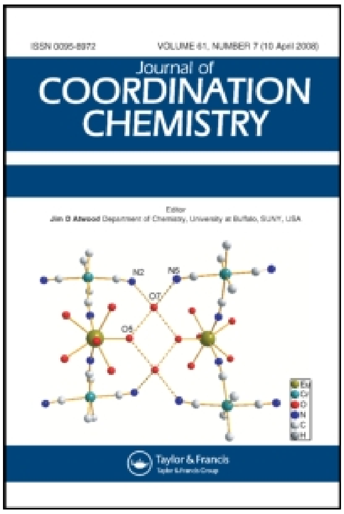

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Synthesis, Structure and Catalytic Activity of An Oxorhenium(V) Complex Containing Chelating Phosphite Ligand

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NOTE

SYNTHESIS, STRUCTURE AND CATALYTIC ACTIVITY OF AN OXORHENIUM(V) COMPLEX CONTAINING CHELATING PHOSPHITE LIGAND

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The new violet oxorhenium(V) complex $ReOCl_3$(pinacop) {pinacop = $(OCMe_2CMe_2O)POCMe_2CMe_2OP(OCMe_2CMe_2O)$} was obtained by reaction of $ReOCl_3(OPPh_3)(SMe_2)$ with a stoichiometric amount of pinacop. Facial geometry was determined by spectroscopic means and preliminary results from an X-ray crystallographic study. The catalytic properties of the title compound in oxygen atom transfer reactions are discussed.

Keywords: oxorhenium(V), chelating phosphite, oxygen atom transfer, X-ray structure

INTRODUCTION

Transition oxo-metal complexes have a prominent function in molecular, heterogeneous and enzymatic catalysis.[1] Some of these complexes exhibit catalytic activity in oxygen atom transfers and/or olefin metathesis reactions.[2] The same applies also to oxorhenium(V) complexes.[3] Among rhenium compounds, phosphiterhenium(V) complexes comprise a relatively small group of compounds.[4] This paper reports the synthesis and structural characterization of the oxorhenium(V) complex $ReOCl_3$(pinacop), containing the bidentate phosphite ligand pinacop $(OCMe_2CMe_2O)POCMe_2CMe_2OP(OCMe_2CMe_2O)$. We also present results concerning catalytic activity of $ReOCl_3$(pinacop) in a model oxygen atom transfer reaction between dimethylsulphoxide and triphenylphosphine. The ligand[5a] was first applied by Bleeke *et al.* in the synthesis of cobalt and rhodium complexes[5b] with phosphite.

RESULTS AND DISCUSSION

Synthesis and characterization of $ReOCl_3$(pinacop)

The violet compound $ReOCl_3$(pinacop) was afforded by reaction (*1*) of $ReOCl_3(OPPh_3)(SMe)_2$[6] with a stoichiometric amount of the chelating phosphite pinacop in boiling toluene, with 86% yield. The crude solid product, sparingly soluble in chloroform, was recrystallized from CH_2Cl_2/Et_2O as the $ReOCl_3(\text{pinacop})\cdot CH_2Cl_2$

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solvate.

$$\mathrm{ReOCl_3(OPPh_3)(SMe_2)+pinacop \xrightarrow[5h]{toluene} ReOCl_3(pinacop)+OPPh_3+SMe_2} \quad (1)$$

Two isomeric forms of the complex are possible, meridional and facial. The FIR spectrum (200–350 cm^{-1}) shows three intense bands, ν(Re-Cl), at 329, 300 and 286 cm^{-1}, which suggests meridional geometry. However, facial arrangement of the chloride ligands could not be excluded.[7] The IR spectrum in the ν(Re-O) range (1000–900 cm^{-1}), displays strong absorptions for the coordinated bidentate phosphite. This prevents unequivocal assignment of the ν(Re-O) frequency.

The electronic spectrum of ReOCl$_3$(pinacop) in CH$_2$Cl$_2$ solution shows two weak absorptions in the visible region at 750 (ε16.9) and 560 nm (ε51), which could be assigned to the $n(dxy)\rightarrow\pi^*(dxz, dyz)$ transitions, characteristic of the 4–5d^2 systems containing the oxo-metal arrangement.[8] The energetically higher intense band at 298 nm (ε4940 M^{-1} cm^{-1}) corresponds to one of the possible CT transitions.

The ^{1}H NMR (100 MHz) spectrum of ReOCl$_3$(pinacop) recorded in C^{2}H$_2$Cl$_2$ shows the resonance signals of the ligand methyl groups as an unresolved multiplet at 1.6 ppm, shifted somewhat downfield in relation to the free ligand (1.11, 1.31 and 1.54 ppm).[5] The ^{31}P{^{1}H} NMR spectrum gives a singlet at 61.7 ppm (free ligand 141.9 ppm) indicating the equivalence of both coordinated phosphorous atoms. The ^{13}C{^{1}H} NMR spectrum shows two sets of four and three signals (in each set). First, four signals at 25.2, 25.8, 26.1 and 26.5 ppm have intensity ratio ca 2:2:1:1 and correspond to twelve nonequivalent methyl group carbons, indicating a lower symmetry for the coordinated ligand with respect to the free.[9] The three signals at 90.2, 92.0, and 93.2 ppm derive from the six quaternary carbon atoms (C—O) of the phosphite ligand. This suggests that four of them in the rings behave as two pairs (possibly at 90.2 and 92.0), while the remaining two carbons (at 93.2 ppm) within the bridge show equivalence. This equivalence is consistent with the ^{31}P NMR equivalence of the two phosphorous atoms and with the nonequivalence of the twelve methyl groups. NMR properties thus suggest that the bidentate phosphite is coordinated in a symmetrical manner and points to facial geometry for ReOCl$_3$(pinacop).

Oxygen transfer reaction

Several oxorhenium(V) complexes undergo reduction, accompanied by oxygen atom transfer,[2a,3,10] but few exhibit catalytic properties. Efficiency of reaction depends on the properties of the ligands coordinated to the oxorhenium group. To measure this dependence, the catalytic activity of ReOCl$_3$(PPh$_3$)$_2$[11] and ReOCl$_3$(pinacop) was compared in the model oxygen atom transfer (*2*).

$$\mathrm{Me_2SO+PPh_3 \xrightarrow{[Re]} Me_2S+OPPh_3} \quad (2)$$

Reaction (*2*) was carried out in C^{2}H$_2$Cl$_2$ solution at 25°C and the abundance of Me$_2$S was monitored by ^{1}H NMR. A tenfold PPh$_3$ and twenty fold Me$_2$SO molar excess with respect to the rhenium compound was used. Reaction (*2*) did not proceed

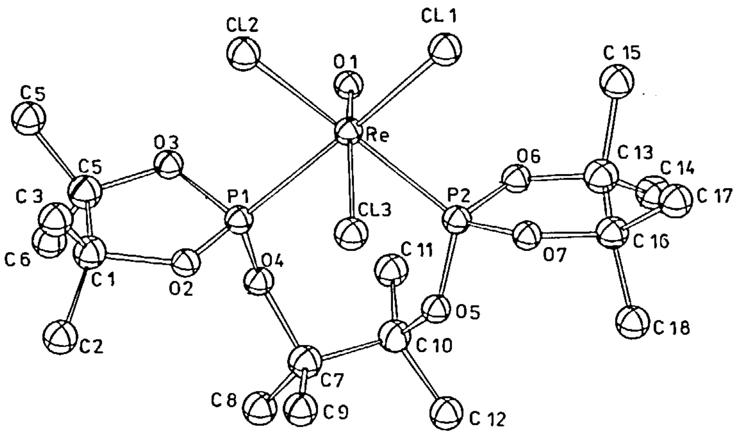

FIGURE 1 Molecular structure of ReOCl (pinacop) based on initial X-ray analysis-[14].

out the rhenium complexes. For $ReOCl_3(PPh_3)_2$, reaction (*2*) was not complete hours and the number of catalytic cycles was 5. For $ReOCl_3$(pinacop), a rapid complete reaction was observed. Even a 100-fold decrease in catalyst entration allows reaction (*2*) to complete 9 catalytic cycles per hour. There was nduction period and linear time-dependence of Me_2S accumulation to about conversion of PPh_3 was observed. The prominent activity enhancement for Cl_3(pinacop) as compared with $ReOCl_3(PPh_3)_2$ and other known oxorhenium pounds[2a,3,6a] could be due to the chelating effect of the bidentate phosphite d. However, the contribution of electronic and steric effects of the ligand in lization of the oxorhenium(V)/rhenium(III)[12] couple cannot be excluded.

order to determine the structural features of the oxorhenium arrangement,[13] as as to confirm the proposed facial structure of the compound, its single crystal y analysis was undertaken. Initial results reveal[14] an octahedral structure for omplex (Fig. 1). The chloride ligands are coordinated facially. The oxorhenium ngement is perpendicular to the plane formed by the rhenium atom and the two valent phosphorous atoms.

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13. The unusually long Re=O bond 1.869(11) (and also apparently weak) resulting from "*trans* influence isomerism" was reported recently for *fac*.$ReOCl_3(PPhEt_2)_2$; V. S. Sergienko and M. A. Porai-Koshits, *Dpkl. Akad. Nauk SSSR*, **309**, 903 (1989).
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