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Oxidative addition of Ph_3SnH to $Pt_3(\mu\text{-}CO)_3(PR_3)_3$ ($R = PCy_3$, P^tBu_3)

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Abstract

The oxidative addition of 1 equiv. of Ph_3SnH to $Pt_3(\mu\text{-}CO)_3(PCy_3)_3$ affords the triangular cluster $[Pt_3(\mu\text{-}CO)_3(PCy_3)_3(Ph_3Sn)H]$ (**1**). The same reaction with the isostructural 42-electron cluster $[Pt_3(\mu\text{-}CO)_3(P^tBu_3)_3]$ gives the 18-electron monomeric complex $[PtH(CO)(P^tBu_3)(SnPh_3)]$ (**2**) instead of the 44-electron product. The structure of both complexes in solution have been established by ^1H, ^{13}C, ^{31}P, ^{195}Pt and ^{119}Sn NMR spectroscopic methods and found to be in accordance with the solid state geometry of **1**.
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Some polynuclear platinum-hydride have already been reported [1–16], most of them based on a Pt_3 core stabilized by bridging bidentate phosphine [4–9,11–13] or phosphido ligands [2,15,16]. To the best of our knowledge the unique hydride derivative of the well known $[Pt_3(\mu\text{-}CO)_3(PR_3)_3]$ 42-electron clusters is the unstable cationic $[Pt_3(\mu_3\text{-}H)(\mu\text{-}CO)_3(PCy_3)_3]^+$ formed by protonation under carefully chosen conditions [14]. Here we report the formation [1] of a stable triangular Pt complex containing both H and Sn(IV) functions $[Pt_3(\mu\text{-}CO)_3(PCy_3)_3(Ph_3Sn)H]$ (**1**) formed in the oxidative addition of Ph_3SnH to $[Pt_3(\mu\text{-}CO)_3(PCy_3)_3]$. Replacing the phosphine ligand in the starting cluster by P^tBu_3 results in the formation of $PtH(CO)(P^tBu_3)(SnPh_3)$ (**2**) instead of the expected analogue of **1**.

Complex **1** (Fig. 1) crystallizes as a solvate with the composition $[Pt_3(SnPh_3)(\mu\text{-}CO)_3(PCy_3)_3H] \cdot 3CH_2Cl_2$. X-ray analysis [2] shows that **1** is a Pt(II)Pt(0)Pt(0) cluster complex where one Pt inserted into the Sn–H bond.

The platinum triangle is almost isosceles, with Pt–Pt distances of 2.65 and 2.70 Å. These bond lengths are similar to the metal–metal distances observed in the

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[1] *$[Pt_3(SnPh_3\mu\text{-}CO)_3(PCy_3)_3H]$ (1)*. Ph_3SnH (30 mg 0.085 mmol) was added to a CH_2Cl_2 solution (25 ml) of $[Pt_3(\mu\text{-}CO)_3(PCy_3)_3]$ (0.127 g, 0.084 mmol), and an immediate colour change from orange-red to yellow was observed. The mixture was stirred for 10 min at room temperature and monitored by IR. Addition of MeOH followed by concentration of the resulting solution gave a yellow solid upon standing overnight at −20 °C (0.116 g, 74% yield). Selected IR data (cm^{-1}): CH_2Cl_2 solution $\nu(C{\equiv}O)$ 1819vs; 1776vs; $\nu(Pt\text{–}H)$: 1985(br) 2034(br). Yellow single crystals were obtained from a CH_2Cl_2 solution standing at 5 °C. *Anal. Calc.* for $C_{75}H_{115}O_3P_3SnPt_3$: C, 48.39; H, 6.22. Found: C, 48.60; H, 6.43. NMR data $\delta(H) = 0.5$, $\delta(P2,3) = 70.4$, $\delta(P1) = 59.2$, $\delta(C1,3) = 229.3$, $\delta(C2) = 261.1$, $\delta(Pt2,3) = -4153.1$, $\delta(Pt1) = -4366.0$, $\delta\ (Sn) = 54.1$, $^1J(Pt1\text{–}H1) = 1018$, $^2J(Sn\text{–}H1) = -140$, $^2J(P1\text{–}H1) = 9$, $^2J(Pt2,3\text{–}H1) = -46$, $^1J(Pt2,3\text{–}P2,3) = 4305$, $^1J(Pt1\text{–}P1) = 2264$, $^2J(Pt2,3\text{–}P1) = 314$, $^2J(Pt1\text{–}P2,3) = 425$, $^2J(Sn\text{–}P1) = -1222$, $^3J(P1\text{–}Pt2,3) = 52.7$, $^3J(P2\text{–}P3) = 55$, $^1J(Pt2,3\text{–}Pt1) = 1128$, $^1J(Pt2,3\text{–}Pt3,2) = 1871$, $^1J(Sn\text{–}Pt1) = 6330$, $^2J(Sn\text{–}Pt2,3) = 498.5$, $^1J(Pt2,3\text{–}C1,3) = 845$, $^1J(Pt2,3\text{–}C2) = 766$, $^1J(Pt1\text{–}C1,3) = 380$.

[2] Empirical formula: $C_{78}H_{121}Cl_6O_3P_3Pt_3Sn$; Formula weight: 2116.32 g/mol; Temperature: 140(2) K; Wavelength: 0.71073 Å; Crystal system: Monoclinic; Space group: P2(1)/n; Unit cell dimensions: $a = 13.9351(5)$ Å, $b = 18.0950(10)$ Å, $c = 32.6165(16)$ Å, $\alpha = 90°$, $\beta = 91.614(3)°$ $\gamma = 90°$; Volume: 8221.2(7) $Å^3$; $Z = 4$; Density (calculated): 1.710 g/cm^3; Absorption coefficient: 5.687 mm^{-1}; $F(000)$: 4176; Crystal size: $0.33 \times 0.18 \times 0.14\ mm^3$; θ range for data collection: 2.74–25.03°; Index ranges: $-16 \leqslant h \leqslant 16$, $-21 \leqslant k \leqslant 21$, $-38 \leqslant l \leqslant 38$; Reflections collected: 47,692; Independent reflections: 13,722 [$R_{int} = 0.0770$]; Completeness to $\theta = 25.03°$ 94.5%; Absorption correction: Empirical (DELABS); Max. and min. transmission: 0.871 and 0.576; Refinement method: Full-matrix least-squares on F^2; Data/restraints/parameters: 13,722/274/844; Goodness of fit on F^2: 0.908; Final R indices [I>2sigma(I)]: $R_1 = 0.0430$, $wR_2 = 0.0800$; R indices (all data): $R_1 = 0.0973$, $wR_2 = 0.1052$; Largest difference peak and hole: 1.918 and −1.929 e/$Å^3$.

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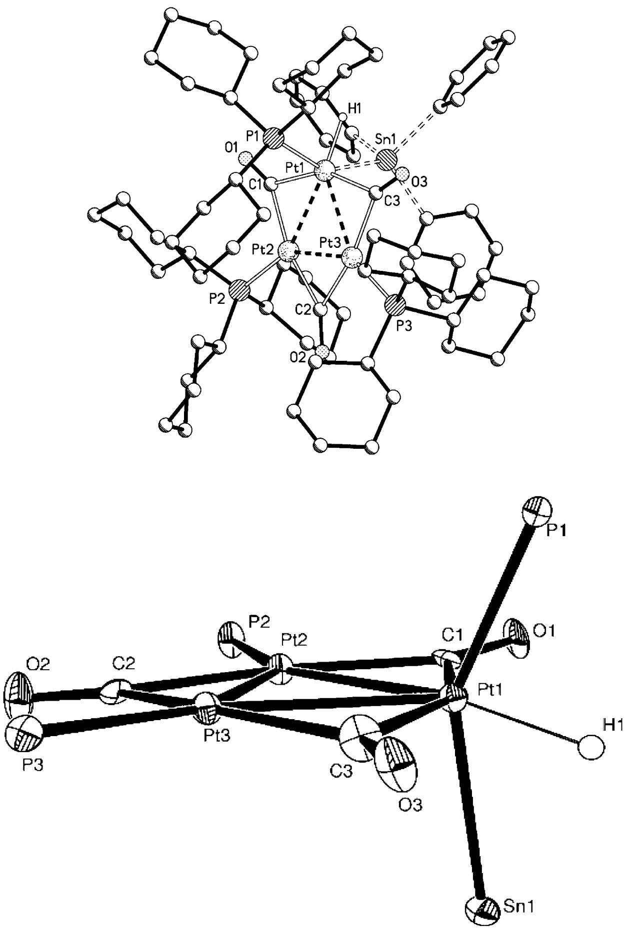

Fig. 1. ORTEP representation of complex **1** and of its metal core ($R = 0.0458$).

starting cluster [17], and are shorter than the corresponding platinum–platinum distances in its 44-electron analogue $[Pt_3(\mu\text{-CO})_3(PCy_3)_4]$ [18]. The P2 and P3 atoms (see Fig. 1 for numbering) stay in the plane of the platinum triangle, while P1 is tipped out from this plane and occupies an opposite side of the core relative to the Sn(IV) unit. The Pt2–P2 and Pt3–P3 distances are almost identical (2.28 and 2.27 Å, respectively) as well as the Pt–C(carbonyl) distances, involving Pt2 or Pt3 metal centres (~2.0 Å). These bond lengths are similar to the corresponding bond lengths observed in the starting [3:3:3] cluster [17]. The Pt1–P1 (2.34 Å) and Pt1–C1,C3 (2.18 and 2.14 Å) bond length – as expected from the increased coordination number of this metal centre – are significantly longer compared to the latter ones.

NMR and IR spectroscopic properties suggest similar stereochemistries of complex **1** in solution and in the solid state. NMR spectra appear as a superimposition of subspectra belonging to the isotopomers differing in the isotopic distribution of these nuclei. δ and J values ^{1} involving Pt2,3 and the ligands bonded to these metal centres are similar to the corresponding values in the parent cluster [19], but large differences are observed in comparison to the corresponding values involving Pt1. This supports that the Pt1 metal centre is inserted into the Sn–H bond and that the P1 phosphine group is tipped out from the plane of the metal core. The observed large ^2J(Sn–P1) value of 1222 Hz is in agreement with this suggestion and suggests a *trans* arrangement of these ligands.

The ^{1}H NMR spectrum presents a hydride signal at 0.5 ppm appearing as a shoulder of the about 160 times more intense multiplet peaks belonging to the methylene protons of the three phosphine-ligands (therefore the ^2J(Sn–H) coupling constant is estimated from gNMR simulation). We have no explanation for the chemical shift value of 0.5 ppm which is unusual, but note that there are other examples where metal-hydrides are unusually low fielded [4,10].

The ^2J(Sn–H) value of 140 Hz suggests a *cis* arrangement of the organotin and hydride ligands [10,20]. Neither the ^{13}C nor the ^{31}P non-decoupled NMR spectra are indicative of the presence of the hydride ligand, because the two-bond couplings involving these nuclei are small relative to the natural line-broadening deriving from couplings with the cyclohexyl protons.

Since the proton spectrum is not clearly indicative for the presence of the hydride ligand, non-decoupled ^{195}Pt NMR measurements have been achieved. No change is noted in the signals belonging to Pt2 and Pt3, while duplication of the peaks belonging to Pt1 metal centre is observed (Fig. 2). The deduced ^1J(Pt1–H) coupling constant value of 1018 Hz is significantly larger than the corresponding coupling constant values of the above referred complexes [4,10] and suggests that the hydride

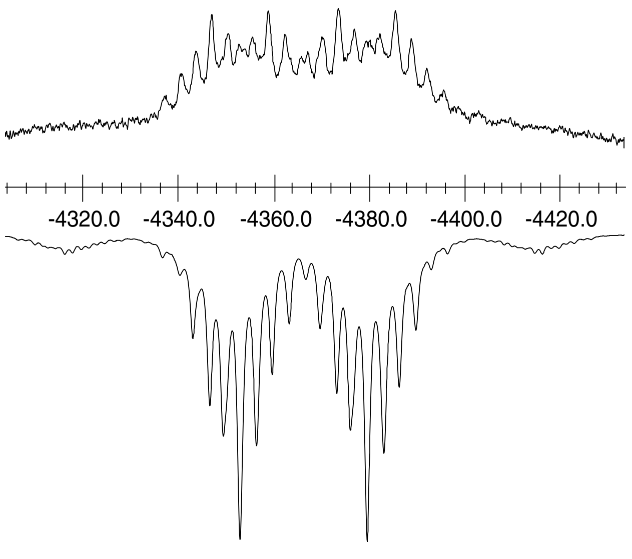

Fig. 2. Hydride indication from non-decoupled (top) and ^{1}H decoupled (bottom) ^{195}Pt spectra of **1** in CD_2Cl_2.

ligand is coplanar with the plane defined by the metal core.

No further reaction occurs in the presence of excess of organotin-hydride. Complex **1** is stable in solution for several hours at room temperature and can be kept for at least several weeks at +5 °C. Decomposition occurs upon standing overnight in solution at room temperature, giving back the starting cluster and other unidentified decomposition products.

The experiment was repeated with the starting cluster containing P^tBu_3 as ligand, which has simpler ^1H NMR features. Ph_3SnH reacts easily with this cluster as well, but surprisingly a monomeric complex $[PtH(SnPh_3)CO(P^tBu_3)]$ (**2**) [3] is obtained instead of the expected hydrido-cluster similar to **1**. Low temperature NMR spectra did not give any indication of the formation of the latter complex down to −90 °C.

The ^1H NMR spectrum clearly indicates the presence of a terminal hydride, presenting twelve lines centered at −1.6 ppm. The central lines are doublet of doublets (^2J(P–H) = −17.8 Hz and ^2J(P–C) = −2.3 Hz), flanked by satellite peaks due to couplings with ^{195}Pt (^1J(Pt–H) = 775 Hz) and ^{119}Sn (^2J(Sn–H) = −36.7). The ^1J(Pt–H) value is in between the corresponding values in *trans*- and *cis*-$[PtH(SnPh_3)(PCy_3)_2]$ (918 and 638 Hz, respectively) found by Clark et al. [20]. The same comparison for ^2J(Sn–H) values (698 and 26 Hz, respectively) rules out a *cis*-Sn–H arrangement in **2**. The ^2J(P–H) value (17.8 Hz) suggests a *cis*-arrangement of these two ligand as well, while ^2J(C–H) (54.4 Hz) indicates a possible *trans*-CO–H arrangement. The coupling constants deduced from $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, $^{195}Pt\{^1H\}$ and $^{119}Sn\{^1H\}$ NMR spectra confirm the ligand arrangement suggested by ^1H NMR.

Supplementary material

CCD 238905 contains supplementary crystallographic data for this paper. These can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retriving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CH2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[3] *$[Pt(SnPh_3)CO(P^tBu_3)_3H]$ (**2**).* $[Pt_3\mu\text{-}CO)_3(P^tBu_3)_3]$ (69 mg, 0.054 mmol) was added to a CH_2Cl_2 solution (20 ml) of Ph_3SnH (57 mg 0.162 mmol) and an immediate colour change from orange to pale yellow was observed. The mixture was stirred for 20 min at room temperature while reaction progress was monitored by IR spectroscopy. Addition of heptane followed by concentration of the resulting solution gave pale yellow microcrystals (0.75 g, 59.5%). Selected IR data (cm^{-1}): CH_2Cl_2 solution $\nu(C\equiv O)$ 2001vs; ν(Pt–H): 2116(s). *Anal. Calc.* for $C_{31}H_{42}OPSnPt$: C, 47.95; H, 5.58. Found: C, 47.56; H, 5.76. NMR data (δ in ppm, J in Hz): $\delta(H) = -1.6$; $\delta(C) = 197.2$; $\delta(P) = 98$; $\delta(Sn) = -64.9$; $\delta(Pt) = -5152$; ^1J(Pt–H) = 775; ^1J(Pt–P) = 2372; ^1J(Pt–C) = 1207; ^1J(Pt–Sn) = 8547; ^2J(P–H) = −17.8; ^2J(C–H) = −54.4; ^2J(Sn–H) = −36.7; ^2J(P–C) = −2.3; ^2J(P–Sn) = −1230; ^2J(C–Sn) = −52.