# Hydridotriplatinum Chemistry and a Stepwise Electrophilic Ligand Substitution Mechanism

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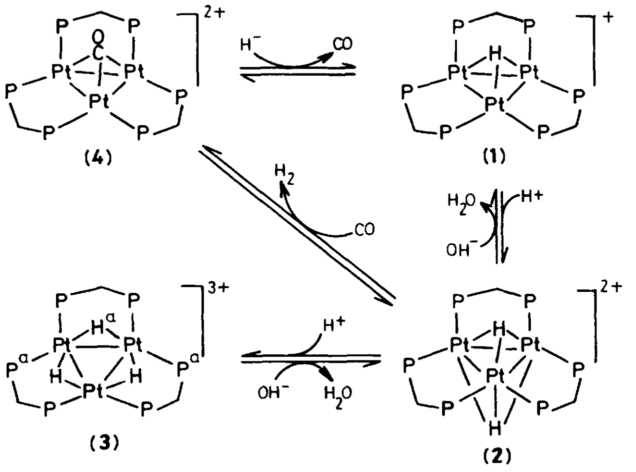
The cluster complex $[Pt_3(\mu_3\text{-}H)(\mu\text{-}dppm)_3]^+$ (1) (dppm = $Ph_2PCH_2PPh_2$) can be protonated rapidly and reversibly to give $[Pt_3(\mu_3\text{-}H)_2(\mu\text{-}dppm)_3]^{2+}$ and $[Pt_3(\mu_2\text{-}H)_3(\mu\text{-}dppm)_3]^{3+}$; auration of (1) with $LAu^+$ (L = $PPh_3$) gives $[Pt_3(\mu_3\text{-}H)(\mu_3\text{-}AuL)(\mu\text{-}dppm)_3]^{2+}$, which can be deprotonated to $[Pt_3(\mu_3\text{-}AuL)(\mu\text{-}dppm)_3]^+$ and then further aurated to $[Pt_3(\mu_3\text{-}AuL)_2(\mu\text{-}dppm)_3]^{2+}$, thus providing a route to novel platinum cluster hydrides and showing clearly how electrophilic ligand substitution at the cluster can occur by a bimolecular, stepwise mechanism.

We report here the easy, reversible protonation, double protonation, or auration of the cluster cation $[Pt_3(\mu_3\text{-}H)(\mu\text{-}dppm)_3]^+$ (**1**) (dppm = $Ph_2PCH_2PPh_2$), which shows how electrophilic ligand substitution occurs in this complex and yields interesting new hydridotriplatinum complexes. Such clusters are important as models for intermediates in heterogeneous platinum-catalysed reactions but are still rare compounds.[1—5] The new chemistry is shown in Schemes 1 and 2.

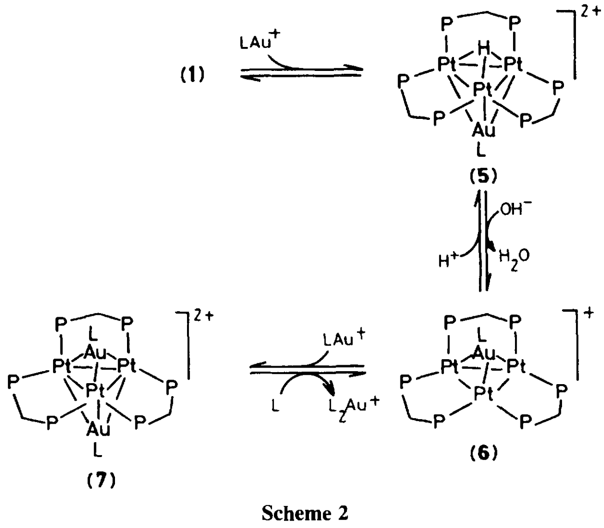
Protonation of complex (**1**)[3] using $HPF_6$ gave the dicationic, dihydride (**2**) and, with a large excess of acid, the tricationic, trihydride (**3**). The reactions could be reversed by addition of base and (**2**) reacted rapidly and quantitatively with CO to give $H_2$ and the known cluster complex (**4**) (Scheme 1).[5] Complex (**4**) was not sufficiently nucleophilic to undergo protonation but is more reactive than (**1**) to addition of nucleophiles.[3,5] For example, (**4**) adds hydride (Scheme 1) but (**1**) does not.

Complexes (**2**) and (**3**) had limited thermal stability and reverted, in part, to (**1**) on attempted isolation, but they could be characterized unambiguously by spectroscopic methods.† The hydride signal in the $^1H$ n.m.r. spectrum of (**2**) integrated as two protons and appeared as a septet, due to coupling to six equivalent $^{31}P$ atoms, with $^{195}Pt$ satellite intensities as expected for a $Pt_3(\mu_3\text{-}H)$ group.[3] The presence of two hydride ligands was confirmed by the extra triplet coupling, due to $^2J$(HPtP), in the $^{31}P$ n.m.r. compared to the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum.‡ In contrast, the hydride signal in (**3**) integrated as three protons and appeared as a triplet, due to coupling to only two $^{31}P$ atoms, with $^{195}Pt$ satellite intensities as expected for a $Pt_2(\mu_2\text{-}H)$ group;[3,6] each phosphorus in the $^{31}P$ n.m.r. was coupled to only one hydride. The large PH coupling is expected to be the *trans*-like coupling between atoms $P^a$ and $H^a$ (Scheme 1). Both (**2**) and (**3**) have a plane of symmetry containing the $Pt_3(\mu\text{-}PCP)_3$ skeleton and therefore give only a single $CH_2P_2$ resonance. Protonation of (**2**) evidently converts the capping $\mu_3$-hydrides to $\mu_2$-hydrides. Complex (**3**) is analogous to the known complex $[Pt_3H_3(\mu\text{-}H)_3(Bu^t{}_3P)_3]$,[1] which has terminal hydrides in place of three of the phosphorus donors in (**3**), but (**2**) is a new type of platinum cluster hydride.

The unit $Ph_3PAu^+$ is isolobal to $H^+$ and undergoes similar reactions with (**1**) as shown in Scheme 2 (L = $PPh_3$, PP =



Scheme 1



Scheme 2

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† *N.m.r. spectroscopic data*: refs. $Me_4Si$ ($^1H$), $H_3PO_4$ ($^{31}P$), or $K_2PtCl_4$ ($^{195}Pt$); multiplicities due to $^{195}Pt$ couplings not given, *J* values in Hz: (**2**), $\delta(^1H)$ −3.6 [sept., 2H, $^1J$(PtH) 420, $^2J$(PH) 20.5, PtH], 5.2 [s, 6H, $CH_2P_2$]; $\delta(^{31}P)$ −8.1 p.p.m. [s, $^1J$(PtP) 3175, $^2J$(PtP) 150, PtP]. (**3**), $\delta(^1H)$ −6.6 [t, 3H, $^1J$(PtH) 605, $^2J$(PH) 72, PtH], 4.8 [s, 6H, $CH_2P_2$]; $\delta(^{31}P)$ −3.28 (s, $^1J$(PtP) 3160, $^2J$(PtP) 151, PtP]. (**5**), $\delta(^1H)$ −0.9 [sept. of d, 1H, $^1J$(PtH) 317, $^2J$(PH) 17, $^3J$(PAuPtH) 11.5, PtH], 5.0, 6.4 [m, 6H, $^2J(H^aH^b)$ 14, $CH^aH^bP_2$]; $\delta(^{31}P)$ 44.6 [sept., 1P, $^2J$(PtP) 503, $^3J$(PP) 19, AuP], −13.4 p.p.m. [d, 6P, $^1J$(PtP) 3155, $^2J$(PtP) 170, $^3J$(PP) 19, PtP]; $\delta(^{195}Pt)$ −2463 p.p.m. (Pt). (**6**), $\delta(^1H)$ 4.11, 6.51 [m, 6H, $^2J(H^aH^b)$ 10, $CH^aH^bP_2$]; $\delta(^{31}P)$ 46.3 [sept., 1P, $^2J$(PtP) 892, $^3J$(PP) 22.5, AuP], −12.6 p.p.m. [d, 6P, $^1J$(PtP) 3020, $^2J$(PtP) 190, $^3J$(PP) 22.5, PtP]. (**7**), $\delta(^1H)$ 5.20 [s, 6H, $CH_2P_2$]; $\delta(^{31}P)$ 44.4 [sept., 1P, $^2J$(PtP) 440, $^3J$(PP) 21, AuP], −16.0 [t, 6P, $^1J$(PtP) 3060, $^2J$(PtP) 134, $^3J$(PP) 21, PtP]; $\delta(^{195}Pt)$ −2207 p.p.m. [tt, $^1J$(PtP) 3060, $^2J$(PtP) 440, PtP].

‡ We note that the n.m.r. data do not preclude less symmetrical but fluxional structures, such as a structure with a $Pt_3H(\mu_3\text{-}H)$ unit. However, the n.m.r. data are unchanged at −80 °C and no terminal Pt–H stretch was observed in the i.r. spectrum, so such structures are improbable. The predicted intensities due to *J*(PtH) are 1:12:49:84:49:12:1 (septet) for a $Pt_3(\mu_3\text{-}H)$ group and 1:8:18:8:1 (quintet) for a $Pt_2(\mu_2\text{-}H)$ group.

dppm). In this case the new complexes (**5**)—(**7**) could be isolated in analytically pure form (as the $PF_6^-$ salts) and were readily characterized by their n.m.r. spectra.§ If the capped compounds (**1**), (**2**), and (**5**)—(**7**) are considered to be formed by consecutive addition to the $a_1$ HOMO of $Pt_3(\mu\text{-dppm})_3$,[7] then the individual Pt–H or Pt–Au bonds are expected to be weaker for the dicapped compounds. This is reflected in the much reduced coupling constants $^1J$(PtH) in (**2**) (420 Hz) or (**5**) (317 Hz) compared to (**1**) (710 Hz), or $^2J$(PtAuP) in (**5**) (503 Hz) or (**7**) (440 Hz) compared to (**6**) (892 Hz). The data also indicate that gold has a greater share of this $a_1$ orbital than does hydrogen in the mixed complex (**5**) [lower $^1J$(PtH), higher $^2J$(PtAuP) compared to the symmetrical compounds (**2**) and (**7**)]. In turn the data can rationalize the selectivity of the substitution reaction defined by the sequence (**1**) $\rightarrow$ (**5**) $\rightarrow$ (**6**) (Scheme 2). This and the sequences (**1**) $\rightleftharpoons$ (**2**) (Scheme 1) or (**6**) $\rightleftharpoons$ (**7**) (Scheme 2) involving symmetrical 'intermediates,' clearly illustrate how electrophilic ligand substitution at the trinuclear site can occur by a bimolecular, stepwise mechanism.

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§ Formation of structures analogous to (**3**) was not observed with excess $Ph_3PAu^+$, presumably due to steric hindrance to edge auration. Only (**7**) and free $Ph_3PAu^+$ were observed by $^{31}P$ n.m.r. spectroscopy.

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