Bis(carboxylato) complexes of platinum(II). Structural and bonding analysis of $[Pt(O_2CR)_2(L-L)] [L-L = 2PPh_3, Ph_2PCH_2PPh_2 \text{ or } Fe(C_5H_4PPh_2)_2; R = Me, CF_3, Pr^i \text{ or } Ph]^{\dagger}$

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Treatment of $[PtCl_2(L-L)] [L-L = 2 PPh_3, Ph_2PCH_2PPh_2(dppm) or Fe(C_5H_4PPh_2)_2(dppf)]$ with Ag(O₂CR) (R = Me, CF₃, Prⁱ or Ph) at room temperature generally gave $[Pt(O_2CR)_2(L-L)]$ in moderate to good yields. The crystal and molecular structures of $[Pt(O_2CMe)_2(dppf)]$ ·H₂O, $[Pt(O_2CPh)_2(dppf)]$ ·CH₂Cl₂ and $[Pt(O_2CCF_3)_2(dppm)]$ have been determined by single-crystal X-ray diffractometry. All these complexes show a mononuclear square-planar structure with a chelating diphosphine and two neighbouring (*cis*) carboxylates in a monodentate mode. These structures contrast those of the parent $[Pt_4(\mu-O_2CMe)_8]$ and its derivative $[Pt_4(en)_4(\mu-O_2CMe)_4]^{4+}$ (en = ethylenediamine) which are tetrameric, based on octahedral Pt^{II}, and contain bridging acetates and direct Pt–Pt bondis interactions. The presence of hard and electronegative ligands like en and acetate incurs a deficiency in σ -electron density, compared to virtually filled non-bonding orbitals; the former is alleviated by Pt–Pt bonding. d⁸ Complexes with ligands like phosphines possessing both σ -donating and π -accepting qualities appear to favour the usual square-planar geometry.

In complexes, carboxylates most commonly adopt a bridging mode.¹ Chelating and monodentate carboxylates are also well known, although many of the latter type are susceptible to chelation² or bridge formation because of the proximity effect and/or high basicity of the pendant oxygen. Complexes with two or more carboxylates can display different bonding modes. However, it is very rare for complexes of neighbouring monodentate carboxylates, *viz. cis*-[M(O₂CR)₂L_n], to be isolated as they are easily converted into bridging, chelating and even dissociated forms. One notable exception is [Pt(O₂CR)₂(PPh₃)₂] (R = Me³ or CF₃⁴) which are stable and have been prepared by oxidation of [Pt(PPh₃)₄]. Although the solid-state structures of these complexes have not been crystallographically identified, there seems no doubt that these species are rare examples of complexes with two monodentate carboxylates.

Two recent reports from Jutand and co-workers⁵ attracted our attention. They described a spontaneous and quantitative self-reduction of $[Pd(O_2CMe)_2(PPh_3)_2]$ at room temperature (r.t.) to give $[Pd(PPh_3)]$, OPPh₃ and $(MeCO)_2O$. Their findings appeared to substantiate (or contradict?) the earlier reports which described the palladium(II) carboxylates as 'stable indefinitely in air' but 'dissociate and decompose readily in warm solvents'.⁶ Jutand's reports not only provide a justification for the established usage of $[Pd(O_2CMe)_2(PPh_3)_2]$ as a source of $[Pd^0(PPh_3)_n]$ (without any added reducing agent) in many C–C coupling reactions,⁷ especially Heck's reactions,⁸ they could explain why complexes with neighbouring monodentate carboxylates are rare, and the considerable difficulties we experienced recently in preparing some related palladium(II) phosphine carboxylates.⁹ Since it is difficult to isolate and structurally characterize these palladium(II) complexes, we decided to carry out a series of X-ray crystallographic work on the established platinum(II) analogues, which model these highly catalytically active palladium(II) species.

There is some confusion in the literature regarding the structures of these complexes: $[Pd(O_2CR)_2(PR_1)_2]$ is generally accepted to be mononuclear with both carboxylates in a monodentate mode while $[{Pd(O_2CR)_2(PR_3)}_2]^{10}$ is dinuclear with bridging and monodentate carboxylates. The former was earlier reported to be a trans complex ⁶ but more recent reports appeared to suggest a cis configuration.¹¹ Both cis and trans products appear to be isolated from the same reaction.¹² Jutand's reports also assumed a trans geometry. The complex $[Pt(O_2CMe)_2(PPh_3)_2]^{13}$ is reported to be 'probably *cis*'¹⁴ but the CF₃CO₂ analogue is, strangely, reported to be trans.¹⁵ Adding further to this confusion, the structure of the parent [Pt(O₂CMe)₂] was found to be tetranuclear with bridging acetates.¹⁶ It is hence best represented as $[Pt_4(\mu-O_2CMe)_8]$. The octahedral geometry about d8-Ptⁿ with Pt-Pt bonds is surprising and, to our knowledge, unexplained. More recently, its ethylenediamine (en) derivative $[Pt_4(en)_4(\mu-O_2CMe)_4]^{4+1}$ was also found to have a similar structure with Pt-Pt bonds and bridging acetates.17 The assumption that complexes $[Pt(O_2CR)_2(L-L)]$ (L-L = bidentate neutral ligand) are mononuclear with chelating L-L and monodentate carboxylate therefore needs verification. In this paper, we describe the structural and bonding properties of such complexes and compare them with the unusual acetate structures in the literature through X-ray crystallography and Fenske-Hall molecular orbital calculations.

Another objective of this work is to examine if the use of a diphosphine [e.g. bis(diphenylphosphino)methane (dppm)] would give isostructural products. In other words, would a diphosphine adopt a bridging mode and hence force changes in the carboxylate bonding mode. It is also uncertain whether two

[†] Supplemetary data available 1 (No.SUP 57136, 9 pp.): tables of platinum orbital coefficients and overlap populations matrices. Non-SI unit employed: $eV \approx 1.60 \times 10^{-19}$ J.



 $R = Me, CF_3, Pr^i$ or Ph

diphosphines having very different bites such as dppm and dppf would give isostructural products. The importance of this study is traced to the first report which described a significantly higher activity in Grignard coupling when $[PdCl_2(dppf)]$ [dppf = 1,1'-bis(diphenylphosphino)ferrocene] was used as the catalyst compared to its PPh₃ counterpart.¹⁸ Since then, there have been many reports on the advantages associated with the use of dppf in catalytic mixtures.¹⁹ Recent work on Cu¹²⁰ and Ag¹²¹ has suggested a variety of phosphine and carboxylate coordination modes which are hard to predict based on solution data.

Results and Discussion

To our knowledge, the only reported dppf or dppm complex of platinum(II) carboxylates [Pt(O₂CCF₃)₂(dppm)].²² For PPh₃, three complexes viz. $[Pt(O_2CR)_2(PPh_3)_2]$ (R = Me, CF₃ or Ph)²³ have been prepared from $[Pt(PPh_3)_n]$ (n = 3 or 4). Treatment of $[PtCl_2(L-L)]$ (L-L = 2 PPh₃, dppm, or dppf with $Ag(O_2CR)$ (R = Me, CF₃, Prⁱ or Ph) at r.t. generally gave [Pt(O₂CR)₂(L-L)] in moderate to good yields. Similar preparations using metathesis have been reported.²⁴ We preferred this to the more established method which uses Pt⁰(L-L)₂ as the precursor because of the inconvenience of going through an air-sensitive platinum(0) species, especially the likes of $[Pt_2(dppm)_3]^{25}$ and $[Pt(dppf)_2]^{26}$ This method is also more direct compared to the use of [Pt(CO₃)(PPh₃)₂] (with MeCO₂H) as precursor. An early attempt at synthesis of phosphine carboxylate complexes from $[Pt(O_2CMe)_2]$ appeared to be unsuccessful.⁶ All the present complexes were characterized by IR and ¹H and ³¹P NMR spectroscopy. The large separation ($\delta v \approx 250 \text{ cm}^{-1}$) between the v_{asym} and v_{sym} bands is usually a diagnostic feature of a carboxylate ligand in a monodentate mode.¹² The complexes synthesized generally show this feature. Although the co-ordination mode of dppf cannot be ascertained from the NMR data, the ³¹P shifts of the present series of carboxylates for each particular phosphine generally lie within a narrow window of ca. 2 ppm. This is indicative of the isostructural nature of the complexes in solution. The large high-field shift of $\delta(P)$ in the dppm complexes is diagnostic of chelating dppm.²⁴

In order to establish the structures and bonding properties of these complexes in the solid state we have carried out singlecrystal X-ray crystallographic analysis of three representatives, *viz.* [Pt(O₂CMe)₂(dppf)] (Fig. 1), [Pt(O₂CPh)₂(dppf)] (Fig. 2) and [Pt(O₂CCF₃)₂(η^2 -dppm)] (Fig. 3).* All three complexes show a square-planar Pt^{II} with two carboxylates *cis* to each other. Selected bond lengths and angles are listed in Table 1.



Fig. 1 An ORTEP²⁷ plot of the molecular structure of $[Pt(O_2CMe)_2(dppf)]$ -H₂O with ellipsoids drawn at the 35% probability level (hydrogen atoms omitted for clarity)



Fig. 2 An ORTEP plot of the molecular diagram of $[Pt(O_2CPh)_2(dppf)]$ -CH₂Cl₂ with ellipsoids drawn at the 35% probability level (solvate removed for clarity)



Fig. 3 An ORTEP plot of the molecular diagram of $[Pt(O_2C-CF_3)_2(dppm)]$ with ellipsoids drawn at the 35% probability level

^{*} Unless otherwise stated, the carboxylate in $[Pt(O_2CR)_2(L-L)]$ is monodentate whilst the phosphine is P,P' bonded.

$(a) [Pt(O_2CMe)_2(d$	lppf)]•H₂O						
Pt-P(1) Pt-O(1)	2.242(1) 2.079(3)	Pt-P(2) Pt-O(3)	2.259(1) 2.073(3)	P(2)-C(34) C(35)-O(2)	1.831(4) 1.221(6)	C(35)–O(1) C(35)–C(36)	1.298(5) 1.502(7)
Fe-C(1-5)	2.039(4)(mean)	Fe-C(6-10)	2.036(4)(mean)	C(37) - O(3)	1.286(5)	C(37)–O(4)	1.210(5)
P(1) - C(1)	1.788(4)	P(1) - C(16)	1.836(4)	C(37)-C(38)	1.515(6)	$O(1w) \cdots O(2a)$	2.916(6)
P(1)-C(22)	1.820(4)	P(2)-C(28)	1.827(4)	$O(1w) \cdots O(4)$	2.836(6)		
P(1)-Pt-P(2)	97.9(1)	P(1)-Pt-O(1)	175.8(1)	Pt-O(3)-C(37)	116.4(2)	O(3)-C(37)-O(4)	124.5(4)
P(2)-Pt-O(1)	86.3(1)	P(1)-Pt-O(3)	89.7(1)	O(3)-C(37)-C(38)	112.5(4)	O(4)-C(37)-C(38)	123.0(4)
P(2) - Pt - (3)	171.9(1)	O(1)-Pt- $O(3)$	86.1(1)	C(1)-P(1)-C(16)	102.8(2)	C(1)-P(1)-C(22)	109.2(2)
Pt-P(1)-C(1)	114.5(1)	Pt-P(1)-C(16)	115.5(1)	C(16)-P(1)-C(22)	101.2(2)	C(6)-P(2)-C(28)	101.9(2)
Pt-P(1)-C(22)	112.4(1)	Pt-P(2)-C(6)	122.3(1)	C(6)-P(2)-C(34)	100.9(2)	C(28)-P(2)-C(34)	107.2(2)
Pt-P(2)-C(28)	116.4(1)	Pt-P(2)-C(34)	106.3(1)	P(1)-C(1)-C(2)	131.0(3)	P(1)-C(1)-C(5)	122.0(3)
Pt-O(1)-C(35)	119.7(3)	O(1)-C(35)-O(2)	124.2(4)	P(2)-C(6)-C(7)	128.2(3)	P(2)-C(6)-C(10)	126.3(3)
O(1)-C(35)-C(36)	114.2(4)	O(2)-C(35)-C(36)	121.6(4)	$O(4) \cdots O(1w) \cdots O(2a)$	138.6(5)		
(b) $[Pt(O_2CPh)_2(d)]$	ppf)]•CH ₂ Cl ₂						
Pt-P(1)	2.219(3)	Pt-P(2)	2.262(3)	P(2)-C(28)	1.79(1)	P(2)-C(34)	1.756(8)
Pt-O(1)	2.034(6)	Pt-O(3)	2.089(6)	C(35) = O(1)	1.28(1)	C(35)-O(2)	1.23(1)
Fe - C(1 - 5)	2.04(1)(mean)	Fe-C(6-10)	2.05(1)(mean)	C(42) - O(3)	1.28(1)	C(42) - O(4)	1.24(1)
P(1)-C(1)	1.802(9)	P(1)-C(16)	1.850(9)	C(35) - C(41)	1.518(9)	C(42) - C(48)	1.46(1)
P(1)-C(22)	1.807(8)	P(2)–C(6)	1.844(7)	C(49) - Cl(1)	1.71(1)	C(49)-Cl(2)	1.694(9)
P(1) - Pt - P(2)	98.1(1)	P(1)-Pt-O(1)	173.8(2)	O(1)-C(35)-O(2)	127.0(7)	O(1)-C(35)-C(41)	113.2(7)
P(1) - Pt - O(3)	90.6(2)	P(2) - Pt - O(1)	86.4(2)	O(2) - C(35) - C(41)	119.9(7)	C(35)-C(41)-C(36)	119.1(7)
P(2)-Pt-O(3)	171.3(2)	O(1) - Pt - O(3)	84.9(2)	C(35) - C(41) - C(40)	120.3(7)	O(3)-C(42)-O(4)	123.5(8)
Pt-P(1)-C(1)	113.4(3)	Pt-P(1)-C(16)	113.2(2)	O(3) - C(42) - C(48)	115.2(7)	O(4)-C(42)-C(48)	121.2(9)
Pt-P(1)-C(22)	115.4(3)	Pt-P(2)-C(6)	122.8(4)	C(1) - P(1) - C(16)	105.1(4)	C(1) - P(1) - C(22)	106.2(3)
Pt-P(2)-C(28)	113.8(3)	Pt-P(2)-C(34)	108.5(3)	C(16) - P(1) - C(22)	102.4(4)	C(6)-P(2)-C(28)	103.7(4)
Pt-O(1)-C(35)	123.9(5)	Pt-O(3)-C(42)	120.2(5)	C(6) - P(2) - C(34)	101.2(4)	C(28) - P(2) - C(34)	104.8(5)
P(1)-C(1)-C(2)	130.8(7)	P(1)-C(1)-C(5)	120.9(5)			. , . , . ,	
(c) [Pt(O ₂ CCF ₃) ₂ (dppm)]						
Pt P(1)	1 111(1)	$\mathbf{P}_{t} - \mathbf{P}(2)$	2 211(2)	C(4) = O(3)	1.260(9)	C(A) = O(A)	1 101(9)
Pt=O(1)	2.222(2)	Pt=O(3)	2.211(2) 2.074(4)	C(4) = C(5)	1.509(8)	C(5) = F(4-6)	1.191(9) 1.34(1)(mean)
C(1) P(1)	1.822(6)	C(1) P(2)	1.874(6)	P(1) = C(11)	1.303(6)	P(1) = C(17)	1.34(1)(mean)
C(1) = I(1) C(2) = O(1)	1.022(0)	$C(1) - \Gamma(2)$ C(2) - O(2)	1.07-(0)	P(2) = C(23)	1.813(6)	P(2) = C(20)	1.791(7)
C(2)=O(1) C(2)=C(3)	1.237(8)	C(2) = O(2) C(3) = F(1-3)	1.195(9) 1.352(9)(mean)	(2) = C(23)	1.815(0)	$\Gamma(2) = C(23)$	1.810(0)
			100.000			5 50 60	
P(1) - P(2)	74.1(1)	P(1) - Pt - O(1)	100.0(1)	C(4) - C(5) - F(4-6)	110.9(6)(mean)	Pt-P(1)-C(1)	95.3(2)
P(1) - Pt - O(3)	174.2(1)	P(2) - Pt - O(1)	171.4(1)	Pt-P(1)-C(11)	115.5(2)	Pt-P(1)-C(17)	119.8(2)
P(2) - Pt - O(3)	102.9(1)	O(1) - Pt - O(3)	82.4(2)	Pt-P(2)-C(1)	94.2(2)	Pt-P(2)-C(23)	119.8(2)
P(1)-C(1)-P(2)	92.6(3)	Pt-O(1)-C(2)	122.0(4)	Pt-P(2)-C(29)	117.1(2)	C(1)-P(1)-C(11)	110.1(3)
Pt-O(3)-C(4)	127.3(4)	O(1)-C(2)-O(2)	129.4(7)	C(1) - P(1) - C(17)	108.4(3)	C(11)-P(1)-C(17)	106.8(3)
O(1)-C(2)-C(3)	112.6(6)	O(2)-C(2)-C(3)	118.0(6)	C(1) - P(2) - C(23)	105.5(3)	C(1)-P(2)-C(29)	108.6(3)
O(3)-C(4)-O(4)	129.5(6)	O(3)-C(4)-C(5)	113.8(6)	C(23)-P(2)-C(29)	109.3(3)		
O(4)–C(4)–C(5)	116.7(6)	C(2)-C(3)-F(1-3)	112.1(6)(mean)			

For four-co-ordinate Pt^{II} a chelating phosphine would necessarily force the carboxylates to adopt a monodentate mode. The pendant oxygens are approximately anti to each other to avoid non-bonding interactions. These oxygens in the acetate complex are, however, hydrogen bonded to a lattice hydrate. A constitutional isomer of this complex [Pt-{C(O)OMe}₂(dppf)] with a methoxycarbonyl group, has recently been structurally characterized.²⁸ Its structure is similar to that of the acetate complex, except that the Pt-P bonds are significantly weaker [2.310(5) and 2.331(5) Å in the methoxycarbonyl complex] which is indicative of the stronger trans influence of the C-bonded methoxycarbonyl ligand compared to the O-bonded acetate. Surprisingly, the carboxylates converge at a larger angle (O-Pt-O) for the smaller acetate [86.1(1)°] than benzoate [84.9(2)°]. This is probably reflective of a slight expansion of the acetates in order to accommodate the hydrate. The minimum influence of the carboxylates exerted on the co-ordination angles at the Pt is also reflected in the near-identical chelate angles of dppf in both complexes [97.9(1) and 98.1(1)°]. The chelate angles are typical among the chelating dppf complexes of PtII.29 Although it is in general difficult to predict the ferrocenyl ring conformation of dppf in its complexes, we have recently pointed out that a gauche (staggered) conformation between the two C_5 rings is the commonest trend for square-planar complexes such as those of Pt^{II} and Pd^{II}.³⁰ The torsional angles τ^* found in the acetate (32.4°) and benzoate (31.6°) complexes are also in agreement with the literature trend. This emphasizes that conformations close to the ideal *gauche* form (τ 36°) are found for planar complexes of Pt^{II}.

The benzoate complex is in general more distorted compared to the acetate and trifluoroacetate complexes. This is best seen by comparing the differences in the Pt-P and Pt-O bonds in the two complexes (Table 1). While the Pt-P bonds in the acetate $[\delta(Pt-P) 0.017(1) \text{ Å}]$ and those of the trifluoroacetate [0.011(2)]Å] complexes are similar and the Pt–O [0.006(3) and 0.006(4) Å] virtually identical, the corresponding bonds in the benzoate complex [δ (Pt-P) 0.043(3) and (Pt-O) 0.055(6) Å] are clearly different from each other. The deviations of the co-ordinating atoms from the platinum planes are also more obvious in the benzoate complex. -0.027 to +0.026 Å for the acetate but significantly greater, -0.035 to +0.051 Å, in the benzoate complex. The deviations of the phosphorus atoms from the C₅ planes are also larger for the benzoate (0.097, 0.169 Å) compared to the acetate (0.017, 0.079 Å) complex. These probably originate from the higher interligand repulsions in the benzoate complex.

^{*} Defined as P(1)-X(1)-X(2)-P(2) where X(1) and X(2) are the centroids of the C₅ rings C(1)-C(5) and C(6)-C(10) respectively.





Although trifluoroacetate is known to be a weaker ligand compared to acetate, the Pt–O bonds in $[Pt(O_2CCF_3)_2(dppm)]$ [mean 2.077(4) Å] and $[Pt(O_2CMe)_2(dppf)]$ [mean 2.076(3) Å] are identical. The C–O bonds of the former [mean C–O 1.259(8), C=O 1.193(9) Å] however, are significantly stronger than those in the latter [1.292(5) and 1.216(6) Å].

An obvious contrast between the dppm and dppf structures is the bite angle (P-Pt-P) differences of the phosphines [74.1(1)° in the dppm complex and 97.9(1) and 98.1(1)° in the dppf complexes]. The acute bite angle of dppm falls short of the ideal 90° favoured by Pt^{II}. The strain imposed on a four-membered dppm chelate is also reflected in the internal angle at phosphorus [mean C-P-Pt 94.8(2)°] which is substantially less than 109°. A natural question follows: why doesn't dppm open up and convert from a chelating mode into its favoured bridging mode, and as a result the carboxylate could also take up its most favoured bridging position? This ligand rearrangement would result in either a dimeric, I or II, or tetrameric (III) structure. Note that, in these structures, half of the carboxylates are dissociated, which is well known especially for the weakly co-ordinating CF₃CO₂⁻. Alternatively, all the carboxylates can stay on the metal core as monodentate ligands. Structure III would resemble that of $[Pt_4(\mu-O_2CMe)_8]$ and $[Pt_4(en)_4(\mu-O_2CMe)_4]^{4+}$ in that the in-plane ligands (O_2CMe or en) are replaced by dppm. This possibility will be addressed below in a molecular orbital (MO) study.

To summarize, the geometric differences of the dppm and dppf chelate rings, although significant, are not sufficiently large to impart any structural changes on these complexes. It is therefore reasonable to conclude that all these platinum complexes, of all the monophosphines and diphosphines examined and regardless of the carboxylates used, are mononuclear in structure with the carboxylates in a monodentate state.

In an attempt to explain why the complexes opt for a mononuclear structure with monodentate acetate while the parent $[Pt(O_2CMe)_2]$ and its derivative $[Pt_4(en)_4(\mu-O_2CMe)_4]^{4+}$ adopt a tetranuclear framework *i.e.* $[Pt_4(\mu-O_2CMe)_8]$ based on an unusual octahedral geometry for Pt^{II} with bridging acetates (and chelating en) and Pt–Pt bonds, we have carried out a series of MO calculations using the Fenske–Hall method. For $[Pt_4(\mu-O_2CMe)_8]$ the molecule is aligned such that the Pt₄ core is approximately in the *xy* plane, and the Pt–Pt bonds are approximately parallel to either the *x* or *y* axis.

The distorted pseudo-octahedral co-ordination of the platinum atoms implies that their d orbitals are roughly split into 't_{2g}' (d_{xy}, d_{xz} and d_{yz}) and 'e_g' (d_{x²-y²} and d_{z²}) sets. The character of the molecular orbitals reveals a significant amount of mixing among the 't_{2g}' orbitals, which also mix a little with the 'e_g' orbitals, possibly to avoid net antibonding Pt–Pt π interactions between filled orbitals. Nevertheless, the calculated electronic populations of the atomic orbitals suggest that the



Fig. 4 Schematic representation of the four molecular orbitals describing Pt-Pt interactions in $[Pt_4(\mu-O_2CMe)_8]$ and the orbital energies

 t_{2g} orbitals are completely filled (Table 2), accounting for six electrons per Pt atom; there are thus two electrons per Pt left. Since the bonds in the z-direction are stronger (*i.e.* the Pt–O distances are shorter), the $d_{x^2-y^2}$ orbitals are pushed higher in energy relative to the $d_{x^2-y^2}$ orbitals. Note that the latter are directed at neighbouring Pt atoms.

There are four molecular orbitals that describe Pt-Pt bonding. Three involve the $d_{x^2-y^2}$ orbitals, while in the fourth, contributions to bonding arise from d_{z^2} (the $x^2 + y^2$ component), d_{xy} (through π -bonding), s, p_x and p_y^* (Fig. 4). Note that two of the $d_{x^2-y^2}$ combinations also include some d_{xy} , s, p_x and p_y contributions, so as to minimize Pt-Pt σ antibonding interactions. One of the $d_{x^2-y^2}$ combinations (which is completely Pt-Pt antibonding) is unoccupied. The Pt-Pt overlap populations are 0.237, 0.234, 0.233 and 0.239, suggesting significant metal-metal bonding character.

Dividing the eight bonding electrons among the four 'bonds', each bond can formally be assigned two electrons. Thus, each Pt atom 'receives' four electrons as a result of metal-metal

^{*} In the fourth orbital, there is some d_{xz} contribution which does not appear to serve any purpose other than the t_{2g} mixing mentioned earlier. The designation of this fourth MO as Pt-Pt bonding could be a subject of some controversy. However, we think it is justified, in view of the sizeable Pt-Pt overlap populations involving d_{z^2} , s and p orbitals. In support of this argument, the breakdown of contributions to the Pt(1)-Pt(2) overlap populations is given as SUP 57136. This bond is parallel to the x axis.

Table 2 Mulliken populations of atomic orbitals on one Pt atom in $[Pt_4(\mu-O_2CMe)_8]$

Orbital	Population	Orbital	Population
d _z ²	1.043	s	0.530
$d_{x^2-y^2}$	1.248	p_x	0.290
d_{xy} d_{xz}	1.985	p_y p_z	0.228
d _{yz}	1.966		

bonding. Adding the eight electrons per Pt from the acetate ligands, each Pt can be assigned 18 electrons.

Focus is next placed on the square-planar geometry of the present complexes. It is generally acknowledged that this planar co-ordination geometry is favoured for d^8 metal complexes, resulting in a total of 16 electrons at the metal centre. While the present complexes $[Pt_4(\mu-O_2CMe)_8]$ and $[Pt_4(en)_4(\mu-O_2CMe)_4]^{4+}$ all possess Pt^{II} and carboxylate ligands, the last two are octahedral, have 18 electrons per Pt atom and Pt–Pt bonds. The question is, why is this so? {especially since the pendant oxygen atoms in $[Pt(O_2CMe)_2(L-L)]$ are nucleophilic, *i.e.* their lone-pair orbitals constitute the two highest-occupied MOs}. To paraphrase the question, what is different when phosphine ligands are introduced?

First, it is important to realize that nitrogen and oxygen donors are more electronegative and less polarizable, hence comparatively little σ -electron density is transferred to Pt. This is especially true for carboxylate ligands, where the formal negative charge causes the platinum orbital energies to increase, thus reducing their capacity to accept electron density. A corollary of this effect is that the electronic population of the platinum orbitals involved in σ -bonding is relatively low, and Pt becomes quite positively charged (Table 3). In contrast, phosphines donate a substantial amount of σ -electron density.

A second important factor is the ability of phosphine to accept electron density from Pt into its empty d orbitals; acetate and en (which do not have valence d orbitals) completely lack this capability. Owing to such π -bonding, the population of the filled 'non-bonding' platinum d orbitals decreases significantly. Such a decrease is not observed with nitrogen and oxygen donors (Table 4).

In the case of $[Pt_4(\mu-O_2CMe)_8]$ and its en derivative, formation of the tetrameric structure alleviates the problem of high positive charge and low σ -electron density. It can be observed from Tables 3 and 4 that in the en complex the charge on Pt decreases significantly and the σ -electron density (in the $d_{x^2-y^2}$, d_{z^2} , s and p orbitals) increases on forming the tetramer.* Reference can also be made to the 18-electron rule, which is based on the ideal of 'spherical' distribution of electron density about the metal centre: formation of the tetramers with concomitant increase in σ -electron density reduces the disparity between the populations of the platinum σ and non-bonding orbitals (as mentioned above, the occupancy of the latter is high because of lack of π back donation).

Another possible electronic factor is that the propensity of phosphine to π bond probably militates against the mixing that was found to stabilize the octahedral environment and Pt–Pt bonding in $[Pt_4(\mu-O_2CMe)_8]$. It should also be noted that phosphine ligands are bulky, and there may be steric problems in incorporating them into a structure like that of the en compound.

As to the question of why platinum(II) acetate does not form a dimeric structure like Rh^{II} in $[Rh_2(O_2CMe)_4]$, the difference

 Table 3
 Calculated Mulliken charges on Pt^{II} in various acetate complexes

Charge
+0.328
+0.217
+0.267
+0.513
+0.591
+0.806
+0.310
+0.470

^{*a*} Square planar; 'cut-and-paste' from $[Pt(O_2CMe)_2(dppf)]$ and tetramer. ^{*b*} Based on structure of tetramer.¹⁷ ^{*c*} Based on structure of $[Pt(O_2CMe)_2(dppf)]$ (this work).

Table 4 Electronic populations of platinum orbitals in $[Pt(O_2C-Me)_2(dppf)]$, square-planar $[Pt(O_2CMe)_2(en)]$ and $[Pt_4(en)_4(\mu-O_2CMe)_4]^{4+}$

	Populatio	Population			
Orbital	dppf complex	en complex	Tetrameric complex ^a		
d2	1.863	1.873	1.236		
$d_{x^2-x^2}$	1.154	0.810	1.300		
d _{xx}	1.698	1.983	1.986		
d.,,	1.823	1.996	1.742*		
d _{v2}	1.835	1.996	1.983		
s	0.601	0.485	0.548		
p _x	0.361	0.185	0.322		
p _v	0.360	0.185	0.325		
p _z	-0.024	-0.024	0.249		

lies in the d^7 state for Rh^{II} and for d^8 for Pt^{II}: the metal orbitals that are directed at each other d_{z^2} if the metal-oxygen bonds are parallel to the xy plane) are half filled for Rh^{II} but completely filled for Pt^{II}. Platinum is probably too large to tolerate the net repulsive interaction between two filled orbitals. Another possible dimeric structure involves two bridging and two chelating acetates, with no Pt-Pt bonds. Such a structure is probably unstable, first because of the above-mentioned problem with the platinum atomic charge and orbital occupancy, and secondly since the lone pairs on oxygen occupy 'sp²' orbitals in the same plane as that of the carboxylate group the orientation of the lone pairs on acetate incurs inefficient overlap (Fig. 5).

As a model of what might happen if Pt is replaced by Pd, calculations were also done on $[Pd(O_2CMe)_2(dppm)]$ {constructed from $[Pt(O_2CCF_3)_2(dppm)]$, with bond lengths adjusted accordingly}, and the results were compared to those of $[Pt(O_2CMe)_2(dppm)]$. It was found that the Pd atom is less positively charged (+0.184 compared to +0.267) and the phosphorus atoms more positively charged (average +0.68 compared to +0.63). This may be attributed to the higher electronegativity of palladium. The movement of electron density from phosphorus to palladium as a result of σ -electron deficiency associated with having carboxylate ligands may explain the decomposition of $[Pd(O_2CMe)_2(PR_3)_2]$, in which one phosphine is oxidized and Pd undergoes a two-electron reduction, as reported by Jutand and co-workers.⁵

Experimental

General

All manipulations were routinely carried out under a dry argon atmosphere using freshly distilled solvents. The instruments used have been previously reported.²⁰ Elemental analyses were performed by the Microanalytical Laboratory in the Chemistry Department in the National University of Singapore.

^{*} All the acetates in $[Pt_4(\mu-O_2CMe)_8]$ are bridging: we did not think it appropriate to do a calculation on a single Pt with four monodentate acetates. The effect is the same, as can be seen from the platinum charge in $[Pt(O_2CMe)_2]$ and $[Pt_4(\mu-O_2CMe)_8]$.



Fig. 5 Orientation of the lone-pair orbitals (syn-syn) in carboxylate ligands and a qualitative assessment of metal-oxygen overlap in various co-ordination modes: (a) bridging a M-M bond (good); (b) chelation (inefficient); (c) bridging, but without M-M bond (inefficient); (d) monodentate (good but unco-ordinated oxygen is nucleophilic)

Molecular-weight measurements were carried out by Galbraith Laboratories, Knoxville, TN, using vapour-pressure osmometry with a Knaüer-Dampfdruck osmometer. Infrared spectra were recorded on samples prepared in KBr discs, NMR spectra in CDCl₃ solutions on Brüker AMX500 (500 MHz for ¹H and 202.46 MHz for ³¹P) or AC300F spectrometers (199.96 and 121.39 MHz respectively). The ¹H and ³¹P spectra were referenced to SiMe₄ and 85% H₃PO₄ respectively.

Syntheses

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[Pt(O₂CMe)₂(dppf)]. Solid Ag(O₂CMe) (0.109 g, 0.64 mmol) was added to an orange-yellow solution of [PtCl₂(dppf)] (0.229 g, 0.28 mmol) in CH_2Cl_2 (ca. 60 cm³). The resultant mixture was stirred, shielded from direct light, for ca. 20 h and filtered through a column of Celite to obtain a yellow solution. The filtrate was then evaporated in vacuo to give a dirty yelloworange residue, which was redissolved in CH2Cl2 and filtered again through Celite to remove any residual silver particles. The filtrate was concentrated and hexane added to induce crystallization. Any silver metal formed during crystallization was removed by Celite filtration. Orange-yellow crystalline [Pt(O₂CMe)₂(dppf)] was obtained (0.167 g, 69%) (Found: C, 51.9; H, 3.9; Fe, 6.1; P, 6.9; Pt, 22.0. C₃₈H₃₆FeO₅P₂Pt requires C, 51.5; H, 4.1; Fe, 6.3; P, 7.0; Pt, 22.0%); $\tilde{v}_{max}/cm^{-1}(CO_2^{-1})$ 1625s, 1595s (sh), 1366s and 1308s; $\delta_{\rm H}$ 1.93 (6 H, s, CH $_{3}),$ 4.39 (4 H, s, C₅H₄), 4.40 (4 H, s, C₅H₄), 7.35-7.49 (12 H, m, Ph) and 7.82–7.89 (8 H, m, Ph); δ_P 5.09 [J(PtP) 3948 Hz].

[Pt(O_2CPh)₂(PPh₃)₂]. A solution of [PtCl₂(PPh₃)₂] (0.155 g, 0.20 mmol) and Ag(O_2CPh) (0.095 g, 0.41 mmol) in CH₂Cl₂ (*ca.* 45 cm³) was stirred, shielded from direct light, at r.t. for *ca.* 18 h. The beige suspension was filtered through a column of Celite to obtain a colourless solution. The solvent was then removed *in vacuo*, CH₂Cl₂ introduced to dissolve the greyish white residue and the solution filtered through Celite to remove any residual silver particles. The CH₂Cl₂ filtrate was concentrated and hexane added to give upon standing an off-white crystalline solid of [Pt(O₂CPh)₂(PPh₃)₂]-0.5CH₂Cl₂

(0.152 g, 81%) [Found: C, 59.45; H, 3.9; Cl, 5.8; P, 7.4; Pt, 22.65%; *M* 972 (CHCl₃). C_{50.5}H₄₁ClO₄P₂Pt requires C, 60.4; H, 4.1; Cl, 3.5; P, 6.2; Pt, 19.4%; *M* 962]; $\tilde{\nu}_{max}/cm^{-1}(CO_2^{-1})$ 1639m, 1616m, 1575m, 1342s (br) and 1326s (sh); δ_{H} 5.29 (1 H, s, CH₂Cl₂), 6.97–7.02 (4 H, m, Ph), 7.10–7.17 (12 H, m, Ph), 7.23–7.28 (8 H, m, Ph), 7.39–7.42 (4 H, m, Ph) and 7.63–7.69 (12 H, m, Ph); δ_{P} 6.55 [*J*(PtP) 3838 Hz].

[Pt(O₂CMe)₂(PPh₃)₂]. A similar reaction between [PtCl₂-(PPh₃)₂] (0.260 g, 0.33 mmol) and Ag(O₂CMe) (0.120 g, 0.72 mmol) in CH₂Cl₂ (80 cm³) gave [Pt(O₂CMe)₂(PPh₃)₂] (0.193 g, 72%) as an off-white microcrystalline solid (Found: C, 56.5; H, 4.2; P, 7.2; Pt, 23.1. C₄₀H₃₆O₄P₂Pt requires C, 57.35; H, 4.3; P, 7.4; Pt, 23.3%); \tilde{v}_{max} /cm⁻¹ (CO₂⁻¹) 1634s (br), 1597m (sh), 1364s (br), 1310 and 1302s; $\delta_{\rm H}$ 1.35 (6 H, s, CH₃), 7.17–7.22 (12 H, m, Ph), 7.30–7.35 (6 H, m, Ph) and 7.54–7.61 (12 H, m, Ph); $\delta_{\rm P}$ 5.13 [J(PtP) 3826 Hz].

[Pt(O₂CCF₃)₂(PPh₃)₂]. A similar reaction between [Pt-Cl₂(PPh₃)₂] (0.150 g, 0.19 mmol) and Ag(O₂CCF₃) (0.092 g, 0.42 mmol) in CH₂Cl₂ (40 cm³) gave [Pt(O₂CCF₃)₂(PPh₃)₂] (0.067 g, 37%) as an off-white microcrystalline solid (Found: C, 50.6; H, 3.1; F, 11.7; P, 7.0; Pt, 19.4. C₄₀H₃₆F₆O₄P₂Pt requires C, 50.8; H, 3.2; F, 12.05; P, 6.55; Pt, 20.6%); \tilde{v}_{max} /cm⁻¹(CO₂⁻) 1727s, 1700s and 1401m; $\delta_{\rm H}$ 7.19–7.25 (12 H, m, Ph), 7.35–7.40 (6 H, m, Ph) and 7.56–7.57 (12 H, m, Ph); $\delta_{\rm P}$ 4.38 [J(PtP) 3933 Hz].

[Pt(O₂CPrⁱ)₂(PPh₃)₂]. A similar reaction between [PtCl₂-(PPh₃)₂] (0.106 g, 0.13 mmol) and Ag(O₂CPrⁱ) (0.085 g, 0.47 mmol) in CH₂Cl₂ (*ca.* 35 cm³) gave [Pt(O₂CPrⁱ)₂(PPh₃)₂]-0.5CH₂Cl₂ (0.080 g, 69%) as an off-white microcrystalline solid (Found: C, 54.9; H, 4.1; Cl, 5.3; P, 6.3; Pt, 20.8. C_{42.5}H₄₁ClO₄P₂Pt requires C, 55.8; H, 4.5; Cl, 3.9; P, 6.8; Pt, 21.3%); \tilde{v}_{max} /cm⁻¹(CO₂⁻⁻) 1627s (br), 1373m and 1341m; δ_{H} 0.59 [6 H, t, J(H_aH_b) 7.5, CH₃], 1.63 [4 H, q, J(H_aH_b), 7.5 CH₂], 5.30 (1 H, s, CH₂Cl₂), 7.16–7.21 (12 H, m, Ph), 7.29–7.34 (6 H, m, Ph) and 7.55–7.61 (12 H, m, Ph); δ_{H} 5.79 [J(PtP) 3818 Hz].

[Pt(O₂CMe)₂(dppm)]. A similar reaction between [PtCl₂-(dppm)] (0.139 g, 0.21 mmol) and Ag(O₂CMe) (0.081 g, 0.48 mmol) in CH₂Cl₂ (*ca.* 50 cm³) gave [Pt(O₂CMe)₂(dppm)] (0.085 g, 57%) as an off-white microcrystalline solid (Found: C, 49.5; H, 4.0; P, 7.7; Pt, 32.9. C₂₉H₂₈O₄P₂Pt requires C, 49.9; H, 4.05; P, 8.9; Pt, 28.0%); $\tilde{v}_{max}/cm^{-1}(CO_2^{-1})$ 1619s (br), 1592(sh), 1366s and 1309s; $\delta_{\rm H}$ 1.96 (6 H, s, CH₃), 4.18 [t, J(PH) 9.9 Hz, CH₂P], 7.37–7.49 (12 H, m, Ph) and 7.76–7.83 (8 H, m, Ph); $\delta_{\rm P}$ – 68.60 [J(PtP) 3463 Hz].

[Pt(O₂CCF₃)₂(dppm)]. A similar reaction between [PtCl₂-(dppm)] (0.145 g, 0.22 mmol) and Ag(O₂CCF₃) (0.107 g, 0.48 mmol) in CH₂Cl₂ (*ca.* 40 cm³) gave [Pt(O₂CCF₃)₂(dppm)] (0.100 g, 56%) as colourless crystals (Found: C, 43.5; H, 2.6; F, 11.5; P, 7.6; Pt, 23.0. C₂₉H₂₂F₆O₄P₂Pt requires C, 43.2; H, 2.75; F, 14.15; P, 7.7; Pt, 24.2%); \tilde{v}_{max} /cm⁻¹(CO₂⁻) 1713s (sh), 1698s (br) and 1406m; $\delta_{\rm H}$ 4.37 [2 H, t, *J*(PH) 10.8, CH₂P], 7.42–7.60 (12 H, m, Ph) and 7.77–7.84 (8 H, m, Ph); $\delta_{\rm P}$ – 66.25 [*J*(PtP) 3404 Hz].

[Pt(O₂CPrⁱ)₂(dppm)]. A similar reaction between [PtCl₂-(dppm)] (0.210 g, 0.32 mmol) and Ag(O₂CPrⁱ) (0.134 g, 0.74 mmol) in CH₂Cl₂ (*ca.* 50 cm³) gave [Pt(O₂CPrⁱ)₂(dppm)] (0.151 g, 65%) as colourless crystals (Found: C, 51.1; H, 4.2; P, 8.4. C₃₁H₃₂O₄P₂Pt requires C, 51.3; H, 4.3; P, 8.5%); \tilde{v}_{max} / cm⁻¹(CO₂⁻) 1616vs, 1373m and 1347m; $\delta_{\rm H}$ 0.89 [6 H, t, *J*(H_aH_b) 7.60, CH₃], 2.22 [4 H, q, *J*(H_aH_b) 7.60, CH₂CO₂], 4.17 [2 H, tt, *J*(PH) 10.0, *J*(PtH) 74.3, CH₂P], 7.35–7.47 (12 H, m, Ph) and 7.80–7.87 (8 H, m, Ph); $\delta_{\rm P}$ – 66.21 [*J*(PtP) 3449 Hz].

[Pt(O_2 CPh)₂(dppm)]. A similar reaction between [PtCl₂-(dppm)] (0.186 g, 0.28 mmol) and Ag(O_2 CPh) (0.149 g, 0.65

	$[Pt(O_2CMe)_2(dppf)] \cdot H_2O$	[Pt(O ₂ CPh) ₂ (dppf)]•CH ₂ Cl ₂	$[Pt(O_2CCF_3)_2(dppm)]$
М	885.5	1076.6	805.50
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P_{2,1/c}$ (no. 14)	$P\overline{I}$ (no. 2)	$P2_1/n$
a/Å	18.915(1)	10.150(1)	10.486(1)
b/Å	10.052(1)	14.187(1)	13.673(1)
c/Å	18.609(1)	17.779(2)	20.991(6)
χ^{0}		70.18(1)	—
β/°	99 00(1)	90.00(1)	90.00(3)
ν/°	_	69.04(1)	
U/\dot{A}^3	3495(2)	2227.4(11)	3009.59(14)
Z	4	2	4
<i>F</i> (000)	1752	1068	1560
$D/g \text{ cm}^{-3}$	1.683	1.605	1.778
$R_{\rm e}$ (from merging of equivalent reflections)	0.078	0.00	0.058
u/mm ³	4.548	3.698	4.84
Meanur	0.728	0.74	
Scan rate	$36 \text{ frames. } \phi = 0-180^\circ$.	60 frames, $\omega = 0-180^{\circ}$.	50 frames $\omega = -30$ to 120°.
Soun futo	$\Delta \omega = 5^{\circ} 10 \text{ min per frame}$	$\Delta \omega = 3^{\circ}$, 10 min per frame	$\Delta \omega = 3^{\circ}$, 9 min per frame
hkl Ranges	-23 to 23 -12 to 12 0-28	-12 to 12 -16 to 17 $0-22$	-13 to 13 -17 to 0 -26 to 26
Observed data n	$5744 [F \ge 5\sigma(F)]$	$6637 [F \ge 5\sigma(F)]$	$4785 [F > 4.0 \sigma(F)]$
No of variables <i>n</i>	425	533	434
10^{6} g In weighting scheme w	2	5	100
R	0.028	0.056	0.041
R'	0.030	0.079	0.037
S	1 78	1 76	1.98
Residual extrema in final difference map/e Å ⁻³	+ 1.09 to 1.49	+1.10 to -1.84	+0.76 to -0.64
* Details in common: $R = \Sigma F_0 - F_c / \Sigma F_0 $; $R' = O_2 CPh$; $S = [\Sigma w(F_0 - F_c)^2 / (n-p)]^{\frac{1}{2}}; w^{-1} = \sigma^2$	$= [\Sigma w(F_{o} - F_{c})^{2} / \Sigma w F_{o} ^{2}]^{\frac{1}{2}}$ $F(F_{o}) + gF^{2}.$	(for O_2CMe and O_2CCF_3), [$\Sigma w^2 (F_0 - F_c)^2 / \Sigma w^2 F_0 ^2]^{\frac{1}{2}}$ (for

mmol) in CH₂Cl₂ (*ca.* 50 cm³) gave [Pt(O₂CPh)₂(dppm)] (0.175 g, 74%) as an off-white crystalline solid (Found: C, 56.8; H, 3.9; P, 7.5; Pt, 25.8. $C_{39}H_{32}O_4P_2Pt$ requires C, 56.9; H, 3.9; P, 7.5; Pt. 23.7%); $\tilde{v}_{max}/cm^{-1}(CO_2^{--})$ 1635m (sh), 1615s (br), 1574m, 1553m and 1333s (br); δ_H 4.29 [t, J(PH) 10.1, CH₂P], 7.24–7.45 (18 H, m, Ph) and 7.89–7.99 (12 H, m, Ph); δ_P – 67.35 [J(PtP) 3437 Hz].

[Pt(O₂CCF₃)₂(dppf)]. A similar reaction between [PtCl₂-(dppf)] (0.127 g, 0.15 mmol) and Ag(O₂CCF₃) (0.082 g, 0.37 mmol) in CH₂Cl₂ (*ca.* 35 cm³) gave [Pt(O₂C-CF₃)₂(dppf)] (0.081 g, 54%) as an orange crystalline solid (Found: C, 46.4; H, 2.9; F, 6.0; Fe, 7.8; P, 5.3; Pt, 22.2. C₃₈H₂₈F₆FeO₄P₂Pt requires C, 46.8; H, 2.9; F, 11.8; Fe. 5.7; P, 6.35; Pt, 20.0%); \tilde{v}_{max} /cm⁻¹ (CO₂⁻) 1725s, 1702s and 1397s; $\delta_{\rm H}$ 4.43 [4 H, d, J(HH) 16, C₅H₄], 4.48 (4 H, s, C₅H₄), 7.37-7.42 (8 H, m, Ph), 7.49-7.54 (4 H, m, Ph) and 7.74-7.81 (8 H, m, Ph); $\delta_{\rm P}$ 5.74 [J(PtP) 4064 Hz].

[Pt(O₂CPrⁱ)₂(dppf)]. A similar reaction between [PtCl₂-(dppf)] (0.137 g, 0.17 mmol) and Ag(O₂CPrⁱ) (0.066 g, 0.36 mmol) in CH₂Cl₂ (*ca.* 35 cm³) gave [Pt(O₂CPrⁱ)₂(dppf)] (0.100 g, 60%) as orange crystals [Found: C, 53.1; H, 4.1; Fe, 5.6; P, 6.6; Pt, 26.8%; *M* 827 (CHCl₃); C₄₆H₃₈FeO₄P₂Pt requires C, 53.6; H, 4.3; Fe, 6.2; P, 6.9; Pt, 21.8%; *M* 896]; \tilde{v}_{max} /cm⁻¹(CO₂⁻) 1604s (br) and 1332s; δ_{H} 0.59 [6 H, t, *J*(H_aH_b) 7.5, CH₃], 1.63 [4 H, q, *J*(H_aH_b) 7.5, CH₂CO₂], 4.39 (8 H, s, C₅H₄), 4.38 (8 H, s, C₅H₄), 7.33-7.47 (12 H, m, Ph) and 7.82-7.88 (8 H, m, Ph); δ_{P} 5.68 [*J*(PtP) 3941 Hz].

[Pt(O₂CPh)₂(dppf)]·0.5CH₂Cl₂. A similar reaction between [PtCl₂(dppf)] (0.250 g, 0.30 mmol) and Ag(O₂CPh) (0.153 g, 0.67 mmol) in CH₂Cl₂ (*ca.* 80 cm³) gave [Pt(O₂CPh)₂(dppf)] (0.207 g, 73%) as orange crystals (Found: C, 56.5; H, 4.0; Fe, 5.2; P, 7.3; Pt, 17.85. C_{48.5}H₃₉ClFeO₄P₂Pt requires C, 56.3; H, 3.8; Fe, 5.3; P. 6.0; Pt, 18.8%); \tilde{v}_{max} /cm⁻¹(CO₂⁻) 1632s, 1356m and 1344s; δ_{H} 4.4 (br, 4 H, s, H₂ of C₅H₄), 4.48 (br, 4 H, s, H₆ of C₅H₄), 6.97-7.02 (4 H, Ph), 7.10-7.15 [2 H, t, *J*(HH) 7.2, Ph], 7.28-7.41 (16 H, m, Ph) and 7.89-7.95 (8 H, m, Ph); δ_{P} 6.69 [*J*(PtP) 3960 Hz].

Crystallography

Single crystals of [Pt(O₂CMe)₂(dppf)]·H₂O (orange-yellow prism, $0.25 \times 0.30 \times 0.40$ mm), [Pt(O₂CPh)₂(dppf)]·CH₂Cl₂ (yellow prism, $0.30 \times 0.40 \times 0.50$ mm) and [Pt(O₂C- $(CF_3)_2(dppm)$] (colourless prism, 0.08 × 0.12 × 0.28 mm) were grown from CH₂Cl₂-hexane mixtures.³ Those suitable for Xray diffraction were mounted on top of glass fibres. Intensity data were measured on a Rigaku RAXIS-IIC ³¹ imaging-plate diffractometer system powered at 50 kV and 90 mA with graphite-monochromatized Mo-K α radiation (λ 0.71073 Å) using the variable ω -scan technique. Two standard reflections were monitored after every 125 data measurements, showing only small random variations. The raw data were processed with the learnt-profile procedure,³² and absorption corrections were applied by fitting a pseudo-ellipsoid to the ψ -scan data for selected strong reflections over a range of 20 angles.³³ All the structures were solved with the Patterson superposition method and subsequent Fourier-difference syntheses. The CF₃ groups in [Pt(O2CCF3)2(dppm)] are disordered. For both dppf structures the final difference map contained residual extrema exceeding $\pm 1 \text{ e} \text{ Å}^{-3}$ in the neighbourhood of the heavy Pt atom. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the organic ligands were generated geometrically (C-H 0.95 Å), assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. The phenyl groups on the phosphines were treated as rigid groups. The other non-hydrogen atoms were refined anisotropically, and the hydrogen atoms of the cyclopentadienyl groups were included in structure-factor calculations with assigned isotropic thermal parameters. All computations were performed with the SHELXTL-PC program package.34 Analytical expressions of neutral-atom scattering factors were employed, and anomalous-dispersion corrections were incorporated.35 Crystal data, data-collection parameters, and results of the analyses are listed in Table 5.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the

CCDC for this material should quote the full literature citation and the reference number 186/31.

Theoretical calculations

The models of the molecules used for the calculations are based on their crystal structures. Those of $[Pt_4(\mu-O_2CMe)_8]$ and $[Pt_4(en)_4(\mu-O_2CMe)_4]^{4+}$ were aligned such that the Pt₄ plane lies on the xy plane and the Pt-Pt bonds along the x and y axes. For $[Pt(O_2CMe)_2(L-L)]$ and related compounds all Pt-P and Pt-O bonds were aligned to be approximately parallel to either the x or the y axis. Where substitutions were made, e.g. MeCO₂ for CF₃CO₂ and Pd for Pt, the bond lengths were adjusted based on the covalent radii of atoms concerned.

Calculations were performed using the self-consistent Fenske-Hall approximate molecular orbital method.³⁶ The basis functions were obtained by fitting the results of X_{α} (Herman–Skillman)³⁷ calculations to Slater orbitals;³⁸ double- ζ functions were used for transition-metal d orbitals and main group p orbitals. As a common practice in Fenske-Hall calculations, the exponents of the platinum valence s and p orbitals were fixed at 2.4, and those of Pd at 2.2. An exponent of 1.2 was used for hydrogen. Mulliken population analyses³⁹ were employed to calculate atomic charges and overlap populations.

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