$PtAu_8Ag$ and $PtAu_8Hg_2$ Metal Cluster Compounds prepared from $Pt(AuPPh_3)_8{}^{2+}$ with Ag^+ and $Hg_2{}^{2+}$ ions

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$[PtAg(AuPPh_3)_8](NO_3)_3$ and $[Pt(AuPPh_3)_7(AuNO_3)(HgNO_3)_2](NO_3)$ are prepared from $PtAu_8(PPh_3)_8{}^{2+}$ with $AgNO_3$ and $[Hg_2(H_2O)_2](NO_3)_2$, respectively.

The addition of nucleophiles to centred Au and Pt cluster ions is well known. In reactions (1) and (2) CO and PPh_3 are added to the central Pt and Au, respectively.[1,2] The cluster electron configurations are changed from $(S^\sigma)^2(P^\sigma)^4$ to $(S^\sigma)^2(P^\sigma)^6$.[3,4] The electrophilic addition of Au^I to centred Au clusters with $(S^\sigma)^2(P^\sigma)^4$ or $(S^\sigma)^2(P^\sigma)^6$ configuration is demonstrated in reactions (3) and (4).[2,5] We now report the electrophilic addition of Ag^+ to $Pt(AuPPh_3)_8{}^{2+}$ and $Pt(CO)(AuPPh_3)_8{}^{2+}$. Reactions (5) and (6) proceed quickly and in high yield in methanol or acetone solutions at room temperature. The cluster ions $PtAg(AuPPh_3)_8{}^{3+}$ (**1**) and $Pt(CO)Ag(AuPPh_3)_8{}^{3+}$ (**2**) can be precipitated as their nitrates by addition of diethyl ether and purified by recrystallisation from methanol/diethyl ether. Cluster (**1**) can easily be converted into (**2**) by reaction with CO at room temperature and atmospheric pressure. Elemental analyses (Pt, Au, Ag, P, C, H, and N) of (**1**) and (**2**) agree with the given composition.

In the $^{31}P\{^1H\}$ n.m.r. spectra of (**1**) at room temperature the lines are rather broad, probably owing to fluxional behaviour. At 40 °C a single P site with a ^2J coupling to Pt and a weak coupling to Ag is observed. This indicates that the phosphines are bonded to the peripheral Au atoms just as in the parent compound. In the metal frame either Pt or Ag must be in the centre. The other hetero-metal, therefore, will be at the periphery as a 'naked' atom. Electrochemical reduction of

$$Pt(AuPPh_3)_8{}^{2+} + CO \longrightarrow Pt(CO)(AuPPh_3)_8{}^{2+} \quad (1)$$

$$Au(AuPPh_3)_7{}^{2+} + PPh_3 \longrightarrow Au(PPh_3)(AuPPh_3)_7{}^{2+} \quad (2)$$

$$Au(AuPPh_3)_7{}^{2+} + AuPPh_3{}^{+} \longrightarrow Au(AuPPh_3)_8{}^{3+} \quad (3)$$

$$\begin{aligned} &Au(AuPMe_2Ph)_{10}{}^{3+} + 2\,AuCl(PMe_2Ph) \\ &\longrightarrow Au(AuCl)_2(AuPMe_2Ph)_{10}{}^{3+} + 2\,PMe_2Ph \end{aligned} \quad (4)$$

$$Pt(AuPPh_3)_8{}^{2+} + Ag^+ \longrightarrow \underset{(\mathbf{1})}{PtAg(AuPPh_3)_8{}^{3+}} \quad (5)$$

$$Pt(CO)(AuPPh_3)_8{}^{2+} + Ag^+ \longrightarrow \underset{(\mathbf{2})}{Pt(CO)Ag(AuPPh_3)_8{}^{3+}} \quad (6)$$

$$\begin{aligned} &Pt(AuPPh_3)_8{}^{2+} + 3\,NO_3{}^- + Hg_2(H_2O)_2{}^{2+} \longrightarrow \\ &\quad Pt(AuPPh_3)_7(AuNO_3)(HgNO_3)_2{}^{+} + 2\,H_2O + PPh_3 \end{aligned} \quad (7)$$

(**1**) in acetone solution occurs in two closely spaced reversible one-electron steps at −0.29 and −0.32 V (*vs.* Ag/AgCl reference electrode), which is 0.6 V higher than the reduction potentials of the parent $Pt(AuPPh_3)_8^{2+}$.[6]

The $^{31}P\{^1H\}$ n.m.r. spectrum of (**2**) shows a single P site with a ^2J coupling to Pt and a weak coupling to Ag. The ^{13}C n.m.r. spectrum of the ^{13}CO derivative, prepared from (**1**) and ^{13}CO, indicates a ^1J(Pt–C) coupling and weak couplings with Ag and P. The i.r. spectrum of (**2**) has a CO stretching frequency at 1960 cm^{-1}, which is very close to that in the spectrum of $Pt(CO)(AuPPh_3)_8^{2+}$.[1] These data suggest that in (**2**) CO is bonded to Pt and the phosphines to the peripheral Au atoms. We cannot decide at the moment whether Ag or Pt is in the centre of the $PtAu_8Ag$ frame. This must wait for an *X*-ray crystal structure determination.

$[Hg_2(H_2O)_2](NO_3)_2$ reacts with $Pt(AuPPh_3)_8^{2+}$ in methanol solution to yield a $PtAu_8Hg_2$ cluster (reaction 7). The same product is obtained in the reaction with $Hg(NO_3)_2$ but the yield is only 40% owing to the oxidation of part of the $Pt(AuPPh_3)_8^{2+}$ with Hg^{II}. The cluster ion $Pt(AuPPh_3)_7(AuNO_3)(HgNO_3)_2^+$ (**3**) can be isolated as its NO_3^- or PF_6^- salt (for PF_6^-, an excess of NH_4PF_6 is added to the reaction mixture) as a precipitate by concentration of the methanol solution. The product can be purified by recrystallisation from CH_2Cl_2/methanol. Elemental analyses (Pt, Au, Hg, P, C, H, N) of the NO_3^- salt and (C, H, N) of the PF_6^- salt of (**3**) are in accordance with the given composition.

$^{31}P\{^1H\}$ n.m.r. spectra indicate a single P site with couplings to Pt and two equivalent Hg atoms. The i.r. spectra show the absorptions of bonded nitrate. The data suggest the product to be a cluster ion with a $PtAu_8Hg_2$ frame and its periphery covered by 7 PPh_3 and 3 NO_3^-, iso-electronic with the long known $Au_{11}(PPh_3)_7Cl_3$.[7] Further details of its structure must wait for an *X*-ray crystal structure determination.

The amphoteric character of the PtAu clusters with regard to their reaction with soft acids and bases is being further explored.

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