

X-Ray crystal structure of (tetraphenylimidodiphosphinato)silver(I): an unexpected tetranuclear complex with two modes of coordination of silver

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Potassium tetraphenylimidodiphosphinate reacts with silver nitrate to give, upon recrystallization from ethanol, an unexpected tetranuclear complex [Ag{N(OPPh₂)₂}]₄·2EtOH, the structure of which is established by X-ray crystallography; preliminary results concerning its use as a catalyst for the aerobic co-oxidation of alkenes and aldehydes are described.

The tetraphenylimidodiphosphinate ligand (TPIP), the 'inorganic' equivalent of β -diketonate ligands, has proven to lead to interesting complexes especially in the field of lanthanide NMR shift reagents.^{1–4} Thus, Pr(TPIP)₃, owing to its high stability with respect to hydrolysis even in the presence of acids (in contrast to β -diketonates), can be used as a shift reagent for carboxylic acids and induces important simplification in their ¹H NMR spectra. Moreover, Pr(TPIP)₃ reacts instantaneously with carboxylates to lead to dinuclear complexes: in the case of acids containing a chiral centre, these complexes can be used to control the optical purity of the starting acids. Along the same lines, the use of Gd(TPIP)₃ as a relaxation agent for carboxylic acids has recently been outlined.⁵ A common feature of all the complexes so far described is the mode of coordination of the TPIP ligand to the metal: as for β -diketonates, TPIP acts as a bidentate ligand.⁴

A second interesting feature of this ligand is its high stability towards oxidants: its preparation from the related phosphine can be carried out in concentrated hydrogen peroxide without noticeable decomposition. This observation and our ongoing efforts to develop new catalysts for the efficient, possibly asymmetric, epoxidation of alkenes, prompted us to carry out the systematic synthesis of various lanthanide and transition metal complexes containing this and related ligands for that purpose.⁶ Among the latter, we were interested in silver complexes containing such ligands. Indeed, silver-based catalysts are used in the epoxidation of ethene;⁷ however, complexes containing this metal have, to the best of our knowledge, not been tested in the aerobic aldehyde alkene co-oxidation system (Mukaiyama reaction).^{8,9}

Moreover, since silver chelates have also found interesting applications in NMR spectroscopy of alkenes,^{10,11} we decided to attempt the preparation of Ag(TPIP).

Here, we describe the synthesis and the unexpected X-ray structure of the new complex Ag(TPIP) and to provide preliminary results concerning its use as an oxidation catalyst.

When aqueous solutions of silver nitrate (0.170 g, 1 mmol; 10 ml H₂O) and of KTPIP (0.46 g, 1 mmol; 10 ml H₂O) were mixed a precipitate formed. Filtration of the solid followed by recrystallization from CH₂Cl₂–EtOH gave colorless crystals (0.34 g, 65% yield) which were stable in the air and in solution, and were suitable for X-ray analysis.† According to the NMR spectrum of the crystals,‡ half an equivalent of EtOH solvent was present in the product and elemental analysis confirmed this observation.

The molecular structure of Ag(TPIP) is shown in Fig. 1. The molecule is built up of four Ag(TPIP) units which are arranged pairwise and which contains two solvent molecules per formula unit. These molecular pairs reside on a crystallographically

imposed centre of symmetry. From a formal point of view, two Ag⁺ cations adopt the preferred^{12,13} linear coordination by combination with two TPIP ligands giving Ag(TPIP)₂[–], with N(1)–Ag(1)–N(2) 172.0(1)°, so leaving three pendent P=O groups, the remaining P=O group being linked *via* a hydrogen bond to ethanol. Two Ag⁺ cations share six P=O ligands and thus hold together the two Ag(TPIP)₂ anions. Moreover, these two anions are also coupled by a pair of Ag...Ag contacts (3.210 Å). The coordination of the two silver atoms to the six suitably oriented P=O groups occurs in such a way as to lead to a central planar Ag₂O₂ ring with O(3)–Ag(2)–O(3') 91.1(2)°, the two oxygen atoms being dissymmetrically bonded to silver with Ag(2)–O(3) 2.269(2) and Ag(2)–O(3') 2.654(2) Å. The coordination around silver is thus distorted tetrahedral with the oxygen atoms of the P=O groups as closest neighbours, the shortest bond occurring between silver and a terminal oxygen atom is Ag(2)–O(1) 2.195 Å.

The P=O bond lengths are comparable or slightly shorter (especially the P=O group linked to ethanol by its oxygen atom) than those found *e.g.* in Pr(TPIP)₃. By contrast, the P–N bonds are in general longer than those observed in Pr(TPIP)₃ (1.620 vs. 1.590 Å) thus confirming their single bond character.¹⁴

Direct comparison of this structure with that of the corresponding unstable silver β -diketonates^{15,16} could unfortunately not be established since the latter structures are so far unknown.

Although a number of mononuclear complexes in which the silver cation is surrounded by four oxygen (or sulfur) atoms giving distorted tetrahedral environment are known,^{17,18} as well

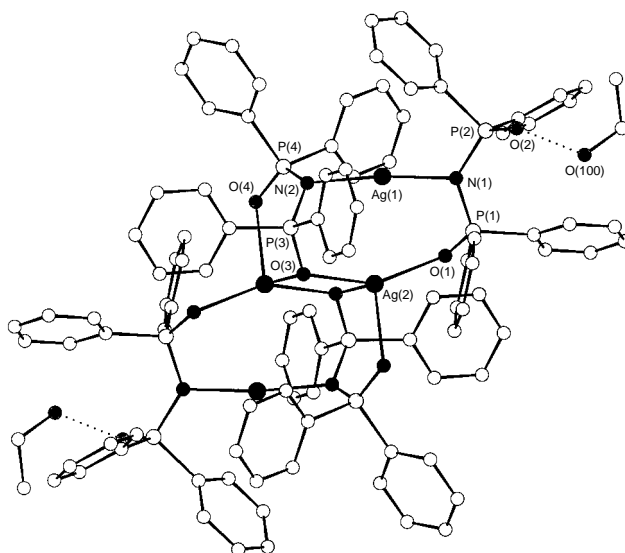


Fig. 1 Molecular structure of [Ag{N(OPPh₂)₂}]₄·2EtOH showing the atomic numbering scheme. Selected distances (Å) and angles (°): Ag(1)–N(1) 2.145(3), Ag(1)–N(2) 2.170(2), Ag(2)–O(1) 2.195(2), Ag(2)–O(3) 2.269(2), Ag(2)–O(3') 2.654(2), Ag(2)–O(4') 2.388(2); N(1)–Ag(1)–N(2) 172.0(2), O(3)–Ag(2)–O(3') 90.84(8), P(1)–N(1)–P(2) 130.7(2), P(3)–N(2)–P(4) 124.6(2).

Table 1 Epoxidation of various alkenes promoted by Ag(TPIP) in the presence of isobutyraldehyde and oxygen in dichloroethane

Entry	Alkene (mmol)	t/h	Yield acid (%)	Yield epoxide (%)	Yield furan (%)	Yield pyran (%)
a	Cyclooctene (0.77)	4	98	100		
b	Oct-1-ene (0.64)	20	98	40		
c	Cholesteryl acetate (0.59)	0.5	50	58 ^b		
	Cholesteryl acetate (0.59)	2	80	100		
d	Linalool (0.57)	3	70	26	30	4
e	Linalool (0.57)	21	99	5	85	10
f	Linalool ^c (5.7)	6	85	65	15	

^a $P(\text{O}_2) = 1$ atm, room temp.; aldehyde/alkene = 7; catalyst = 1 mol%. ^b α/β isomers: 32/68. ^c Linalool (1 ml), aldehyde (4 ml), catalyst (50 mg), dichloroethane (20 ml).

as an example of a trinuclear complex in which the silver atoms adopt both a linear and a tetrahedral coordination,¹⁹ the central planar dinuclear structure with the two linear Ag^- moieties found in the present complex is, to the best of our knowledge, unique.

Preliminary results of the catalytic properties of this complex in the oxidation of alkenes are promising. Many transition metals bearing various groups (usually β -diketonato ligands) are active in the aerobic co-oxidation of alkenes and aldehydes into epoxides and acids. However, one major problem is linked to the high rate of oxidation of the aldehyde to the acid: in such cases, the conversion of the alkenes into epoxides drops considerably, unless a large excess of aldehyde is used. We have now found that on the one hand that the lanthanide complexes (Pr, Eu, Dy) containing TPIP can be used for the epoxidation of alkenes: their activity are comparable to that of more classical complexes of Co and Mn.⁶ On the other hand, as shown in Table 1, a series of alkenes gave, in the presence of Ag(TPIP), the corresponding epoxides (and their rearrangement products for linalool²⁰) in yields and rates comparable to, or even higher than those observed for other metal TPIP complexes and also for the more classical metal β -diketonates ($M = \text{Mn}, \text{Co}$).^{8,9,21,22} Although cyclooctene and cholesteryl acetate (entries a and c) are readily oxidized alkenes, the result achieved with Ag(TPIP) is striking since high rates and quantitative conversions into the epoxide are observed. However, and as for other catalysts, the results were rather sluggish for monosubstituted terminal alkenes (entry b). Finally, for linalool, the conditions could be varied in order to obtain either the epoxides or their rearrangement products²⁰ (entries d–f).

Footnotes and References

† *X-Ray structure determination*: X-ray quality crystals were obtained by slow evaporation of CH_2Cl_2 from a solution of the silver complex in CH_2Cl_2 –EtOH. Data were collected at room temperature on a Nonius CAD4 diffractometer. Empirical absorption correction using PSISCAN was applied. Anomalous dispersion terms and correction of secondary extinction were applied. The structure was solved by SHELXS²³ and refined by

least-squares analysis using anisotropic thermal parameters for all non-hydrogen atoms. H atoms were located on a difference Fourier map, and their coordinates were refined as free atoms with an overall isotropic thermal parameter. 9260 reflections, with $F_o > 3\sigma(F_o)$ were used to solve and refine the structure to $R = 0.0338$ and $R_w = 0.0324$, 708 least-squares parameters. The programs used were CRYSTALS and CAMERON.^{24,25}

Crystal data: $\text{C}_{100}\text{H}_{92}\text{O}_{10}\text{N}_4\text{P}_8\text{Ag}_4$, $M = 2189$, triclinic, space group $P\bar{1}$, $a = 12.424(2)$, $b = 13.563(2)$, $c = 16.200(5)$ Å, $\alpha = 74.22(2)$, $\beta = 69.06(2)$, $\gamma = 71.24(2)^\circ$, $U = 2375(1)$ Å³, $Z = 1$, $D_c = 1.53$ g cm⁻³. CCDC 182/629.

‡ *Selected data*: ¹H NMR (C_6D_6) δ 7.97 (m, 8 H), 6.97 (m, 12 H), 3.43 (q, 0.5 H, OCH₂), 1.02 (t, 0.75 H, CH₃). Analysis. Calc.: C, 54.87; H, 4.22; N, 2.42. Found: C, 54.24; H, 4.22; N, 2.56%.

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