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A convenient synthetic route to bi- and tri-nuclear palladium and platinum complexes. The crystal structures of [M₃(μ₃-CO)(Cl) (μ-dppm)₃]Cl, M = Pd, Pt, dppm = bis(diphenylphosphino)methane

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Abstract—Simple new one-pot syntheses from metal salts, CO, dppm and NaBH₄ and the crystal structures of [M₃(μ₃-CO)(Cl)(μ-dppm)₃]Cl (M = Pd, Pt) are reported. The structure of the triangulo Pd₃-containing cation is very similar to that already reported with a CF₃COO⁻ anion, including the disorder at the CO and Cl ligands. There is no disorder in the Pt cation. The CO asymmetrically caps one side of the Pt₃ face and the Cl⁻ ligand on the other side is weakly associated with only one of the Pt atoms. Convenient, high-yield syntheses of additional Pt-dppm and Pt-dppm-CO complexes are also reported. © 1997 Elsevier Science Ltd

We have reported earlier that reactions between Ni[II] [1], Co[II] [2] and Fe[III] [3] ions with NaBH₄ or LiAlH₄ in the presence of bis(diphenylphosphino)methane (dppm) and CO are very convenient routes to a wide variety of complexes with the outcome of a particular reaction determined by suitable adjustment of reaction conditions. In the case of Pd(II) or (IV), Pd₆(μ₂-CO)₆(μ-dppm)₃ [4] and a fluxional Pd₃ system [5] have been obtained as products of similar reactions, along with several complexes previously made by other routes. Similar reactions involving Pt[II] are even more complex, and from reactions involving one or other of these metals, the compounds [M₃(μ₃-CO)(Cl)(μ-dppm)₃]⁺X⁻, M = Pd, **1** X = Cl, and M = Pt, **2** X = Cl have now been obtained in one simple experimental step. For the Pt reactions, modification of conditions leads to the formation of any one of several other Pt complexes.

The literature on complexes of the type [M₃(L)(L′)(μ-dppm)₃]⁺X⁻ is very extensive, more so for Pt than Pd [6,7]. The complexes have an essentially planar arrangement of M₃P₆ atoms, the M₃ being triangular, with L and L′ on opposite sides of the plane in positions which range from symmetrically capping to weakly bound terminally to one of the metal atoms. Structurally characterized complexes for M = Pd, include L = CO, L′ = Cl **1**, X = CF₃COO [8]; L = CO, L′ = I, X = CF₃COO [9]; L = CO, L′ = CF₃COO, X = CF₃COO [7]; L = PF₃, L′ = Cl, X = PF₆ [10] and L = PF₃, L′ = I, X = I [11]. For M = Pt, there are examples where L = L′ and both are symmetrically capped, L = μ₃-, L′ = terminal, and L and L′ are both terminal [7,12]. The steric effects [13] and the site preference [14] for L and L′ have been discussed.

The previously published synthesis of **1** X = CF₃COO was by the addition of halide to [Pd₃(μ₃-CO)(μ-dppm)₃][CF₃COO]₂ and in the structure, disorder at both the CO and Cl resulted in some uncertainty in the precise position of the Cl above the Pd₃ face [7,9]. Attempts to resolve this *via* the structure

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of **1** X = Cl, along with the structure of the Pt analogue, **2** X = Cl, where no disorder in the cation is present, are now reported. In addition, a brief account of considerably more convenient, high-yield, syntheses of several known Pt complexes, obtainable by small variations in the conditions under which these reactions are carried out, is included.

EXPERIMENTAL

Reagents, solvents and measurements

LiBH$_4$ was obtained from Strem and dppm, K$_2$PtCl$_4$ and NaBH$_4$ were purchased from either Strem or Aldrich. The LiBH$_4$ was stored in a desiccator under nitrogen and was recrystallized according to published procedures [15]. All solvents were degassed prior to use by purging with nitrogen. Both samples and reagents were handled under an inert atmosphere during weighing and data collection. Microanalyses for C, H and N were acquired in our laboratories with a Control Equipment Corporation model 240XA analyzer and using V$_2$O$_5$ as a combustion aid. Infrared spectra (for Nujol mulls between NaCl plates and in solution) were recorded on either a Beckman IR-4250 or a Bruker IFS 66 FTIR spectrophotometer. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker AC-E 200 spectrometer. Chemical shifts are reported as δ values with positive shifts for ^{1}H downfield of the signal of Me$_4$Si (TMS) while those for ^{31}P are downfield of the signal of external 85% H$_3$PO$_4$.

Syntheses of the compounds [M$_3$(μ_3-CO)(Cl)(μ-dppm)$_3$]Cl M = Pd, Pt

The following syntheses represent typical preparations, the various steps of which were carried out under a flow of pure nitrogen or carbon monoxide as appropriate. Isolation and recrystallization procedures were carried out in a nitrogen-filled glove box.

Preparation of [Pd$_3$(μ_3-CO)(Cl)(μ-dppm)$_3$]Cl, (1)

K$_2$PdCl$_6$ (0.42 g, 1.1 mmol) and dppm (0.46 g, 1.2 mmol) were dissolved in toluene/ethanol (1 : 1, 30.0 cm^3). CO was passed through the stirred orange solution for 15 min and then NaBH$_4$ (0.10 g, 2.6 mmol) in ethanol (15.0 cm^3) was added dropwise over 2 min. The reaction mixture was then filtered and hexane (300 cm^3) added to the brown filtrate which yielded, over a 24 h period, brown crystals. These were recrystallized from acetone/ether, CH$_2$Cl$_2$/hexane or acetone/hexane. In each case the precipitate was filtered off and dried under reduced pressure. Yield 25%. All samples showed the presence of varying amounts of solvents, particularly ethanol. A crystal suitable for X-ray purposes was grown by successive additions of hexane (30.0 cm^3), approximately every third day over

a 3 week period, to the above filtrate following the addition of the initial 300 cm^3 of hexane. The cation was characterized from its spectroscopic properties which were in full agreement with those reported [9] for **1** X = CF$_3$COO. Analytical data were consistent with the presence of between 2 and 3 molecules of ethanol per unit of **1** X = Cl, and the presence of this was confirmed by both ^{1}H NMR measurements and the crystal structure.

Preparation of [Pt$_3$(μ_3-CO)(Cl)(μ-dppm)$_3$]Cl · C$_6$H$_6$ (2)

K$_2$PtCl$_4$ (0.61 g, 1.5 mmol) and dppm (0.56 g, 1.5 mmol) were suspended in CH$_3$CN (30 cm^3) and left to stir under a slow, steady stream of CO for 20–30 min. Freshly-recrystallized LiBH$_4$ (0.064 g, 2.9 mmol) was dissolved in diethyl ether (10 cm^3) and added to the reaction solution over 1–2 min, turning the solution yellow, then orange. CO was bubbled through the reaction solution for a further 15 min, or until a white solid, **(3)**, appeared. After filtering the reaction solution, the crude solid product was dissolved in benzene (25 cm^3), stirred for several min, and then filtered. An excess of diethyl ether (40 cm^3) was carefully layered over the deep, dark-red solution and orange crystals of **2** appeared over about 24 h. Yield: 29%. ^{31}P{^{1}H} NMR (25°C, CD$_2$Cl$_2$): δ − 12.5 (singlet centred on multiplet, $^1J_{PtP}$ 3711, $^2J_{PtP}$ 170, $^3J_{PP}$ 170 Hz), ^{1}H NMR (25°C, CD$_2$Cl$_2$): δ 5.63 and 5.24 (ABX$_2$ pattern, PH^{a}H^{b}P, $^2J_{HH}$ 14.9, $^3J_{PtH}$ 78.1 Hz). IR: ν_{CO} 1750 (wk) cm^{-1}. Found: C, 51.5; H, 4.0. Calc. for Pt$_3$Cl$_2$P$_6$OC$_{82}$H$_{72}$: C, 51.4; H, 3.8%. (Samples contained varying amounts of solvent as reflected in the above analyses which require one benzene in the lattice. The particularly well-formed crystal used in the structural determination contained no solvent.)

Alternatively, K$_2$PtCl$_6$/dppm/NaBH$_4$ (1 : 1 : 5) in benzene/ethanol react under CO to produce **2** X = Cl over about 20 h with no visible evidence for the formation of **3** during the reaction.

Syntheses of other Pt complexes

The clean and high-yield syntheses reported below, starting with a simple Pt^{II} salt, of the known complexes **3** [16], **4** [17] and **5** [18] are alternative procedures to those previously reported. Physical properties were in full agreement with those recorded elsewhere.

Preparation of Pt$_2$(μ-CO)(CO)$_2$(μ-dppm)$_2$, (3)

K$_2$PtCl$_4$ (0.23 g, 0.55 mmol) and dppm (0.21 g, 0.55 mmol) were suspended in CH$_3$CN (20 cm^3) and stirred under a slow stream of CO for 30 min. The rate of passing CO was increased (to approximately 0.5 l/min) and solid NaBH$_4$ (0.10 g, 2.7 mmol) was added in one portion to the reaction solution turning it light

orange. CO was passed through the solution at this increased rate until an off-white precipitate formed (about 60 min). The product was filtered, quickly washed with methanol (10 cm^3) and pentane (20 cm^3). Yield: 80%.

Preparation of PtCl$_2$(dppm), (4)

K$_2$PtCl$_4$ (0.29 g, 0.69 mmol) and dppm (0.27 g, 0.69 mmol) were suspended in CH$_3$CN (25 cm^3), and CO was passed through the suspension for 60 min. The flow of CO was stopped and the solution was left to stir for 24 h after which time a bright white precipitate had formed. The solid was recovered, washed with water (20 cm^3), C$_6$H$_6$ (20 cm^3) and pentane (20 cm^3), and then dried under reduced pressure. Yield: 88–90%.

Preparation of Pt$_2$(μ-dppm)$_3$ (5)

K$_2$PtCl$_4$ (0.21 g, 0.51 mmol) and dppm (0.59 g, 1.5 mmol) were suspended in CH$_3$CN (25 cm^3) and allowed to mix for 1–2 min. Solid NaBH$_4$ (0.096 g, 2.5 mmol) was then added to the suspension in one portion. The reaction solution was left to stir for 12 h, after which a reddish-brown precipitate had formed. The solid was recovered, washed with pentane (20 cm^3) and dried briefly under reduced pressure. Yield: 98%.

Crystal structure determinations

X-ray crystallographic data collection was carried out on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Mo$_{K_\alpha}$ radiation at 293 K. Crystal structure refinement calculations were carried out on a PC Express computer with the SHELX program system [19]. NRCVAX programs were used for scaling and data reduction [20]. Unit cell parameters were obtained by least squares analysis of 25 low angle reflections. The stability of the crystal was measured by monitoring periodically three standard reflections; no systematic intensity variations were observed. Intensity data were corrected for Lorentz and polarization factors. An absorption correction was applied (for 2).

Heavy atoms in both structures were found using direct methods; cycles of Fourier and difference Fourier calculations were used to find the remaining atoms. Because of refinement difficulties with the phenyl C atoms, (of 2), the phenyl rings were refined as rigid hexagons with isotropic thermal displacement parameters. Calculated ideal locations for the hydrogen atoms of methylene carbon atoms (both) and phenyl rings of dppm ligands (1 only) were included but not refined. All remaining atoms were refined with anisotropic thermal displacement parameters. Relevant data concerning the crystal, data collection and struc-

ture solution are found in Table 1. Atomic scattering factors were taken from tabulated values [21]. Compound 1 shows disorder in both the capping CO and Cl ligands. The final model resulted in relative occupancies of 0.83 and 0.17. In addition, there is solvent disorder. In 2 there is no disorder in the cation, but the Cl$^-$ anion is disordered.

The several large positive and negative peaks remaining near the Pt atoms in 2, ranging from 1.51 to 4.95 and -1.54 to -2.41 $e/\text{Å}^3$, illustrate problems with modelling heavy atoms. There are several additional positive peaks (1.47 to 2.45 $e/\text{Å}^3$) at least 3 Å from atoms of the cation, but many near the Cl$^-$. In 1, the largest remaining positive peak was 1.22 $e/\text{Å}^3$ near one of the ethanol solvent molecules and the largest negative peak was -1.47 $e/\text{Å}$ close to a Pd atom. Atomic coordinates for 1 and 2 have been deposited with the Cambridge Crystallographic Data Center.

RESULTS AND DISCUSSION

The syntheses of Pd$_6$(μ_2-CO)$_6$(μ-dppm)$_3$ [4] and the fluxional [Pd$_3$(μ_2-CO)$_3$(dppm)$_2$]$_n$ ($n = 1$ or 2) [5] from reactions of Pd^{II} or Pd^{IV}, BH$_4^-$, CO and dppm have already been described. In addition the reaction also produces, under appropriate conditions, 1 X = Cl, as described in this paper, in contrast to the synthesis of 1 X = CF$_3$COO, made by coordinating the halide to the [Pd$_3$(μ_3-CO)(μ-dppm)$_3$] dication [8]. The analogous 1 X = Br with a coordinated Br can be made by reacting together PdBr$_2$(COD), dppm, CO and NaBH$_4$, but although convincing spectroscopic evidence for its formation was obtained (IR, ^{31}P and ^{1}H NMR essentially the same as for 1 X = Cl), the acquisition of good analytical data was frustrated by widely varying amounts of solvent always present in the lattice.

Reductions of K$_2$PtCl$_4$ by either LiBH$_4$ or NaBH$_4$ in solutions containing CO and dppm are much more complex. Amongst the compounds readily produced in the reactions described here (in addition to 2 X = Cl) are Pt$_2$(μ-CO)(CO)$_2$(μ-dppm)$_2$ [16], 3, PtCl$_2$(dppm) [17], 4, and Pt$_2$(μ-dppm)$_3$ [18], 5, and since the syntheses are not only in very high yield but also more convenient than those reported previously, a brief description is included in the experimental section. The following known complexes also have been observed and identified by characteristic ^{31}P NMR chemical shifts and coupling constants as products in reactions carried out under a variety of conditions: Pt$_2$Cl$_2$(μ-dppm)$_2$ [18], Pt$_2$Cl$_2$(μ-CO)(μ-dppm)$_2$ [18], [Pt$_2$H$_2$(μ-H)(μ-dppm)$_2$]$^+$ [18], [Pt$_2$H$_2$(μ-Cl)(μ-dppm)$_2$]$^+$ [18], [Pt$_2$Cl$_2$(μ-H)(μ-dppm)$_2$]$^+$ [18], [Pt$_2$(CO)$_2$(μ-dppm)$_2$]$^{2+}$ [22], and [Pt$_6$(μ_2-CO)$_6$(μ-dppm)$_3$] [23]. In addition, there are several other compounds that have not yet been identified.

These direct syntheses from a simple starting material are therefore extremely convenient routes to

Table 1. Crystal data and structure refinement for $[Pd_3(Cl)(\mu_3\text{-CO})(\mu\text{-dppm})_3]Cl \cdot 2.72C_2H_5OH$ (1) and for $[Pt_3(Cl)(\mu_3\text{-CO})(\mu\text{-dppm})_3]Cl$ (2)

	(1)	(2)
Empirical formula	$C_{81.44}H_{66}Cl_2O_{3.72}P_6Pd_3$	$C_{76}H_{66}Cl_2OP_6Pt_3$
Formula weight	1680.06	1776.75
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\text{-}1$	$P2_1$
a Å	14.506(9)	10.949(5)
b Å	14.468(4)	26.660(12)
c Å	20.743(6)	14.331(5)
α^0	75.08(2)	
β^0	69.60(3)	100.01(4)
γ^0	2.88(3)	
V (Å³)	3841(3)	4120(3)
Z	2	2
D_{calc} (g/cm³)	1.453	1.432
Absorption coefficient (mm⁻¹)	0.937	5.298
$F(000)$	1693	1656
Range (°)	1.06–25.97	1.53–23.98
Index ranges	$-16 \leqslant h \leqslant 17, 0 \leqslant k \leqslant 17, -24 \leqslant l \leqslant 25$	$-12 \leqslant h \leqslant 12, 0 \leqslant k \leqslant 30, 0 \leqslant l \leqslant 16$
Reflections collected	15,042	6607
Independent reflections	15,042 [R(int) = 0.0000]	6607 [R(int) = 0.0000]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	15,042/39/933	6607/19/298
Goodness-of-fit on F^2	0.997	0.992
Final R indices[a]	$R1 = 0.0535, wR2^b = 0.12259$ [10,663 $F_o > 4\sigma(F_o)$]	$R1 = 0.0914, wR2 = 0.2448$ [4347 $F_o > 4\sigma(F_o)$]
R indices (all data)	$R1 = 0.0838, wR2 = 0.1400$	$R1 = 0.1359, wR2 = 0.2735$
Largest diff. peak and hole ($e/Å^3$)	1.275 and -1.574	4.853 and -2.345

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{0.5}$.

many Pt-CO-dppm complexes. For example, the earlier synthesis of 2 X = Cl [7] was via the precursor $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3][CF_3CO_2]_2$, the synthesis of which was carried out from $[Pt(CF_3CO_2)_2(dppm)]$ and CO at 4 atmospheres pressure and 100°C over 71 h. In the present work, 2 X = Cl, is readily produced from the $K_2PtCl_4/dppm/CO/BH_4^-$ system, via the in situ production of the dinuclear Pt^0 compound 3, which precipitates as an intermediate. The chloride required in the formation of 2 is carried through from the K_2PtCl_4 or it can be abstracted from chlorinated solvents. For example, we find that 3 abstracts chloride from CH_2Cl_2 to form 2 X = Cl and in a related, vigorous, reaction with $C_2H_2Cl_4$, produces the known [18] compound $[Pt_2(Cl)(CO)(\mu\text{-dppm})_2]^+$ which was isolated after addition of $NaPF_6$ to the solution. Using K_2PtCl_6 as the starting salt, no precipitate of 3 appears, probably due to its fast reaction with the large excess of Cl^- present. The overall mechanism for the formation of 2 is probably similar to that already discussed [7,9] for the formation of trinuclear systems by other routes, although the syntheses described here are considerably more convenient. Reduction of 2 X = Cl with $CO/NaBH_4$ in acetone

produces 3. Note also that 3 reacts readily [16] with other sources of halide.

ORTEP views of the trimeric units of 1 and 2 X = Cl are shown in Figs 1 and 2, respectively, and the relevant bond lengths and angles are recorded in Table 2. The cations contain an approximately planar arrangement of an equilateral M_3 triangle and six P atoms from three μ_2-dppm ligands. On opposite sides of this plane is a symmetrically bonded μ_3-CO group and an asymmetrically oriented Cl atom.

The structures of the Pd complexes 1 X = Cl (reported here) and 1 X = CF_3COO [8] are very similar. They crystallize in the same space group ($\sim 3C_2H_5OH$ v one H_2O in the lattice), have the same Pd—Pd bond lengths and disorder at the capping ligands. The most frequent of the two positions of the CO in 1 X = Cl [(C(4)—O(1), present in 83% of the asymmetric units] is shown in Fig. 1, the second position being found on the opposite side of the Pd_3P_6 plane. Pd—C(4) distances are 2.153(9), 2.168(8) and 2.153(9) Å, with Pd(3) being the closest [2.10(2)–2.23(1) in 1 X = CF_3COO [8]]. Also in 1 X = Cl, the Pd—Cl(1) distances are 2.638(3), 2.875(3) and 3.001(3) Å compared to the maximum and minimum
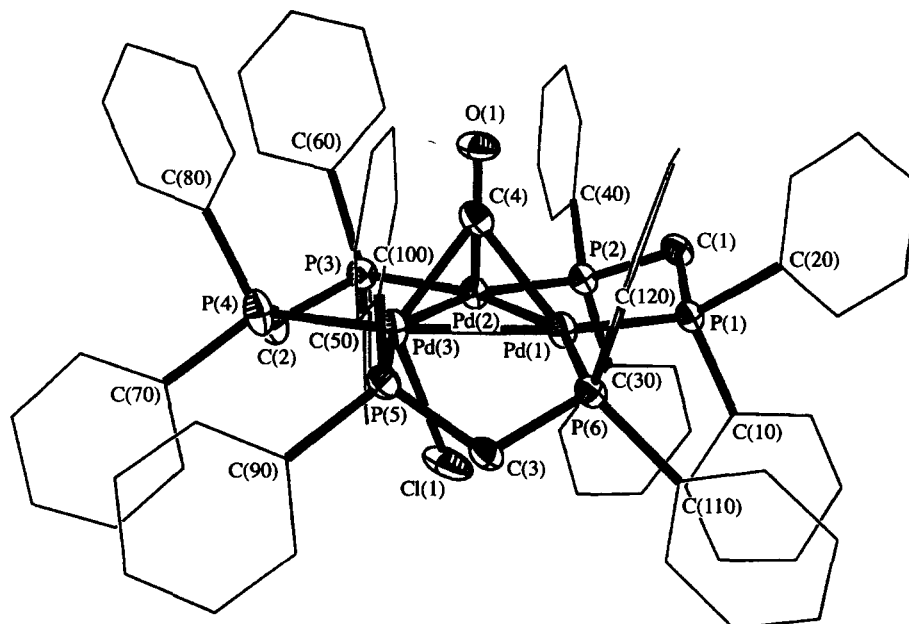
Fig. 1. ORTEP diagram of complex 1 X = Cl.

Fig. 2. ORTEP diagram of complex 2 X = Cl.
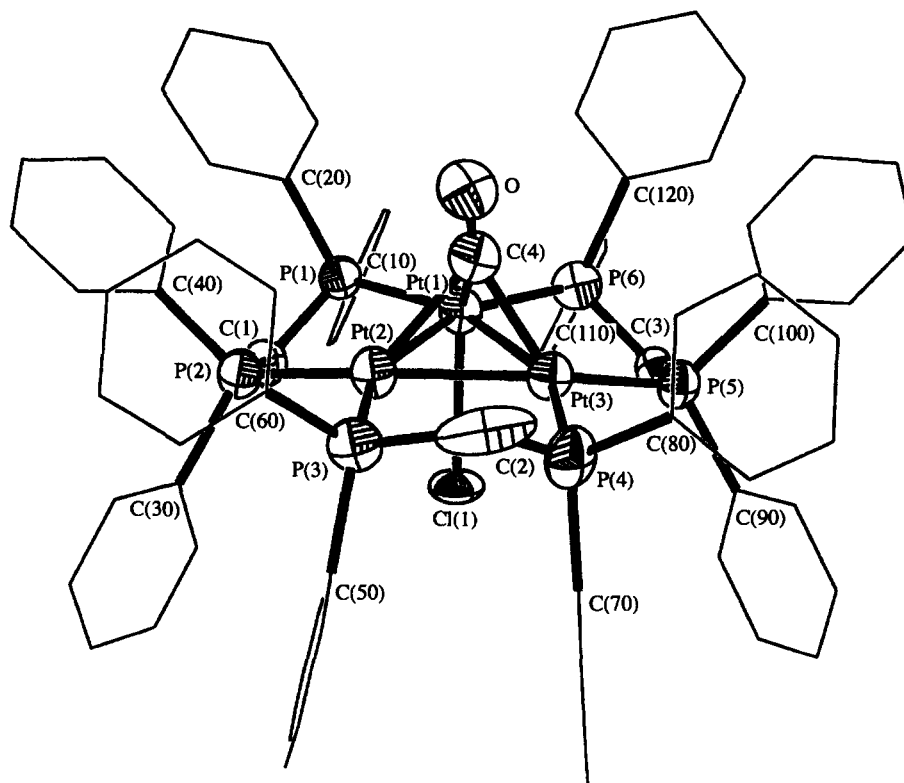
distances of 2.741(4)–3.161(4) for 1 X = CF$_3$COO. The most significant difference between the structures of 1 X = Cl and X = CF$_3$COO is that the capping CO is symmetrical in the chloride compound. Also, the

asymmetry of the Cl is less pronounced than in 1 X = CF$_3$COO.

The structure of 2 X = Cl has not been reported before. The rms deviation of the Pt$_3$P$_6$ atoms from

Table 2. Selected bond lengths (Å) and angles (°) for [Pd₃(Cl)(μ₃-CO)(μ₃-dppm₃]
Cl · 2.72C₂H₅OH (1) (top) and [Pt₃(Cl)(μ₃-CO)(μ-dppm)₃]Cl (2) (bottom)

Pd(1)—C(4)	2.188(8)		Pd(2)—P(3)	2.294(2)	
Pd(1)—P(1)	2.298(2)		Pd(2)—P(2)	2.299(2)	
Pd(1)—P(6)	2.306(2)		Pd(2)—Pd(3)	2.604(2)	
Pd(1)—Pd(2)	2.5611(9)		Pd(3)—C(4)	2.153(9)	
Pd(1)—Pd(3)	2.6025(13)		Pd(3)—P(5)	2.320(2)	
Pd(2)—C(4)	2.168(8)		Pd(3)—Pd(4)	2.329(2)	
			Pd(3)—Cl(1)	2.638(3)	
C(4)—Pd(1)—P(1)	114.8(2)		P(3)—Pd(2)—Pd(3)	96.20(5)	
C(4)—Pd(1)—P(6)	119.1(2)		P(2)—Pd(2)—Pd(3)	155.98(4)	
P(1)—Pd(1)—P(6)	108.05(6)		Pd(1)—Pd(2)—Pd(3)	60.50(3)	
C(4)—Pd(1)—Pd(2)	53.6(2)		C(4)—Pd(3)—P(5)	115.7(2)	
P(1)—Pd(1)—Pd(2)	94.89(5)		C(4)—Pd(3)—P(4)	113.2(2)	
P(6)—Pd(1)—Pd(2)	155.87(4)		P(5)—Pd(3)—P(4)	111.53(6)	
C(4)—Pd(1)—Pd(3)	52.6(2)		C(4)—Pd(3)—Pd(1)	53.8(2)	
P(1)—Pd(1)—Pd(3)	155.44(4)		P(5)—Pd(3)—Pd(1)	94.26(6)	
P(6)—Pd(1)—Pd(3)	96.24(6)		P(4)—Pd(3)—Pd(1)	154.07(5)	
Pd(2)—Pd(1)—Pd(3)	60.56(4)		C(4)—Pd(3)—Pd(2)	53.2(2)	
C(4)—Pd(2)—P(3)	114.2(2)		P(5)—Pd(3)—Pd(2)	152.96(4)	
C(4)—Pd(2)—P(2)	116.9(2)		P(4)—Pd(3)—Pd(2)	95.15(5)	
P(3)—Pd(2)—P(2)	107.60(6)		Pd(1)—Pd(3)—Pd(2)	58.93(3)	
C(4)—Pd(2)—Pd(1)	54.3(2)		C(4)—Pd(3)—Cl(1)	111.6(2)	
P(3)—Pd(2)—Pd(1)	156.66(4)		P(5)—Pd(3)—Cl(1)	102.88(7)	
P(2)—Pd(2)—Pd(1)	95.59(5)		P(4)—Pd(3)—Cl(1)	100.49(8)	
C(4)—Pd(2)—Pd(3)	52.7(2)		Pd(1)—Pd(3)—Cl(1)	69.88(6)	
			Pd(2)—Pd(3)—Cl(1)	66.52(6)	
Pt(1)—C(4)	2.00(4)		Pt(2)—C(4)	2.26(5)	
Pt(1)—P(6)	2.276(13)		Pt(2)—P(2)	2.283(13)	
Pt(1)—P(1)	2.301(12)		Pt(2)—P(3)	2.300(12)	
Pt(1)—Pt(2)	2.612(2)		Pt(2)—Pt(3)	2.619(2)	
Pt(1)—Pt(3)	2.620(2)		Pt(3)—C(4)	2.08(5)	
Pt(1)—Cl(1)	2.785(8)		Pt(3)—P(4)	2.273(13)	
			Pt(3)—P(5)	2.282(12)	
C(4)—Pt(1)—P(6)	111(2)		P(2)—Pt(2)—P(3)	107.7(5)	
C(4)—Pt(1)—P(1)	118(2)		C(4)—Pt(2)—Pt(1)	47.8(10)	
P(6)—Pt(1)—P(1)	111.2(4)		P(2)—Pt(2)—Pt(1)	95.9(3)	
C(4)—Pt(1)—Pt(2)	56.8(14)		P(3)—Pt(2)—Pt(1)	155.7(3)	
P(6)—Pt(1)—Pt(2)	154.5(4)		C(4)—Pt(2)—Pt(3)	49.8(13)	
P(1)—Pt(1)—Pt(2)	94.0(3)		P(2)—Pt(2)—Pt(3)	153.2(4)	
C(4)—Pt(1)—Pt(3)	51.4(13)		P(3)—Pt(2)—Pt(3)	95.5(3)	
P(6)—Pt(1)—Pt(3)	94.6(3)		Pt(1)—Pt(2)—Pt(3)	60.12(7)	
P(1)—Pt(1)—Pt(3)	154.0(3)		C(4)—Pt(3)—P(4)	122.7(12)	
Pt(2)—Pt(1)—Pt(3)	60.06(6)		C(4)—Pt(3)—P(5)	119(2)	
C(4)—Pt(1)—Cl(1)	125.5(11)		P(4)—Pt(3)—P(5)	107.4(5)	
P(6)—Pt(1)—Cl(1)	93.8(6)		C(4)—Pt(3)—Pt(2)	56(2)	
P(1)—Pt(1)—Cl(1)	95.0(5)		P(4)—Pt(3)—Pt(2)	95.5(4)	
Pt(2)—Pt(1)—Cl(1)	79.9(3)		P(5)—Pt(3)—Pt(2)	152.2(3)	
Pt(3)—Pt(1)—Cl(1)	80.0(3)		C(4)—Pt(3)—Pt(1)	48.8(11)	
C(4)—Pt(2)—P(2)	124.0(13)		P(4)—Pt(3)—Pt(1)	155.0(4)	
C(4)—Pt(2)—P(3)	118.1(11)		P(5)—Pt(3)—Pt(1)	95.5(3)	
			Pt(2)—Pt(3)—Pt(1)	59.82(7)	

their least squares best plane is 0.199 Å, the maximum deviation being 0.379(0.015) Å for P(2). Two methylene C atoms, C(1) and (3), of dppm are almost 1 Å to one side of this plane, with the third being a similar amount on the other side (the CO side). The latter dppm has an almost eclipsed conformation for the P atoms of P(3)—Pt(2)—Pt(3)—P(4) [torsion angle 4(1)°]. The P atoms of the other two dppm ligands (on the Cl side) deviate significantly from an eclipsed conformation [P(1)—Pt(1)—Pt(2)—P(2), torsion angle at 10.9(8)° and P(6)—Pt(1)—Pt(3)—P(5), torsion angle −10.7(7)°], probably as a result of steric

interactions between the phenyl rings on the adjacent P atoms, P(1) and (6). (In **1** X = Cl, all Pd—P bonds in each of the three dppm ligands are approximately eclipsed, with torsion angles ranging from 0.57(7) to 3.28(6)°.)

In **2** X = Cl, the μ_3-CO and Cl are closer to Pt(1) than to the other Pt atoms. Pt—C distances are 2.01(4), 2.26(5) and 2.08(5) Å for Pt(1), (2) and (3) respectively. The distance of the chloride, Cl(1), from Pt(1) is 2.785(8), while Pt(2) and (3) are 3.469(8) and 3.476(8) Å respectively from Cl(1). Interaction between Pt(1) and Cl(1) is therefore very weak (the distance is almost 0.5 Å longer than sum of the covalent radii) and clearly there is no bonding between Cl(1) and the other two Pt atoms. In fact **2** might best be described as a $[Pt_3(\mu_3\text{-CO})(\mu_2\text{-dppm})]^{2+}$ cation interacting very weakly (ionically) with Cl$^-$.

In fact, the structure of **2** X = Cl is quite similar to structures containing the $[Pt_3(\mu_3\text{-CO})(L)(\mu\text{-dppm})_3]^{1\text{or}2+}$ unit, where L = CN [12b], SCN [24a] or P(OR)$_3$ [24b], all of which have major asymmetry in the positions of CO and, especially, L.

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