



The interactions between the sterically demanding trimesitylphosphine oxide and trimesitylphosphine with scandium and selected lanthanide ions



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ARTICLE INFO

Article history:

Received 12 October 2015

Received in revised form

26 January 2016

Accepted 26 January 2016

Available online 1 February 2016

Keywords:

Phosphine oxide

Lanthanide

Scandium solution NMR

X-ray crystal structure

ABSTRACT

The reactions between lanthanide nitrates, $\text{Ln}(\text{NO}_3)_3$ and scandium and lanthanide trifluoromethane sulfonates, $\text{Ln}(\text{Tf})_3$ with trimesitylphosphine oxide, Mes_3PO show that coordination to the metal ions does not lead to crystalline complexes. Investigation of the reactions by ^{31}P NMR spectroscopy shows that weak complexes are formed in solution. The crystal structures of $\text{Mes}_3\text{PO} \cdot 0.5\text{CH}_3\text{CN}$ (**1**) and $[\text{Mes}_3\text{PO}]_3\text{H}_3\text{O} \cdot 2\text{CH}_3\text{CN} \cdot \text{Tf}$ (**2**), formed in the reaction between ScTf_3 and Mes_3PO , are reported. Trimesitylphosphine, Mes_3P , is protonated by scandium and lanthanide trifluoromethane sulfonates and lanthanide nitrates in CD_3CN and the structure of $[\text{Mes}_3\text{PH}]\text{Cl} \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ (**3**) is reported.

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1. Introduction

The coordination chemistry of phosphine oxides with lanthanide ions has attracted interest for a number of years because of the potential the complexes have in a variety of applications [1,2].

Complexes of lanthanide nitrates have been studied in some detail in the solvent extraction separation of lanthanide from actinides carried out in nitric acid solutions [3–5]. We have previously studied the effect on structures and solution properties of increasing the size of the R group in R_3PO where we found that solid state structures and solution properties depend on a balance between steric and electronic effects of the phosphine oxides and the size of the lanthanide ions [6–8]. Cone angles, are not available for phosphine oxides, and as a result we have used the cone angles of the parent phosphine [9] as a proxy for the steric demands of the oxides. Previous studies on trialkyl phosphine oxides R_3PO (R = Et [6], ^tBu [7], cyclohexyl [10] and ^tBu [8]) have shown that significant differences in the properties of the lanthanide nitrate complexes result with changes in the steric and electronic properties of the ligands.

We have extended our studies to include the more highly

sterically demanding trimesitylphosphine oxide, for which the cone angle of the parent phosphine is 212° [9].

Lanthanide ions do not form complexes with soft donors such as phosphines in the presence of competition from hard donor ligands such as water. We have previously found that sterically crowded phosphine oxides are able to hydrogen bond to lanthanide-coordinated water molecules [11,12]. Theoretical studies of hydrogen bonding between phosphines and a variety of hydrogen donors have indicated that such bonding can give rise to stable complexes [13–15] and an $\text{HF} \cdot \text{PH}_3$ dimer has been identified in the gas phase [16]. In view of this we have conducted a brief investigation into the interaction of the sterically demanding Mes_3P with hydrated lanthanide salts to investigate whether hydrogen bonding to coordinated water occurred.

2. Results and discussion

2.1. Synthesis and solid state structures

Attempted synthesis of complexes of Mes_3PO with representative lanthanide nitrates across the series (Ln = Pr, Nd, Gd, Ho, Er, Lu) was carried out in ethanol solution. The phosphine oxide is poorly soluble in warm ethanol but on addition of solutions of lanthanide nitrates clear solutions were obtained which implied that

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interaction with the metal had taken place. Attempts to obtain crystalline materials from these reactions by slow evaporation, cooling to $-30\text{ }^{\circ}\text{C}$ or slow diffusion with diethylether or toluene followed by cooling were not successful. The reactions led to either recovery of unreacted Mes_3PO , no solid materials or to the formation of oils. The reason for the apparent lack of coordination with $\text{Ln}(\text{NO}_3)_3$ is probably a combination of the high affinity of lanthanide ions for nitrate and the increased steric demands of the ligand limiting access of the phosphoryl oxygen to the coordination sites on the metal.

Clearly there is some interaction between Mes_3PO and the lanthanide nitrates in solution, but this does not result in the formation of complexes which are sufficiently stable to permit isolation. The reactions of lanthanide and scandium trifluoromethane sulfonates (triflates) were examined as the triflate ion has a low coordinating ability and might thus lead to a less crowded coordination environment around the metal. In reactions with LnTf_3 ($\text{Ln} = \text{La, Nd, Eu, Er, Lu}$) in ethanol the initial suspensions of Mes_3PO cleared on addition of the lanthanide salt, again implying some complex formation. The reaction mixtures, however, failed to yield characterisable materials.

In order to assess the steric congestion around the oxygen in trimesitylphosphine oxide the crystal structure of $\text{Mes}_3\text{PO} \cdot 0.5\text{CH}_3\text{CN}$ (**1**) was determined. The structure is shown in Fig. 1 details of the data collection and refinement are given in Table 1 and selected bond distances and angles in Table 2. The compound crystallises with two Mes_3PO molecules and one CH_3CN in the unit cell. There are no close contacts between the acetonitrile and the phosphine oxide. Comparison of this structure with Ph_3PO , which forms stable complexes with all simple lanthanide salts, indicates that the structure of Mes_3PO changes to reduce steric interactions between the methyl groups and in doing so increases the crowding of the environment around the O-atom, as described below. The P=O bond distance is 1.486 Å which is very similar to those reported for Ph_3PO , for example 1.483 [13] and 1.487 [14]. The C–P–C angles widen to reduce steric interactions between the methyl groups in Mes_3PO with an average of 110.2° compared to 106.4° in Ph_3PO . There is also a significant increase in the P–C bond distance compared with Ph_3PO from 1.800 Å to 1.828 Å which will further reduce steric crowding between the methyl groups. The structure

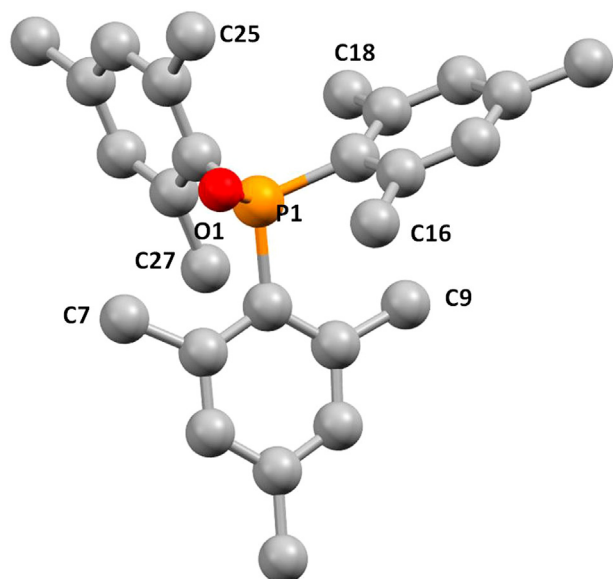


Fig. 1. The structure of $\text{Mes}_3\text{PO} \cdot \text{CH}_3\text{CN}$. The acetonitrile molecule is omitted for clarity.

shows that, compared to Ph_3PO , reduction in steric strain by widening of the C–P–C angle has the effect of making the methyl groups effectively shield the phosphoryl oxygen and this probably limits the availability of the P=O group to coordinate to the lanthanide ion, where the environment around the metal will already contain coordinated nitrate ions and/or water molecules.

The reaction with scandium triflate in CH_3CN did produce crystalline material which was suitable for x-ray diffraction study. The solid does not, however, contain scandium but is $[\text{Mes}_3\text{PO}]_3\text{H}_3\text{O}^+ \text{CF}_3\text{SO}_3^- \cdot 2\text{CH}_3\text{CN}$ (**2**). The hydronium ions are formed almost certainly by acid hydrolysis of hydrated Sc^{3+} . The structure is shown in Fig. 2 and details of the data collection and refinement are included in Table 1. Three Mes_3PO molecules are coordinated to H_3O^+ via hydrogen bonding and the CH_3CN and triflate ions are not involved in hydrogen bonding interactions. The P=O bonds are slightly longer (average 1.493 Å) than in Mes_3PO as expected on coordination to a positively charged centre. Larger increases in bond distances in similar structures such as $\text{Ph}_3\text{PO} \cdot \text{HBr}$ (1.550 Å) [15] and $\text{Ph}_3\text{PO} \cdot \text{HNO}_3$ (1.499 Å) [16] are probably due to the proton being coordinated to one phosphine oxide rather than three as in this study.

Trimesitylphosphine oxide is bulkier than trialkylphosphine oxides such as ${}^t\text{Bu}_3\text{PO}$ (the cone angle ${}^t\text{Bu}_3\text{P}$ is 182°) which forms only 1:2 complexes with lanthanide nitrates [8]. Trimesitylphosphine itself forms complexes with a number of metals and coordination compounds with Hg [17], Ag [18], Pt [19] and Au [20] have been characterised. The inability of Mes_3PO to form stable complexes might thus be considered to be surprising as the cone angle of the oxide will certainly be lower than that of the phosphine. A comparison of some of the parameters which might be relevant to their relative coordinating ability are given in Table 3.

The approach of Mes_3PO to the metal centre will be restricted by steric interaction with the methyl groups. The proximity of the methyls to the coordinating atoms indicates that the environments in Mes_3P and Mes_3PO are similar with P ... O and C ... O distances relatively short. Although the distances could be considered as indicative of hydrogen bonding (C ... O average in Mes_3PO is 2.89 Å compared to a sum of Van der Waals radii for C and O of 3.2 Å and C ... P average in Mes_3P is 2.72 Å compared to a sum of Van der Waals radii for P and C of 3.5 Å), it is more likely that these distances are imposed by the geometrical constraints of the molecules [21].

The differences in coordinating ability probably lies in the strong hydration of the lanthanide and scandium ions which combines with the steric congestion of the ligand to make coordination impossible under the conditions employed. In addition the metal ions coordinated to Mes_3P are likely to be less strongly solvated (for example using $\text{CH}_2\text{Cl}_2/\text{THF}$ as the reaction medium) and hence the effective size of the metal ions will be lower than hydrated lanthanide or scandium ions.

2.2. Solution NMR investigation

Given that there is clearly some interaction between the lanthanide ions and Mes_3PO several lanthanide triflate/ Mes_3PO systems were investigated by ^{31}P NMR spectroscopy.

The results are shown in Table 4. The absence of any large coordination shifts with the paramagnetic lanthanide ions indicates that there is no direct interaction between the phosphine oxide and the metal. However, the lines are broad and show a significant temperature dependence of the chemical shifts which whilst smaller than that observed for $\text{Ln}=\text{O}=\text{P}$ systems, is an order of magnitude greater than that of free Mes_3PO . We recently reported the structures of $[\text{Ln}(\text{H}_2\text{O})_5(\text{Cy}_3\text{PO})_2] \cdot 2\text{Cy}_3\text{PO} \cdot 3\text{X}$ ($\text{X} = \text{Cl, Br}$) [11,12] where $\text{Cy} = \text{cyclohexyl, C}_6\text{H}_{11}$ in which the Cy_3PO are either directly bonded to the metal ion or through hydrogen bonding to the

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