such as sodium borohydride, and thus we obtained the hydridonitrosyl complex described below, $ReH_2(NO)(PPh_3)_3$. It is the second example of a rhenium hydridonitrosyl, the other being the recently reported $ReH(NO)_2(PPh_3)_2$ [4]. While a manganese analogue of the latter is also known [5], this is not the case for our compound.

Results and discussion

The direct reactions of $[Re(NO)X_5]^{2-}$ with sodium borohydride in solution were unsuccessful. Variation of the reaction conditions (solvent, temperature, concentrations) led in all cases to complete decomposition of the pentahalogeno complexes to metallic rhenium. We therefore tried a two-phase procedure, as previously used for the preparation of some rhenium hydrides [6,7]. The parent pentahalogenonitrosyl is suspended in boiling ethanol containing an excess of triphenylphosphine, and $NaBH_4$ is added in small portions. Refluxing gives a yellow precipitate of $ReH_2(NO)(PPh_3)_3$ in good yield. The compound is diamagnetic. It reacts with halogens in solvents such as benzene attending to equation 1. The reaction leads to the complete elimination of the hydridic hydrogens and to the oxidation of the metal atom by the halogen. The gas evolved was measured and identified by GLC. The products $Re(NO)X_3(PPh_3)_2$ can be isolated by use of appropriate conditions. The chloro and bromo compounds had been previously obtained by a different route [1], but the iodo analogue was unknown.

$$ReH_2(NO)(PPh_3)_3 + 3/2\ X_2 \rightarrow Re(NO)X_3(PPh_3)_2 + H_2 + PPh_3 \qquad (1)$$

$(X = Cl, Br, I)$

The reactions with hydrogen halides in benzene also give rise to gas formation (identified as hydrogen by GLC) but the nature of the reaction is not so clear. When the process is carried out in open air, the compounds $Re(NO)X_3(PPh_3)_2$ are again obtained. On the other hand, under an inert atmosphere, extremely unstable products are formed, difficult to analyze, which may be tentatively formulated as $Re(NO)X_2(PPh_3)_2$. (This type of complex, with $X = Cl$, was recently obtained by another method [8]). It is clear that in the former case the oxidation of the metal is due to atmospheric oxygen and the reaction occurs readily if oxygen is bubbled through the solution.

The reaction of $ReH_2(NO)(PPh_3)_3$ with carbon monoxide was also examined; in toluene with CO at atmospheric pressure the known, unstable species $Re(NO)(CO)_2(PPh_3)_2$ [4] is obtained, but the reaction is slow.

An alternative synthesis of the dihydridonitrosyl complex involves a similar procedure but from the trihalogenonitrosyl compounds $Re(NO)X_3(PPh_3)_2$. The reactions occur readily and in good yields.

When the crude powdered product $ReH_2(NO)(PPh_3)_3$ obtained by both methods is crystallized from a suitable solvent, it can give crystals containing trapped solvent molecules. This is the case with benzene, the product being $ReH_2(NO)(PPh_3)_3 \cdot \frac{1}{2}\ C_6H_6$, as shown by a single crystal X-ray analysis [9]. The IR spectrum of this species in the solid (Nujol mull) exhibits three characteristic bands: at 1950m and 1800s cm^{-1}, assigned to the Re—H stretching modes, and at 1640vs cm^{-1}, due to the $\nu(NO)$ mode. The IR spectra in solution show exactly similar bands. When $ReH_2(NO)(PPh_3)_3$ is crystallized from CS_2, solvent molecules are again trapped in the crystals, as indicated by the solid state IR spectrum, which shows, in addition to the usual bands, a strong band at 1520 cm^{-1} characteristic of the free solvent.

The presence of two Re—H bands, which are exceptionally strong when compared with the corresponding bands in other rhenium hydrides, is an indication of the mutually *cis* position of the two hydridic hydrogen atoms. This fact has been confirmed by a structure determination [9], which also showed the linearity of the Re—N—O interaction. The compound has a markedly distorted octahedral geometry, as illustrated in Fig. 1.

The NMR spectrum in the hydridic hydrogen region exhibits a multiplet centered at τ 11.5 (see Fig. 2). It is interpreted as involving the partial overlap of two quartets (1:3:3:1), at τ 10.9 and at τ 12.1 respectively, with J(P—H)

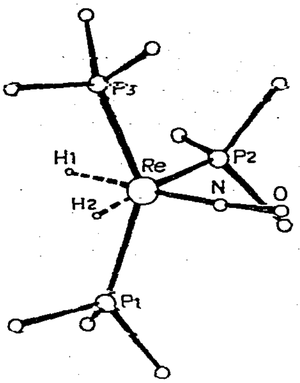

Fig. 1. Schematic view of the inner coordination sphere of the molecule $ReH_2(NO)(PPh_3)_3$.

equal to 30 Hz in both cases, each peak being split with a J(H—H) of 5 Hz. Upon raising the temperature from —40 to 72°C the main features remain essentially unchanged, but with a moderate decrease of overlap at lower temperatures and a moderate increase at higher temperatures. Since a stereochemically rigid molecule of this kind would give rise to a quartet (1:3:3:1) plus two triplets (1:2:1), as was found in similar complexes, e.g. in $RuH_2(CO)(PPh_3)_3$ [10], $OsH_2(CO)(PEtPh_2)_3$ [11] and $[IrH_2(CO)(PPh_3)_3]^+$ [12], there seems to be a fluxional situation in our case. It is noteworthy that the values of these hydridic resonances are the lowest ever found for a rhenium complex.

Experimental

Reagent grade solvents and chemicals were used unless otherwise stated. IR spectra were recorded on Perkin—Elmer grating spectrometers mod. 237 and mod. 621. Magnetic moments were measured on a Gouy balance. Elemental analyses were carried out at the Microanalysis Laboratory of the University of Milan.

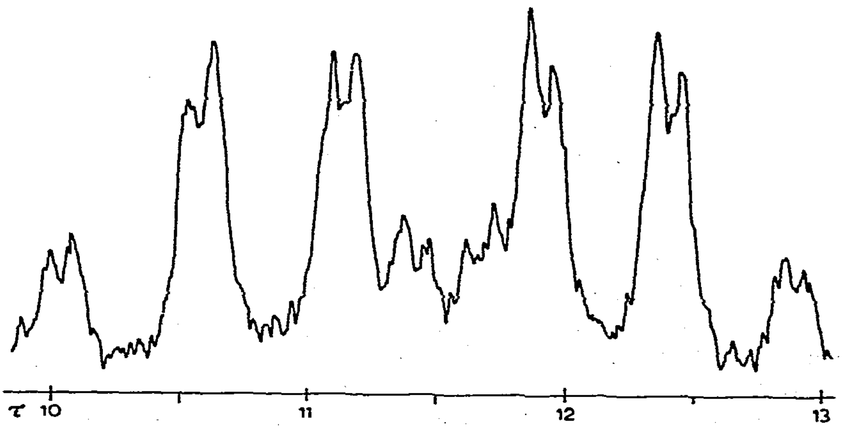

Fig. 2. High field region of the ^1H NMR spectrum of $ReH_2(NO)(PPh_3)_3$ recorded at 60 MHz in CS_2 solution.

Dihydridonitrosyltris(triphenylphosphine)rhenium

(a) Pentahalogenonitrosylrhenate and triphenylphosphine (molar ratio 1:5) were suspended in 30 ml of ethanol. The mixture was refluxed for 15 min and then $NaBH_4$ was added in very small portions (30 min). A vigorous evolution of gas occurred and the green suspension turned yellow. The hot suspension was filtered and the precipitate washed with hot ethanol to give a yellow powdered product which was recrystallized from a mixture of benzene /ethanol. Yield: 60%.

(b) Trihalogenonitrosylbis(triphenylphosphine)rhenium and triphenylphosphine (molar ratio 1:2) were suspended in 30 ml of ethanol. The mixture was refluxed for 15 min and $NaBH_4$ is added in small portions until the suspension became yellow. The procedure was then as in *a*. Yield: 60%. Analysis: found: C, 64.9; H, 4.45; N, 1.31. $C_{21}H_{20}NOP_3Re$ calcd.: C, 65.5; H, 4.82; N, 1.34%. M.p. 178°C. The compound is soluble in benzene, chloroform and carbon disulphide, and insoluble in hexane and alcohols.

Trichloronitrosylbis(triphenylphosphine)rhenium

Dihydridonitrosyltris(triphenylphosphine)rhenium was dissolved in benzene and benzene saturated with chlorine was added dropwise at room temperature. The yellow solution rapidly turned red and gas was evolved. After a few minutes a purple precipitate was obtained by addition of hexane. Yield: 75%. Analysis: found: C, 51.9; H, 3.50; N, 1.65. $C_{36}H_{30}Cl_3NOP_2Re$ calcd.: C, 51.2; H, 3.54; N, 1.65%. M.p. 230°C. The compound is slightly soluble in benzene, insoluble in other organic solvents.

Tribromonitrosylbis(triphenylphosphine)rhenium

Dihydridonitrosyltris(triphenylphosphine)rhenium was dissolved in benzene and then a benzene solution of bromine was added dropwise at room temperature. The yellow solution rapidly turned deep green and gas was evolved. After a few minutes a deep green precipitate was obtained by addition of hexane. Yield: 75%. Analysis: found: C, 43.6; H, 2.96; N, 1.39. $C_{36}H_{30}Br_3NOP_2Re$ calcd.: C, 44.1; H, 3.06; N, 1.43%. M.p. 215°C. The compound is slightly soluble in benzene, insoluble in other organic solvents.

Triiodonitrosylbis(triphenylphosphine)rhenium

Similarly use of iodine gave a brick red compound. Yield: 60%. Analysis: found: C, 38.7; H, 2.65; N, 1.23. $C_{36}H_{30}I_3NOP_2Re$ calcd.: C, 38.5; H, 2.75; N, 1.25%. The compound is soluble in benzene and chloroform and insoluble in other organic solvents.

Dicarbonylnitrosylbis(triphenylphosphine)rhenium

Dihydridonitrosyltris(triphenylphosphine)rhenium was dissolved in toluene and carbon monoxide was bubbled through for 6 h during which the yellow solution turned red. It was concentrated under vacuum and addition of ethanol gave a red precipitate in 40% yield. Analysis: found: C, 57.8; H, 3.66; N, 1.69. $C_{38}H_{30}NO_3P_2Re$ calcd.: C, 57.2; H, 3.76; N, 1.76%. M.p. 180°C (dec.). The compound is unstable in air.

Acknowledgements

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