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A Novel Dinuclar Nitrosylruthenium(II) Complex. X-ray Structure Determination of $(RuCl_2(NO)[(EtO)_2PO]_2H)_2$

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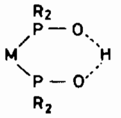
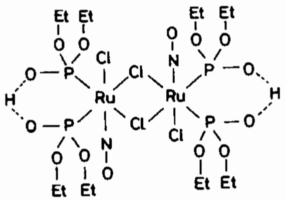
Introduction

Recently, platinum subgroup metal complexes containing the hydrogen bis(diphenylphosphinite) or hydrogen bis(dialkylphosphonite) groups as in I have attracted attention as possible precursors for inorganic oligomers with chains of mixed metal atoms [1, 2]. Furthermore, the existence of very short (~2.4 Å) O••H••O distances in these derivatives [3] implies that information of fundamental importance to strong hydrogen bonding may be available from studies of the P–O–H–O–P bond system in I.



(I)

We report here that $RuCl_3 \cdot xH_2O$ in the presence of tertiary phosphites and a source of nitrosyl leads in one step to a novel centrosymmetric dinuclear nitrosylruthenium(II) complex *1* for which an accurate X-ray structure determination has shown that two six membered heterometallocycles Ru–P–O—H—O–P are bridged by two chlorine atoms. This compound is, to our knowledge, the first example of a non-platinum subgroup metal complex shown to contain the hydrogen bis(diethylphosphonite) anion as in *1*.



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Results and Discussion

In an attempt to prepare $Ru(NO)Cl_3(P(OR)_3)_2$, *2* according to the general procedure leading to analogous phosphine derivatives [3] via refluxing during 24 hr a mixture of $RuCl_3 \cdot xH_2O$ (4 mmol), N-methyl, N-nitrosoparatoluenesulfonamide (6 mmol) and an excess (16 mmol) of triphenylphosphite in dry ethanol we obtained, beside phenol formation, the bright yellow compound *1* (55%; m.p. 240–242 °C). The same product *1* could be isolated from a similar reaction sequence but using the triethylphosphite (77%). The molecular weight (942 ± 20) calculated from the unit cell volume and experimental density, was consistent with the formula corresponding to *1* (954.57).

Infrared spectra of *1* showed one broad nitrosyl absorption band at 1900 cm^{-1} and absorptions at 342, 287 and 237 cm^{-1} indicating both terminal and bridging RuCl bonds.

The ^1H nmr spectrum exhibited three signals of relative intensity 12:8:1 [δ ppm ($CDCl_3$): 1.43–1.37 (double triplet) $^3J_{H-H}$: 7Hz); 4.37 (multiplet) and 13.25 (broad singlet)]. The two first signals correspond to the two types of $POCH_2CH_3$ groups. The last signal which disappeared on addition of D_2O was attributed to two equivalent P–O–H protons. A proton decoupled ^{31}P nmr spectrum showed only one singlet at +79.1 ppm downfield from H_3PO_4 in $CDCl_3$ indicating the equivalence of phosphorus nuclei at 35 °C. These results led us to suggest for *1* the arrangement $[RuCl_2(NO)[(EtO)_2PO)_2H]_2$ which was confirmed by a single crystal X-ray structure determination.

Crystal Data

$Ru_2Cl_4P_4O_{14}C_{16}H_{42}$, space group $P\bar{1}$, $a = 9.370(2)$, $b = 10.248(5)$, $c = 10.933(6)$, $\alpha = 93.89(0.03)$, $\beta = 101.33(0.04)$, $\gamma = 113.82(0.06)$, $V = 928.9$ Å^3, $D_c = 1.71$, $D_{ex} = 1.69$, $Z = 1$. Intensity data ($0.05 < \sin\theta/\lambda < 0.7$) were recorded on a NONIUS C.A.D.4 diffractometer with graphite monochromated MoKα radiation. The 3921 unique observed intensities were not corrected for absorption. The structure was solved by direct methods. Positional and anisotropic thermal parameters for all non hydrogen atoms were refined by full matrix least squares. The hydrogen atoms located on a difference Fourier synthesis were refined with isotropic thermal factors to $R = 0.043$ and $R_w = (\Sigma w\Delta^2/wF_o^2)^{1/2} = 0.044$.

A perspective view of the structure is given in the figure. The molecule contains linear nitrosyl ligands with *trans* terminal chlorines (Ru–N–O(1), 177.60(24)°; N–Ru–Cl(2), 177.58(0.1)°), equivalent Ru–P(1) and Ru–P(2) bond lengths of 2.301(1) and 2.302(1) Å respectively and almost symmetrical

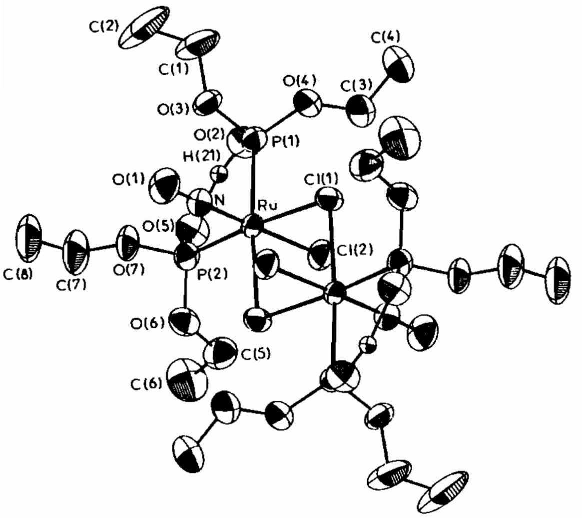

Figure. Molecular structure of $\{RuCl_2(NO)[(EtO)_2PO]_2H\}_2$, *1*.

bridging Ru–Cl, bond distances (Ru–Cl(1), 2.494(1) Å; Ru–Cl(1)′, 2.484(1) Å). The most significant feature is the six-membered ring Ru–P–O–H–O–P geometry for which the bridging H(21) has been located. The non-bonded distance O(2)- - -O(5) (2.432(5) Å) is in the range normally expected for strong symmetrical hydrogen bonds [5] yet both P–O [P(1)–O(2), 1.526(2); P(2)–O(5), 1.508(2) Å] and O–H [O(2)–H(21), 1.00(5); O(5)–H(21), 1.45(5) Å] distances are suggestive of some asymmetry in the P–O–H–O–P moiety. It is also interesting that in this structure and in both of the other two X-ray analyses [3, 6] of metal complexes containing $Ph_2PO\cdots H\cdots OPPh_2$ groups the O···H···O distances are shorter than 2.44 Å despite the presence of different groups on phosphorus and ligands *trans* to phosphorus of very different *trans* influence. The hydrogen bonds in these systems are clearly some of the strongest known and we are currently exploring the use of other techniques to characterise their potential wells.

The synthesis of *1* can be understood by the initial formation of *2*; Compound *2* (R = Ph) could be obtained in the same fashion as *1* but using dry tertiary butanol instead of ethanol. The solvolysis of *cis* coordinated phosphino acetylenes [3] or tertiary phosphinites or phosphites [6–8] leading to the formation of six-membered rings as in *1* is well documented for palladium and platinum complexes. In the present case the nitrosyl ligand probably plays a significant role in preventing the formation of an $RuCl_3Ru$ bridge which would lead to an unsymmetrical complex [9]. The formation of this new type of six coordinated nitrosyl ruthenium dimer can be extended to other phosphite ligands.

Acknowledgements

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