

Palladium–gold oxo complexes†‡

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Treatment of L_2PdCl_2 ($L_2 = 4,4'$ -di-*tert*-butyl-2,2'-bipyridine) with $[(L'Au)_3(\mu_3-O)]BF_4$ ($L' = PPh_3$) has yielded cationic oxo complexes with core formulas $Pd_2Au_2O_2$ and Pd_4AuO_3 thereby doubling the number of structurally characterized Pd oxo complexes.

Late-transition metal oxo complexes^{1,2} have been of interest for many years due to their importance in various catalytic processes³ and in biological systems.⁴ Our attention has been on the heavier members of the late transition metals and we have prepared a number of oxo complexes of Rh, Ir, Pt and Au.^{1b} In contrast, Pd oxo complexes have been very difficult to obtain^{1b,5} and are still very rare with only two structurally characterized Pd oxo complexes, $Pd_6Cu_4(\mu_2-Cl)_{12}(\mu_4-O)_4(HMPA)_4$ ^{6a} and $Pd_4(dpm)_4(\mu_2-Cl)_2(\mu_4-O)$ ^{6b} ($dpm =$ dipivaloylmethanato), reported to date. Here we report the isolation and structures of two new Pd(II) oxo complexes. One of these complexes has an unusual structure consisting of a trigonal-bipyramidal arrangement of four Pd atoms and an Au atom with three of the faces capped by oxygen atoms.

The complexes are prepared from the oxo–chloro exchange reaction^{1b} of $[(L'Au)_3(\mu_3-O)]BF_4$ ($L' = PPh_3$) with L_2PdCl_2 ($L_2 = 4,4'$ -di-*tert*-butyl-2,2'-bipyridine) in methylene chloride (Scheme 1). The identity of the isolated complex depends on the molar ratio of the reactants. A 1 : 1 ratio gives yellow air-stable $[(L_2Pd)_2(\mu_3-O)_2(AuL')_2](BF_4)_2$ **1**. The structure of **1** was determined by X-ray diffraction (Fig. 1)[§] and consists of a planar $L_2Pd(\mu-O)_2PdL_2$ diamond core with out-of-plane $L'Au^+$ groups linearly coordinated to the oxo ligands in an *anti* orientation. Close contacts between the Pd and Au atoms ($d_{PdAu} = 2.994(1), 3.260(1)$ Å) indicate closed-shell Pd(II)–Au(I) interactions. Though uncommon, such interactions have been reported in other Pd(II)–Au(I) complexes.⁷ The average Pd–O bond distance in **1** of 2.006(2) Å is similar to those found in the μ_4 -oxo containing complexes $Pd_4(dpm)_4(\mu_2-Cl)_2(\mu_4-O)$ ($dpm =$ dipivaloylmethanato) (2.024 Å),^{6b} and $Pd_6Cu_4(\mu_2-Cl)_{12}(\mu_4-O)_4(HMPA)_4$ (2.03(1) Å),^{6a} and in the binary oxide PdO (2.01 Å).⁸ The Pd–N distances match those reported for Pd(II) 4,4'-di-*tert*-butyl-2,2'-bipyridine complexes^{3e,9} and the Au–O and Au–P distances in **1** are essentially identical to those found in $[(L'Au)_3(\mu_3-O)]^+$ ($L' = PPh_3$).¹⁰

The solution NMR data for **1** are consistent with the inversion and near two-fold (along the Pd–Pd vector) symmetry of the solid-state structure. The ³¹P NMR spectrum shows a single peak at 25.7 ppm, slightly downfield of the parent complex $[(L'Au)_3(\mu_3-O)](BF_4)$ at 24 ppm.¹⁰ The ¹H NMR spectrum shows, in addition to the phosphine ligand phenyl groups, aromatic peaks and a single sharp aliphatic singlet associated with the 4,4'-di-*tert*-butyl-2,2'-bipyridine ligand.

Another Pd–Au oxo complex (**2**) is isolated by decreasing the reactant ratio to 3 : 4 ($[(L'Au)_3(\mu_3-O)]BF_4$ to L_2PdCl_2) or by treating Pd–Au oxo complex **1** with additional L_2PdCl_2 (Scheme 1).

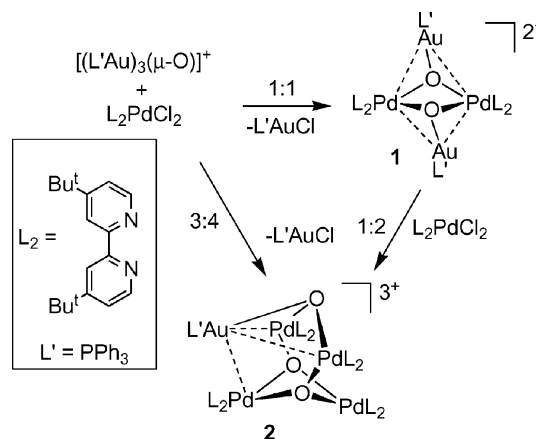
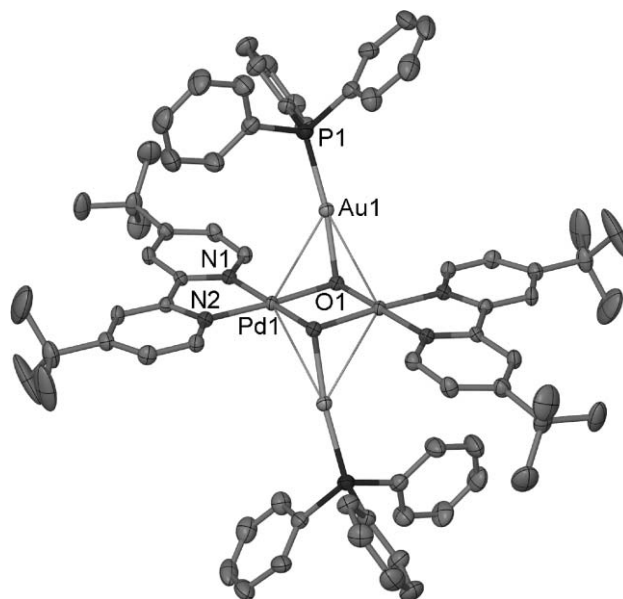
Scheme 1 Synthesis of **1** and **2**.

Fig. 1 Molecular structure of the cationic portion of **1** (50% probability ellipsoids). Hydrogen atoms omitted for clarity. Labeled and unlabeled atoms are inversion related. Selected distances (Å) and angles (°): Au1–Pd1 2.9853(3), Au1–Pd1' 3.2436(3), Pd1–Pd1' 2.990(5), Pd1–O1 2.017(2), Pd1–O1' 1.995(2), Au1–O1 2.038(2), Pd1–N1 2.010(3), Pd1–N2 1.997(3); O1–Pd1–O1' 83.64(9), O1–Au1–P1 172.19(6), Pd–O–Pd' 96.36(9), Pd–O–Au 107.05(10), Pd'–O–Au 94.80(9), N2–Pd–N1 80.60(11). Primed and unprimed atoms are inversion related.

Orange $[(L_2Pd)_4(\mu_3-O)_3(AuL')](BF_4)_3$ **2** shows a single peak at 26.6 ppm by ³¹P NMR spectroscopy, slightly downfield from **1**. The ¹H NMR spectrum of **2** is more complicated than that of **1** and shows, in addition to peaks for the phosphine ligand, four equal intensity resonances for the 4,4'-di-*tert*-butyl-2,2'-bipyridine ligand indicating a more complex structure. Crystals of **2** are readily obtained from CH₂Cl₂–toluene. However, these crystals are very unstable and quickly decompose outside the mother-liquor. A low-temperature data set was obtained with these crystals and the structure was solved but the definition

† This article is dedicated to the late Professor Ian Rothwell and his many contributions to chemistry.

‡ Electronic supplementary information (ESI) available: Experimental section; colour versions of Figs. 1 and 2. See <http://www.rsc.org/suppdata/dt/b5/b504808g/>

was very poor. More stable crystals are obtained from CH_2Cl_2 -*p*-xylene. These gave good results[§] allowing a clear determination of the non-solvent portions but with some unresolved solvent disorder. A drawing of the core of the cationic portion of **2** is shown in Fig. 2.

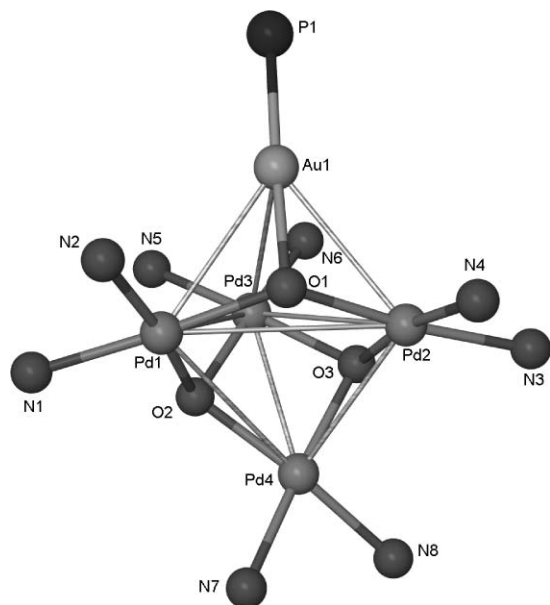


Fig. 2 Drawing of the core structure of **2** emphasizing the trigonal-bipyramidal arrangement of the metal atoms. Lines connecting metal atoms do not necessarily represent bonds. Atoms are drawn as arbitrary sized spheres. Selected distances (Å) and angles (°): Au1–Pd1 3.071(1), Au1–Pd2 3.065(1), Au1–Pd3 3.211(1), Pd1–Pd2 3.671(1), Pd1–Pd3 3.243(1), Pd1–Pd4 3.406(1), Pd2–Pd3 3.425(1), Pd2–Pd4 3.034(1), Pd3–Pd4 2.907(1), Au1–O1 2.020(7), Pd1–O1 1.979(8), Pd1–O2 1.968(8), Pd2–O3 2.007(7), Pd3–O3 1.977(8); P1–Au1–O1 173.2(3), O2–Pd1–O1 93.7(3), O3–Pd2–O1 95.5(3), O3–Pd3–O2 82.1(3), O3–Pd4–O2 82.5(3), Pd1–O1–Au1 100.3(3), Pd2–O1–Au1 99.1(4).

Complex **2** is related to **1** in that it also contains an $\text{L}_2\text{Pd}(\mu\text{-O})_2\text{PdL}_2$ diamond core. However, the two $\text{L}'\text{Au}^+$ fragments of **1** have been replaced by an $[(\text{L}_2\text{Pd})_2(\mu_3\text{-O})\text{AuL}']^+$ fragment, a unit of **1** with an $\text{L}'\text{AuO}^-$ removed. The resulting structure has near mirror symmetry in the Au1,O1,Pd3,Pd4 plane resulting in four equivalent sets of Bu^t groups consistent with the solution ¹H NMR data. The structure of **2** can be viewed as a trigonal-bipyramidal arrangement of the five metal atoms (Au1 in an axial position) with oxygen atoms capping three of the faces. This view is emphasized in Fig. 2. As in **1**, close contacts between the Pd(II) and Au(I) atoms (3.064(1)–3.211(1) Å) indicate closed-shell interactions. The average Pd–O bond distance in **2** of 2.00(2) Å is the same as that in **1** and is again similar to those found in the other two Pd oxo complexes.⁶ Other metrical parameters are also comparable to those of **1**.

In conclusion, we have successfully prepared and isolated two new Pd–Au oxo complexes by oxo–chloro exchange reactions thereby doubling the number of structurally characterized Pd oxo complexes. Both structures show short Pd–Au distances consistent with closed-shell interactions that likely help stabilize the complexes. The success of the preparations appears to rely on the 4,4'-di-*tert*-butyl-2,2'-bipyridine ligand since previous attempts to prepare Pd oxo complexes with phosphine, COD, DBCOD (dibenzo-1,5-cyclooctadiene), and NBD ligands have failed for Pd(II) but been successful for Pt(II), Rh(I), and Ir(I).^{16,5}

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Notes and references

[§] Crystal data for **1**: $\text{C}_{72}\text{H}_{78}\text{N}_4\text{Au}_2\text{B}_2\text{F}_8\text{O}_2\text{Pd}_2 \cdot 2\text{CH}_2\text{Cl}_2$, $M = 2043.52$, monoclinic, space group $P2_1/c$, $a = 13.5307(5)$, $b = 15.3927(6)$, $c = 18.8517(7)$ Å, $\beta = 96.0220(10)^\circ$. $U = 3904.7(3)$ Å³, $T = 173$ K, $Z = 2$, $D_c = 1.738$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 4.4$ mm⁻¹, 27964 reflections measured, 8644 unique ($R_{\text{int}} = 0.035$) which were used in all calculations. $wR(F^2) = 0.0634$ (all data). CCDC reference number 267185. Crystal data for **2**: $\text{C}_{90}\text{H}_{111}\text{N}_8\text{AuB}_3\text{F}_{12}\text{O}_3\text{PPd}_4 \cdot n\text{C}_8\text{H}_{10}$, $M = 2266.93$ (without solvent), monoclinic, space group $P2_1$, $a = 18.385(3)$, $b = 17.993(3)$, $c = 21.862(4)$ Å, $\beta = 109.413(3)^\circ$. $U = 6820.6(19)$ Å³, $T = 173$ K, $Z = 4$, $D_c = 1.283$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 1.6$ mm⁻¹, 45296 reflections measured, 25199 unique ($R_{\text{int}} = 0.0458$), $R = 0.0740$, $R_w = 0.1844$ ($I > 2\sigma$). CCDC reference number 267186. Crystal data were measured at -100 °C on a Bruker P4 diffractometer with Mo-K α radiation and ω and ϕ -scans. The structures were solved by direct methods and refined anisotropically on F^2 (program SHELXL-97, G. M. Sheldrick, University of Göttingen) Absorption correction: multi-scan. Special refinement details: Crystals of **2** are unstable to solvent loss and contain loosely held solvent. As a result the structure contains isolated residual peaks that represent unresolved solvent molecules. See <http://www.rsc.org/suppdata/dt/b5/b504808g/> for crystallographic data in CIF or other electronic format.

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