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Synthesis of some pentanuclear platinum clusters $[Pt_5(CO)_6(L)_4]$. The X-ray structure of $[Pt_5(\mu-CO)_5(CO)(PCy_3)_4]$

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Abstract

[Pt₅(μ -CO)₅(CO)L₄] (L = PPh₃ **1**, PPh₂Bz **2**, AsPh₃ **3**, PEt₃ **4**, PCy₃ **5**) have been synthesized by reacting [Pt₃(μ -CO)₃(PR₃)₃] with H₂O₂ (**1** and **2**), by reduction of *cis*-[PtCl₂(CO)(PEt₃)] with Zn dust (**4**), and by the Zn reduction of [Pt₃(μ -CO)₃(PCy₃)₃] in the presence of [PtCl₂(CH₃CN)₂] (**5**). Complex **5** has not been observed previously and has been characterized by X-ray crystallography. Oxidation of the phosphine ligands with H₂O₂ is a new way to synthesize **1** and **2**. The first complete NMR characterization of these complexes has also been achieved, and showed that these pentanuclear cluster complexes exhibit similar stereochemistries in solution and in the solid state. The observed ¹*J*_{Pt-Pt} values do not have any correlation with the corresponding bond lengths, again pointing out the irregular behaviour of such parameter in Pt complexes.

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1. Introduction

Pentanuclear platinum cluster complexes with the formula $[Pt_5(\mu-CO)_5(CO)(L)_4]$ have been known for some time. The first synthesis was reported by Chatt and Chini [1] in 1970, who obtained the complexes with PPh₃ and PPh₂Me from $[Pt_3(\mu-CO)_3L_4]$ under CO atmosphere, and the AsPh₃ derivative from alkali-tetra-chloroplatinate(II). They postulated these complexes as being tetranuclear on the basis of IR spectroscopic evidence and elementary analysis. In 1978, Braunstein and coworkers [2] investigated the formation of metalmetal bonds between transition metals and found that the reaction of *cis*-[PtL₂Cl₂] (L = PPh₃ and PEt₃) with two equivalents of Na[Mn(CO)₅] led to the formation of

the homopentanuclear Pt clusters $[Pt_5(\mu-CO)_5(CO)L_4]$ and $[Mn_2(CO)_{10-n}L_n]$ (n = 0 to 2). The crystal structure of the PPh₃ derivative has been reported [2]. The same group investigated the formation of these pentanuclear species during the elution of $[Pt_3(\mu-CO)_3(PPh_3)_4]$ on chromatographic columns containing different inorganic supports with various eluents. In the early 1980s, Mingos and coworkers [3–5] investigated the substitution of carbonyl ligands by SO₂ and described the formation of $[Pt_5(\mu-CO)_2(\mu-SO_2)_3(-CO)(PPh_3)_4]$. In 1994, Burrows et al. [6] reported the synthesis of a pentanuclear platinum cluster with a functionalized phosphine and its reaction with xylylisocyanide.

We report here the synthesis of the new pentanuclear cluster $[Pt_5(\mu-CO)_5(CO)(PCy_3)_4]$ (5) and a novel synthetic route to the derivatives containing PPh₃ (1), PPh₂Bz (2) and PEt₃ (4). Since very few information, some ¹⁹⁵Pt NMR parameters of complex 1 [7] and some ³¹P NMR chemical shifts [4–6], are available about the solution

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characteristics of these complexes, a complete NMR characterization has been achieved in addition.

2. Results and discussion

2.1. Structures in solution

The IR spectra in solution or in solid state (nujol mull) of complexes 1 and 5 are indicative of the presence of a terminally bonded (strong absorbance at ~ 2000 cm⁻¹) and four bridging carbonyls (four strong bands in the range 1770–1900 cm⁻¹). The observed stretching bands are in accordance with the previously reported values for 1 [2], 2 [1], 3 [1,2] and 4 [1,4].

¹⁹⁵Pt NMR spectra of complexes 1-4 present four distinct Pt chemical environments (an example is given in Fig. 2), indicating that C_s symmetry is preserved in solution. The chemical shifts relative to Na₂[PtCl₆] are decreasing with the metal-like character of the Pt centres, e.g., in all cases Pt(5) is the most highly shielded and Pt(1) is the lowest shielded metallic centre. Due to the metal-metal and metal-phosphorus or if used ¹³C labelled CO: metal-carbon scalar couplings, the spectra are complex and not analysable in the first order. Simulation of the ¹⁹⁵Pt, ³¹P and ¹³C spectra of each complex (except for 5, as no ¹⁹⁵Pt spectrum could be obtained due to its very low solubility) using gNMR 4.1 gave the homo and heteronuclear coupling constants summarized in Tables 1-3, respectively. All spectra are the superimposition of subspectra belonging to 32 isotopomers differing in the content of the ¹⁹⁵Pt isotope.

Corresponding ${}^{1}J_{Pt-Pt}$ and ${}^{2}J_{Pt-Pt}$ values (see Table 1) are similar to each other. Comparison of the ${}^{1}J_{Pt-Pt}$ values of complex 1 with the corresponding bond lengths in the solid state [2] clearly shows that there is no correlation between these two parameters. Although the longest Pt(2)-Pt(3) or Pt(2)-Pt(4) bond lengths (2.92 Å) correspond to the smallest one bonded Pt-Pt coupling constant (824 Hz), they are just slightly smaller than the ${}^{1}J_{Pt1-Pt3,4}$ value, which corresponds to platinum-platinium distances which are about 0.15 Å shorter (2.77 Å). In contrast, the value of the ${}^{1}J_{Pt2-Pt3,4}$ is significantly smaller than that of ${}^{1}J_{Pt3-Pt4}$ value which corresponds to a slightly shorter Pt-Pt distance (2.86 Å). The reasons for these observations are not clear as well as why the observed ${}^{1}J_{Pt1-Pt5}$ coupling constant in 3 is significantly smaller (220 Hz) than the corresponding values in the other three complexes (~800 Hz). However, it is known that ${}^{1}J_{Pt-Pt}$ values do not always correlate well with related metal-metal distances in the solid state [8,9]. Recently, Ziegler et al. [10] investigated the irregular behaviour of the one-bonded platinum-platinium coupling constant in Pt(I) dimeric complexes using DFT. They concluded that CO ligands axial to the Pt-Pt bond drastically diminish the ${}^{1}J_{Pt-Pt}$ constant. Unfortunately, in the case of pentanuclear cluster complexes these findings could not be used to rationalize the tendency observed in the metal-metal coupling constants in structures where axial ligands are absent.

The ${}^{31}P{}^{1}H{}$ NMR spectra of complexes 1, 2, 4 and 5 present three distinct phosphine environments with significant overlapping of the corresponding lines. Spectral data observed from computer simulation are listed in Table 2. In all cases, the values of ${}^{1}J_{Pt3,4-P3,4}$ and ${}^{1}J_{Pt5-P5}$ coupling constants are found to be significantly larger (4600–5100 Hz) than the ${}^{1}J_{Pt1-P1}$ values (3700–4100 Hz). In the case of 5, this trend is in accordance with the Pt–P bond lengths in the solid state. The ${}^{2}J_{Pt-P}$ values show significant differences. For example, ${}^{2}J_{Pt1-P5}$ and $^{2}J_{\text{Pt5-P1}}$ (~500 Hz) are significantly larger than, for example, ${}^{2}J_{\text{Pt2-P3,4}}$ or ${}^{2}J_{\text{Pt3,4-P1}}$ (~100 Hz). These differences can be explained considering the molecular structure of 5 (Fig. 1), since P(5) and P(1) are coplanar with the Pt(1)Pt(2)Pt(5) triangle, while the two other P atoms are in the plane defined by Pt(1)Pt(3)Pt(4). This is in accordance with the corresponding coupling constants of $[Pt_3(\mu-CO)_3(PR_3)_3]$ ([3: 3: 3]) complexes, where all three phosphine ligands are in the plane of the metal core [11]. In the case of the $[Pt_3(\mu-CO)_3(PR_3)_4]$ complexes [12], smaller ${}^{2}J_{Pt-P}$ values are also observed for the two phosphines which are flipped from the plane of the metals, relative to the ${}^{2}J$ values of the other two which are in the Pt₃ plane. The ${}^{3}J_{P-P}$ values are in accordance with the latter conclusion as well; thus ${}^{3}J_{P1-P5}$ and ${}^{3}J_{P3,4-P4,3}$ values are similar to the ${}^{3}J_{P-P}$ values of the [3: 3: 3] complexes [11] while ${}^{3}J_{P5-P3,4}$ and ${}^{3}J_{P1-P3,4}$ are smaller than these and similar to the values of the corresponding [3: 3: 4] complexes [12].

Due to a large number of different couplings, the ${}^{13}C{}^{1}H$ NMR spectra of these complexes are the most complicated ones. In accordance with IR spectra, the



Fig. 1. Core structure of $[Pt_5(\mu-CO)_5(CO)(PCy_3)_4]$ (5) (cyclohexyl rings are omitted for clarity), idealized C_s symmetry with symmetry plane passing through Pt(5) Pt(2) Pt(1).



Fig. 2. Observed (top) and simulated (bottom) ¹⁹⁵Pt{¹H} NMR spectrum of 2 in CD₂Cl₂.

Table 1 Selected ¹⁹⁵Pt NMR data (δ in ppm, J in Hz)

			/	
L	PPh ₃ 1	$PPh_2 Bz 2$	AsPh ₃ 3	PEt ₃ 4
$\delta_{\rm Pt1}$	-3571	-3621	-3734	-3628
$\delta_{\rm Pt2}$	-4066	-3960	-4172	-3874
$\delta_{\text{Pt3.4}}$	-4305	-4256	-4468	-4206
δ_{Pt5}	-4725	-4575	-4785	-4517
${}^{1}J_{\mathrm{Pt1-Pt2}}$	1854	1497	1787	1695
${}^{1}J_{\rm Pt1-Pt3.4}$	866	879	632	944
$^{1}J_{\mathrm{Pt1-Pt5}}$	1132	1180	221	1187
$^{1}J_{\mathrm{Pt2-Pt5}}$	1875	1866	2010	1781
$^{1}J_{\mathrm{Pt3-Pt4}}$	1906	1950	1950	1840
${}^{1}J_{{\rm Pt3,4-Pt2}}$	824	957	918	926
${}^{2}J_{\rm Pt3,4-Pt5}$	-333	-328	-398	-268

Table 2 Selected ³¹P NMR data (δ in ppm, J in Hz)

	PPh ₃ 1	PPh ₂ Bz 2	PEt ₃ 4	PCy ₃ 5
$\delta_{\rm P1}$	44.4	49.2	40.0	62.8
$\delta_{P3,4}$	50.2	51.1	47.2	68.5
$\delta_{ m P5}$	44.9	43.5	39.7	53.2
${}^{1}J_{\rm P1-Pt1}$	4117	3878	3732	3768
${}^{1}J_{P34-Pt34}$	5117	4948	4647	4635
${}^{1}J_{\rm P5-Pt5}$	5027	4982	4617	4640
${}^{2}J_{\rm P1-Pt2}$	363	367	381	401
${}^{2}J_{\rm P1}$ Pt 3 4	104	112	108	97
${}^{2}J_{\rm P1-Pt5}$	537	568	487	551
${}^{2}J_{P5-Pt1}$	556	554	472	500
${}^{2}J_{P5-Pt2}$	309	309	269	285
${}^{2}J_{P34-Pt1}$	287	287	273	279
${}^{2}J_{P3,4-Pt2}$	74	74	73	59
${}^{2}J_{\mathrm{P3,4-Pt4,3}}$	439	461	376	358
³ J _{P1 P5}	40	42	41	37
${}^{3}J_{P3} 4_{P4} 3$	48	51	48	52
${}^{3}J_{\rm P1-P3.4}$	~4	~4	~6	~5
${}^{3}J_{P3 4-P5}$	~ 3	~3	~ 4	~ 3
${}^{3}J_{\rm P5-Pt3,4}$	30	31	20	53

Table 3 ¹³C chemical shifts (δ in ppm) and one bonded ¹⁹⁵Pt–¹³C coupling constants (*J* in Hz)

L	PPh ₃ 1	PPh ₂ Bz 2	AsPh ₃ 3	PEt ₃ 4	PCy ₃ 5
$\delta_{C1,2}$	220.3	221.2	219.9	224.9	224.9
δ_{C3}	248.8	251.0	245.3	257.7	255.6
δ_{C4}	203.8	206.3	201.0	211.2	211.4
δ_{C5}	241.5	243.1	239.9	247.1	243.9
$\delta_{\rm C6}$	247.7	254.0	250.5	258.3	258.1
${}^{1}J_{C1.2-Pt3.4}$	880	869	934	849	829
${}^{1}J_{\rm C1.2-Pt1}$	283	277	270	257	307
$^{1}J_{\rm C3-Pt5}$	928	918	811	865	978
${}^{1}J_{C3-Pt1}$	676	766	931	752	678
${}^{1}J_{C4-Pt2}$	2286	2250	2340	2195	2290
${}^{1}J_{\rm C5-Pt2.5}$	2287	897	936	875	875
${}^{1}J_{\rm C6-Pt3,4}$	2287	740	755	714	729

¹³C NMR spectra (an example is shown in Fig. 3) present one terminal ($\delta \sim 200$ ppm) and four (C(1) and C(2) are chemically equivalent due to C_s symmetry) bridging carbonyl environments (in the 220–250 ppm range). Corresponding ${}^{1}J_{C-Pt}$ values of the different complexes are similar. The ${}^{1}J_{C4-Pt2}$ values (~ 2200 Hz) are similar to terminal Pt–CO coupling values found in other polynuclear platinum species [10,13].

In an intermolecular comparison, the ${}^{1}J_{C(bridging)-Pt}$ values are significantly different, e.g., ${}^{1}J_{C1,2-Pt1}$ is significantly smaller than the others, while for example C(1) is bridging the Pt(1) and Pt(3) metal centres, the corresponding one bonded couplings with the two metal centres are different. These differences are in accordance with the bond length (Table 4) differences in complex 5 observed in the solid state. Thus, ${}^{1}J_{C1,2-Pt3,4}$ (829 Hz) in complex 5 corresponds to a shorter Pt–C(carbonyl) distance (2.016 and 1.996 Å, respectively) than ${}^{1}J_{C1,2-Pt1}$ (307 Hz), which corresponds to a 0.2 Å longer bond length (2.205 and 2.243 Å, respectively). Similarly, the observed ${}^{1}J_{C3-Pt5}$ in complex 5 is 300 Hz larger than



Fig. 3. Observed (top) and simulated (bottom) ¹³C NMR spectrum of 2 in CD₂Cl₂ at 298 K.

Table 4 Selected bond distances (Å) and angles (°) for cluster ${\bf 5}$

	• • •				
Pt(1)-Pt(2)	2.8629(7)	Pt(4)–P(4)	2.281(3)	Pt(4)-C(6)	2.090(13)
Pt(1)–Pt(3)	2.7660(7)	Pt(5)–P(5)	2.273(3)	Pt(5)–C(3)	1.976(12)
Pt(1)-Pt(4)	2.7625(7)	Pt(1)-C(1)	2.205(12)	Pt(5)-C(5)	2.074(13)
Pt(1)–Pt(5)	2.7231(7)	Pt(1)–C(2)	2.243(14)	O(1)–C(1)	1.156(14)
Pt(2) - Pt(3)	2.8861(7)	Pt(1)-C(3)	2.111(13)	O(2)–C(2)	1.164(16)
Pt(2)–Pt(4)	2.9136(6)	Pt(2)-C(4)	1.849(14)	O(3)–C(3)	1.166(13)
Pt(2)–Pt(5)	2.6514(7)	Pt(2)-C(5)	2.030(14)	O(4)–C(4)	1.142(14)
Pt(3)–Pt(4)	2.6610(6)	Pt(3)–C(1)	2.016(13)	O(5)–C(5)	1.117(14)
Pt(1) - P(1)	2.357(3)	Pt(3)–C(6)	2.074(13)	O(6)–C(6)	1.138(14)
Pt(3)–P(3)	2.295(3)	Pt(4)-C(2)	1.996(15)		
Pt(3)–Pt(1)–Pt(2)	61.663(17)	P(1)-Pt(1)-Pt(2)	166.11(8)	C(3) - Pt(1) - Pt(3)	151.7(3)
Pt(4) - Pt(1) - Pt(2)	62.358(17)	P(1)-Pt(1)-Pt(3)	104.63(8)	C(2)-Pt(1)-Pt(4)	45.6(4)
Pt(5) - Pt(1) - Pt(2)	56.607(17)	P(1) - Pt(1) - Pt(4)	109.42(8)	C(1) - Pt(1) - Pt(5)	93.7(3)
Pt(4) - Pt(1) - Pt(3)	57.544(16)	P(1) - Pt(1) - Pt(5)	136.40(8)	C(2) - Pt(1) - Pt(5)	87.5(3)
Pt(5)-Pt(1)-Pt(3)	112.65(2)	P(3)-Pt(3)-Pt(1)	151.56(8)	C(3)-Pt(1)-Pt(4)	139.2(3)
Pt(5) - Pt(1) - Pt(4)	109.29(2)	P(3)-Pt(3)-Pt(2)	127.12(8)	C(3) - Pt(1) - Pt(5)	46.1(3)
Pt(1)-Pt(2)-Pt(3)	57.515(16)	P(3)-Pt(3)-Pt(4)	146.79(8)	C(4) - Pt(2) - Pt(1)	147.8(4)
Pt(1)-Pt(2)-Pt(4)	57.131(16)	P(4) - Pt(4) - Pt(1)	150.09(8)	C(4) - Pt(2) - Pt(3)	94.4(4)
Pt(5)-Pt(2)-Pt(1)	59.035(17)	P(4) - Pt(4) - Pt(2)	127.34(8)	C(4) - Pt(2) - Pt(4)	94.9(4)
Pt(5)-Pt(2)-Pt(3)	111.09(2)	P(4) - Pt(4) - Pt(3)	148.27(8)	C(4) - Pt(2) - Pt(5)	153.0(4)
Pt(5)-Pt(2)-Pt(4)	106.92(2)	P(5)-Pt(5)-Pt(1)	146.81(8)	C(5)-Pt(2)-Pt(5)	50.5(4)
Pt(3)-Pt(2)-Pt(4)	54.618(15)	P(5)-Pt(5)-Pt(2)	148.50(8)	C(1)-Pt(3)-Pt(1)	52.1(3)
Pt(1)-Pt(3)-Pt(2)	60.821(17)	Pt(3)-C(1)-Pt(1)	81.7(5)	C(6)-Pt(3)-Pt(4)	50.6(3)
Pt(4) - Pt(3) - Pt(1)	61.162(17)	Pt(5)-C(3)-Pt(1)	83.5(5)	C(2)-Pt(4)-Pt(1)	53.4(4)
Pt(4)-Pt(3)-Pt(2)	63.217(17)	Pt(2)-C(5)-Pt(5)	80.5(5)	C(6) - Pt(4) - Pt(3)	50.0(3)
Pt(1)-Pt(4)-Pt(2)	60.511(16)	Pt(3)-C(6)-Pt(4)	79.4(5)	C(3) - Pt(5) - Pt(1)	50.4(4)
Pt(3)-Pt(4)-Pt(1)	61.294(17)	C(1) - Pt(1) - Pt(2)	76.0(3)	C(5)-Pt(5)-Pt(2)	49.0(4)
Pt(3)-Pt(4)-Pt(2)	62.165(17)	C(2) - Pt(1) - Pt(2)	76.7(3)	O(4) - C(4) - Pt(2)	175.9(12)
Pt(2)-Pt(5)-Pt(1)	64.358(18)	C(1) - Pt(1) - Pt(3)	46.2(3)		

the ${}^{1}J_{C3-Pt1}$ value, while the corresponding bond length is 0.15 Å shorter. This is in accordance with the observed two (undistinguishable) ${}^{1}J_{C5-Pt2,5}$ and ${}^{1}J_{C6-Pt3,4}$ values, which correspond to almost identical Pt–C distances (2.030 (2.074) and 2.074 (2.090) Å, respectively).

3. Crystal structure of $[Pt_5(\mu\text{-CO})_5(CO)(PCy_3)_4]\cdot C_7H_8\cdot 1/2C_6H_{14}\ (5)$

Slow diffusion of hexane in a toluene solution of 5 gave deep red crystals, which belong to the mono-

clinic system with C2/c space group. The compound crystallizes with a disordered toluene and half of a hexane molecule, and is isostructural with the pentanuclear cluster containing triphenylphosphine ligands [2,14] or functionalized phosphines [6]. The cluster has an edge-bridged tetrahedral skeletal geometry. It contains one terminal carbonyl and four tricyclohexylphosphine ligands. Five edges of the cluster are bridged by carbonyls, while the remaining two edges are unbridged.

The Pt–Pt distances (Table 4) are in the 2.65–2.92 Å range (Pt(3)–Pt(4) being the shortest and Pt(3,4)–Pt(5) being the longest distances). These distances are similar to the corresponding metal-metal bond lengths in the isostructural complex containing PPh₃ ligands [2,14] and are shorter than those of a similar cluster, where three of the five bridging carbonyls are substituted by SO₂ [3,4]. Cluster 5 has a total of 70 electrons, again showing that platinum clusters have a count short of the effective atomic number (EAN) rule [4,15]. The observed long Pt-Pt bond lengths corresponding to the Pt(3,4)-Pt(2) distances (~2.90 Å) in complex 1 led to the suggestion [2,14] that these clusters may be more correctly described as two orthogonal triangulo-cluster fragments, which share a common metal atom. Later, Mingos and Evans classified the polyhedral platinum clusters [16] and concluded that condensed platinum clusters have 4 electrons less than the number of electrons observed for a carbonyl cluster compound with the same metal skeletal geometry, but derived primarily from conical M(CO)₃ fragments. These pentaplatinum clusters can be described as edge-bridged-tetrahedrons having 70 valence electrons, 4 less than the corresponding 74-electron clusters obeying the EAN rule, derived from a tetrahedron and a triangle. In complex 5, other platinum-platinum distances are also elongated in addition to Pt(3,4)-Pt(2), Pt(1)-Pt(2) is close to 2.9 Å as well. Thus, in order to describe the structure as two almost orthogonal triangles one has to pick arbitrarily two Pt-Pt distances as non-bonding interactions. However, the structural description in terms of interconnected triangles has the advantage to explain the almost flat arrangements of the ligands in the Pt₃ triangles.

The bridging carbonyls are almost coplanar with the corresponding Pt_3 triangles, only the two chemically equivalent carbonyl groups containing C(1) and C(2) are flipped from the Pt(1)Pt(3)Pt(4) plane due to the steric demand of the phosphine groups P(1), P(3) and P(4). The Pt–C bond lengths are in the 1.85–2.20 Å range, the terminal Pt(5)–C(4) distance being the shortest and the Pt(1)–C(4) distances the longest.

This is understandable when considering that the Pt(1) centre has the largest coordination number. The metal-carbonyl distances are similar to the corresponding bond lengths in isostructural complexes [6].

4. Conclusions

Oxidation of $[Pt_3(CO)_3(PR_3)_3]$ (PR₃ = PPh₃ and PBzPh₂) by H_2O_2 is an easy way of preparing pentaplatinum carbonyl phosphine complexes, while reduction of $[Pt_3(\mu-CO)_3(PCy_3)_3]$ by Zn dust in the presence of [PtCl₂(CH₃CN)₂] under CO led to the formation of the novel homologue containing PCy₃. NMR spectroscopic measurements confirmed that these pentanuclear species exhibit similar stereochemistries in solution and in the solid state. Simulation of the NMR spectra is needed, since due to the low symmetry they are not analysable in the first order. Comparison of ${}^{1}J_{Pt-Pt}$ with the corresponding bond lengths shows that there is no straightforward relation between these two molecular parameters, while ${}^{n}J_{Pt-P}$ and ${}^{n}J_{Pt-C}$ values do show correlations and are clearly indicative of the position of the phosphine and carbonyl groups relative to the metal core.

5. Experimental

All manipulations were carried out under nitrogen atmosphere using standard Schlenk techniques. All solvents were dried by conventional methods and distilled prior to use. $[Pt_3(CO)_3(PPh_3)_3]$, $[Pt_3(\mu-CO)_3(PBzPh_2)_3]$, [PtCl₂(CH₃CN)₂] and [PtCl₂(COD)₂] were prepared by literature methods [17–19]. The ¹³C isotopically labelled derivatives were prepared similarly using 13 CO. H₂O₂ (Fluka), Zn dust (Fluka) and carbon monoxide (99% ¹³CO Cambridge Isotope Laboratory Inc.) were used as received. Infrared spectra (CaF2 cells) were recorded on a Perkin-Elmer 2000 FT IR spectrometer and NMR spectra on a Bruker DRX 400 spectrometer. Chemical shifts (δ) are referred to external TMS (¹³C), 85% H₃PO₄ (³¹P) and Na₂[PtCl₆] (¹⁹⁵Pt). Simulations were performed with the gNMR 4.1, considering only the relative population of platinum isotopomers since all samples for ${}^{13}C{}^{1}H$ NMR were enriched to 99% ¹³CO. All NMR spectra were recorded in CD₂Cl₂ as solvent except for 5 where toluene- d_8 was used. In the case of 5, no ¹⁹⁵Pt NMR spectrum could be obtained due to its low solubility.

5.1. Synthesis of $[Pt_5(CO)(\mu - CO)_5(PPh_3)_4]$ (1)

A solution of $[Pt_3(\mu-CO)_3(PPh_3)_3]$ (0.70 g, 0.48 mmol) in THF (60 ml) was stirred with an excess of CO at room temperature and then treated with 0.2 ml (1.90 mmol) of H₂O₂ (30%). The reaction mixture was stirred for 20 h until pentaplatinum cluster **1** was formed (the reaction progress was monitored by IR spectroscopy). The redbrown solution was evaporated to dryness in vacuo, the residue was dissolved in toluene and filtered through a neutral Al₂O₃ pad (10 cm × 6 cm²) and eluted with toluene. The eluate was reduced to a small volume. The product precipitated by *n*-heptane and recrystallized from dichloromethane/heptane as red microcrystals. Yield 0.45 g (71 %). *Anal.* Calc. for C₇₈H₆₀O₆P₄Pt₅: C, 42.73; H, 2.76. Found: C, 42.58; H, 2.80%. IR (THF): 2003 vs, 1896 w, 1862 m, 1817 s, 1793 vs cm⁻¹.

5.2. Synthesis of $[Pt_5(CO)(\mu-CO)_5(PBzPh_2)_4]$ (2)

As for 1 starting with $[Pt_3(\mu-CO)_3(PBzPh_2)_3]$ (0.65 g, 0.434 mmol), treated with 0.15 ml (1.5 mmol) of H_2O_2 (30%) and stirred for 2 days. Yield 0.51 g (87%) as red microcrystals. *Anal.* Calc. for $C_{82}H_{68}O_6P_4Pt_5$: C, 43.80; H, 3.05. Found: C, 43.66; H, 3.05%. IR (CH₂Cl₂): 2001 s, 1893 w, 1847 m, 1803 vs, 1775 vs; (nujol mull): 1989 s, 1895 w, 1851 m, 1798 s, 1773 s cm⁻¹.

5.3. Synthesis of $[Pt_5(CO)(\mu-CO)_5(AsPh_3)_4]$ (3)

This complex was prepared following the method reported by Mingos et al. [5], starting with $[PtCl_2(AsPh_3)_2]$ (2.7 g, 3.07 mmol). Yield 0.51 g (35%) as red microcrystals. *Anal.* Calc. for $C_{78}H_{60}As_4O_6Pt_5$: C, 39.56; H, 2.55. Found: C, 39.82; H, 2.64%. IR (CH₂Cl₂): 2001 vs, 1890 w, 1856 m, 1807 vs, 1783 vs; (Nujol mull): 1996 vs, 1891 w, 1853 m, 1811 s, 1783 vs cm⁻¹.

5.4. Synthesis of $[Pt_5(CO)(\mu - CO)_5(PEt_3)_4]$ (4)

A suspension of [PtCl₂(CH₃CN)₂] (1.6 g, 4.6 mmol) in THF was saturated with an excess of CO for 3 h. PEt₃ (0.57 ml, 3.9 mmol) was added, the mixture stirred for 10 h, and the reaction progress was followed by IR spectroscopy. When the maximun concentration of the carbonyl intermediate cis-[PtCl₂(CO)(PEt₃)] $(v(CO) = 2103 \text{ cm}^{-1})$ was observed, zinc dust (1.5 g, 23) mmol) was added and the mixture stirred until the initially developing green colour turned red and its IR spectrum showed the disappearance of the v(CO)absorption at 2103 cm⁻¹ and the appearance of a strong absorption at 1989 cm⁻¹ (terminal CO) together with those of bridging COs: 1877 m, 1843 s, 1797 vs, 1776 vs and 1765 vs. After 60 h, the excess of zinc dust was filtered off and the solvent removed in vacuo. The residue was extracted with dichloromethane, transferred to the top of a chromatographic column (18 cm \times 16 cm²) packed with silica gel (70–230 mesh) and eluted with dichloromethane. The first orange-red fraction was reduced to ca. 20 ml and treated with methanol (70 ml). The solution was evaporated until all the dichloromethane was removed and cooled to -20 °C overnight. The red crystals of 4 were filtered, washed with cold methanol and dried in vacuo. Yield 0.95 g (64%).

Anal. Calc. for $C_{30}H_{60}O_6P_4Pt_5$: C, 22.29; H, 3.74. Found: C, 22.15; H, 3.70%. IR (THF): 1988 vs, 1877 m, 1843 s, 1798 vs, 1776 vs, 1765 vs cm⁻¹.

5.5. Synthesis of $[Pt_5(CO)(\mu - CO)_5(PCy_3)_4]$ (5)

A THF solution (150 ml) containing [Pt₃(µ-CO)₃(PCy₃)₃] (1.0 g, 0.662 mmol) and [PtCl₂(CH₃CN)₂] (0.19 g, 0.546 mmol) was saturated with CO (45 ml). An excess of zinc dust (0.371 g, 5.7 mmol) was added and the reaction mixture vigorously stirred under CO at room temperature for 6 days. The excess of zinc dust was filtered off and the solution was chromatographed on a column (35 cm \times 7 cm²) packed with silica gel (70-230 mesh). Elution with THF/n-hexane (2:1) gave a first red-brown fraction containing unreacted $[Pt_3(\mu-CO)_3(PCy_3)_3]$ together with other non identified mono- and polynuclear carbonyl derivatives, which were discarded. Subsequent elution with THF gave orangered solution. Concentration of this solution followed by standing and cooling overnight at -22 °C deposited 5 as red microcrystals. Overall yield based on Pt, 0.83 g (72%). Anal. Calc. for C₇₈H₁₃₂O₆P₄Pt₅: C, 41.36; H, 5.87. Found: C, 41.33; H, 5.70%. Single crystals were grown from toluene by slow diffusion of n-hexane at 5 °C. IR (THF) 1983 vs, 1868 w, 1829 m, 1794 vs, 1772 vs cm⁻¹.

Crystal data for $C_{78}H_{132}O_6P_4Pt_5 \cdot C_7H_8 \cdot 0.5C_6H_{14}$; $M/g \text{ mol}^{-1}$ 2400.39; T/K 140(2); crystal system: monoclinic; space group C2/c; a/A 25.9603(10); b/A17.6303(9); $c/\text{\AA}$ 42.7560(15); $\beta/^{\circ}$ 97.012(3); $V/\text{\AA}^{3}$ 19422.5(14); Z 8; $D_c/g \text{ cm}^{-3}$: 1.642; F(000) 9384; crystal dimensions $0.43 \times 0.26 \times 0.18 \text{ mm}^3$; μ/mm^{-1} 7.288; θ range 3.43 to 25.03°; reflections collected/unique 57147/11165 [R_{int} 0.0741]; R_1 0.0564, wR_2 [$I > 2\sigma(I)$] 0.0941. The crystal was analysed on a Stoe IPDS system equipped with Mo radiation. More than 11% of the volume of the cell is empty, this means that more than 1 toluene and half *n*-hexane should be placed in the asymmetric unit (but this is very difficult due, the disorder affecting the solvent and the very weak diffracting power of such atoms compared to the cluster). The potential solvent molecules which occupy the void in the cell were not detected from the electron density map; therefore, these molecules are not included in the final model. Intensities were integrated and corrected for Lorentz and polarization effects. An absorption correction based on the crystal habitus was computed with the help of the XPREP [20] program. The decay during the measurements was negligible. The structures were solved with the help of DIRDIF-99 [21] and refined by means of SHELXS-97 [22]. All non-hydrogen atoms were refined anisotropically, except the atoms of the solvent molecules, and all hydrogens were made to ride isotropically on their associated carbons.

6. Supplementary material

CCDC 238571 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033."

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