


 Cite this: *Chem. Commun.*, 2015, 51, 6746

 Received 16th February 2015,
 Accepted 6th March 2015

DOI: 10.1039/c5cc01446h

www.rsc.org/chemcomm

Bis(triphenylphosphine)silver(i) perrhenate, a cyclic dimer†

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The 1 : 4 and 1 : 2 complexes of silver perrhenate and triphenylphosphine, [(Ph₃P)₄Ag]⁺ ReO₄⁻ and [(Ph₃P)₂AgReO₄]₂, have been prepared and their structures determined in the solid state by X-ray diffraction. The former is composed of independent ions, while in the latter the ions are aggregated into cyclic dimers. The silver centers are tetracoordinated including contact with two bridging perrhenate anions, setting this structure apart from that of its gold analogue [(Ph₃P)₂Au]⁺ ReO₄⁻ where the gold centers are strictly two-coordinate.

The perrhenate anion ReO₄⁻ is a common component of many salt-like compounds^{1–4} where it is associated with a large variety of monoatomic or more complex onium cations M⁺[ReO₄]⁻.^{5–16} Owing to the very similar structure and charge characteristics of the anions, there are many analogies not only with the congeners, permanganate MnO₄⁻ or pertechnetate TcO₄⁻, but also with perchlorate ClO₄⁻, perbromate BrO₄⁻ and periodate IO₄⁻. To mention an example, the cesium salts Cs[ReO₄] and Cs[BrO₄] are isotypical.¹⁷ However, in an earlier report it has been noticed that the structural analogy does not lead to a set of comparable physical properties, and this is particularly true for silver(i) salts: a striking difference has been noticed between the very high solubility of AgClO₄ in both water and benzene on the one hand, and the very low solubility of AgReO₄ in the same pair of solvents on the other.¹⁸ This observation suggests a much stronger donor–acceptor interaction of the ReO₄⁻ anion with the silver(i) centers, which is not

overcome upon solvation with water or the formation of arene complexes, respectively.¹⁹

However, compounds in which the perrhenate anion is coordinatively attached to acceptor atoms, or forms covalent bonds with a substituent, are generally rare and in most cases of limited stability.^{1,2} This is particularly true for the highly unstable esters of perrhenic acid ROReO₃, showing an analogy with the explosive esters of permanganic, pertechnetate and perchloric acids.¹⁸ An exceptional stability was found only for the silyl esters R₃SiOREO₃ which can be readily prepared and are stable at ambient temperature.²⁰ The crystal structure of Me₃SiOREO₃ has been determined and has been shown to have a single discrete Si–O–Re linkage.²¹ Detailed ^{185,187}Re NQR measurements have confirmed that in this ester the ReO₄ tetrahedron is indeed strongly distorted.²² Similar overall characteristics were found for organogermanium, -tin and -indium perrhenates.^{23–27}

The combination of perrhenate with the heavy coinage metals, Ag and Au, is poorly presented in the literature. Contrary to silver(i) perrhenate AgReO₄,^{5,28} gold(i) perrhenate AuReO₄ is still an unknown compound. In a report published in 2013 on complexes with triphenylphosphine as the ligand it has been shown that in the 1 : 2 complex, [(Ph₃P)₂Au]⁺ ReO₄⁻, the gold center has no acceptor affinity for the anion and remains strictly linearly two-coordinate.²⁹ This result has recently been confirmed for a series of other gold(i) complexes with tertiary phosphines, where again the ReO₄⁻ counterion is not part of the coordination sphere of the metal atoms.³⁰ In subsequent investigations attempts have been made to synthesize the corresponding silver(i) complexes, where perrhenate complexation and hence activation may arise because relativistic effects, which strongly favour two-coordination at gold(i), are strongly reduced at silver(i) centres.^{31,32}

Upon the reaction of a mixture of AgReO₄ with PPh₃ in the molar ratio of 1 : 2 in dry acetonitrile at reflux temperature under nitrogen and with protection against incandescent light a crystalline product could be isolated in 92% yield. The pale rose colour of the primary product vanished upon careful

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† Electronic supplementary information (ESI) available: Preparation of the described compounds, ATR-IR spectra, NMR and elemental analysis data, selected crystallographic data, details on structure solution and refinement, and additional figures. CCDC 1052824 and 1052825. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc01446h



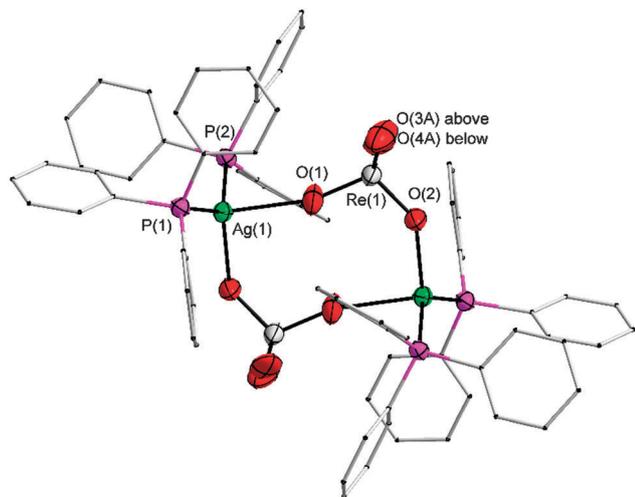


Fig. 1 Molecular structure of $[(\text{Ph}_3\text{P})_2\text{AgReO}_4]_2$. Thermal displacement parameters are shown at the 70% level at 123 K. H atoms are omitted and the C atoms are shown as a wire-frame for the sake of clarity. Only one orientation of the disordered O3 and O4 atoms is shown.

crystal growth in acetonitrile. The expected 1 : 2 composition of the product was confirmed by an elemental analysis (ESI†). Solutions in acetonitrile- d_3 showed a sharp single resonance in the ^{31}P NMR spectrum with δ 11.25 ppm at 25 °C. No couplings $^1J(^{107/109}\text{Ag}-^{31}\text{P})$ were observed even upon lowering the temperature to the solubility limit, probably owing to the rapid ligand exchange, very common for silver(I) complexes of tertiary phosphines.^{33,34} The spectrum also suggests that the eight-membered ring found in the crystal structure is flexible or subject to partial dissociation in solution, which is rapid on the NMR time scale.

The IR spectrum of the solid (on ATR crystals) shows that the prominent $\nu_3(\text{Re}-\text{O})$ vibrational mode, which appears as a single band for the undistorted tetrahedral anionic ReO_4^- unit near 910 cm^{-1} (see below), is split into two bands at 896 and 925 cm^{-1} suggesting a significant distortion. In a single crystal X-ray diffraction analysis it has been shown that the perrhenate anions are indeed strongly coordinated to the silver atoms as shown in Fig. 1 (triclinic, space group $P\bar{1}$, for further crystallographic details see Table S1 in the ESI†).

Two formula units are associated into a cyclic dimer in which the ReO_4^- anions form triatomic bridges O–Re–O between the silver cations. The silver atoms are thus tetra-coordinated with Ag–P and Ag–O bond lengths at 2.3997(8)/2.4227(7) and 2.366(2)/2.511(2) Å, respectively. The P–Ag–P angle of $133.38(3)^\circ$ shows a strong deviation from the linear geometry observed in the gold analogue.²⁹ The point group symmetry of the cyclic dimer is C_i , as it resides around a crystallographic inversion center. The Re–O distances for the Ag–O–Re bridges are observed for Re–O(1) 1.718(2) and Re–O(2) 1.705(2) Å. Due to the disorder of the terminal O atoms, a direct comparison of the distances to the terminal oxygen atoms (Re–O(3A/B) 1.60(2)/1.81(2) and Re–O(4A/B) 1.78(1)/1.65(2) Å) is not meaningful, but as expected the former Re–O distances are similar to, and the latter shorter than the reference distance

in an undistorted ReO_4^- tetrahedron which is present in the gold analogue [1.710(7)–1.716(7) Å].²⁹ However, it is interesting to note that in crystals of AgReO_4 (Scheelite-type), where all four oxygen atoms of the anion are in close contact with the silver cations,⁵ the Re–O distances are as long as 1.732(2) Å, showing the strong influence of silver multiple-coordination on the structure of the anion. The strong donor properties of the perrhenate anion for silver(I) are also evident from a comparison with the corresponding tetrafluoroborate $[(\text{Ph}_3\text{P})_2\text{Ag}]^+\text{BF}_4^-$. When this compound is prepared in acetonitrile, its 1 : 1 solvate $[(\text{Ph}_3\text{P})_2\text{Ag}(\text{NCMe})]^+\text{BF}_4^-$ with a tricoordinate silver atom is formed.³⁴ By contrast, perrhenate competes favourably with the solvent molecules and only perrhenate complexation is obtained.

Experiments with a molar ratio of 1 : 4 of the reactants in a mixture of dry acetonitrile and benzene [2 : 5 v/v] at 25 °C under nitrogen and protection against light led to the formation of the complex $[(\text{Ph}_3\text{P})_4\text{Ag}]^+\text{ReO}_4^-$ in 89% yield. A compound of this composition has been prepared in a previous report, but no structural data are available.¹⁸ Crystals grown from the reaction mixture were colourless and stable to air, moisture and light. Their composition was confirmed by elemental analysis (ESI). Solutions in acetonitrile- d_3 at 25 °C showed a singlet resonance at δ 10.8 ppm in the ^{31}P NMR spectrum, again without $^{107/109}\text{Ag}-^{31}\text{P}$ couplings. The crystals (trigonal, space group $R\bar{3}$) are related to those of known compounds containing the $[(\text{Ph}_3\text{P})_4\text{Ag}]^+$ cation associated with other tetrahedral anions like ClO_4^- or BF_4^- (space groups $R\bar{3}$, heavily disordered tetrahedral anions due to site symmetry).^{35,36} It is possible that for these cases the space group type $R\bar{3}$ would be a better choice as well. For crystallographic details, information on the choice of the space group, and crystal structure solution and refinement, see the ESI.†

The bond lengths and angles of the cations are within the range of data collected in earlier studies. The tetrahedron of the anion is largely undistorted as also seen in the IR spectrum of the crystals, where only a single sharp band is observed for the $\nu_3(\text{ReO})$ mode at 906.8 cm^{-1} . Attempts to prepare crystals of compounds with the 1 : 1 and 1 : 3 stoichiometry were unsuccessful.

In summary, in the present work structural details of silver-perrhenate coordination have been provided for a molecular system. The results help us to explain the unusual silver-perrhenate affinity suggested by a number of earlier qualitative observations. This affinity causes distinct differences in the structural chemistry of silver(I) and gold(I) compounds. The radii of Ag^+ and Au^+ are known to be virtually the same for both the two- and four-coordinate states owing to strong relativistic contraction of the frontier orbitals of the latter.^{37,38} The differences in the Ag/Au ← O–ReO₃ acceptor strengths are the result of the distinct preference for two-coordination with high s-character in the two dative bonds at gold(I), which is less pronounced for silver(I). Along the same lines, the higher donor strengths of the perrhenate anion as compared to *e.g.* the perchlorate anion (the former is coordinated to Ag, while the latter is not) are related to strong relativistic effects on rhenium which strongly modify the donor properties of the ReO_4^- anion through electronegativity enhancement and orbital rehybridization affecting the nature of the Re–O bonds.^{39,40}



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