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Preparation and X-ray structure of a platinum(II) hydroxycarbonyl, $Pt(CO_2H)\{C_6H_3(CH_2PPh_2)_2\text{-}2,6\}$, containing a *trans*-spanning, tridentate P,C,P-ligand *,**

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Abstract

The ligand 1,3-{bis(diphenylphosphino)methyl}benzene, $1,3\text{-}C_6H_4(CH_2PPh_2)_2$ (**3a**) undergoes cyclometallation on heating in 2-methoxyethanol either with $PtCl(CH_3)(COD)$ or, in the presence of 2-methylaminoethanol, with $PtCl_2(COD)$ to give $PtCl\{C_6H_3(CH_2PPh_2)_2\text{-}2,6\}$ (**6**). In this complex, the tridentate anionic ligand $C_6H_3(CH_2PPh_2)_2\text{-}2,6$ (**2a**) is attached to platinum via a σ-bonded carbon atom and mutually trans-phosphorus atoms. Successive treatment of **6** with $AgBF_4$ and KOH gives the hydroxo-complex Pt(OH)(**2a**) (**11**), which reacts with CO to give the corresponding hydroxycarbonyl $Pt(CO_2H)$(**2a**) (**12**). The structure of $\mathbf{12}\cdot 1.5C_6H_6$ was determined by X-ray diffraction methods and shown to consist of a dimer in which two planar *trans*-$Pt(CO_2H)$(**2a**) units are joined by hydrogen-bonded carboxylate groups. The hydrogen-bonded O ··· O distance [2.750(4)Å] is significantly larger than that in *trans*-$Pt(CO_2H)(C_6H_5)(PEt_3)_2$ (**1**) [2.695(8)Å], which may be related to the greater tendency of **2a** to form a monomer in dichloromethane.

1. Introduction

An interesting feature of the chemistry of monomeric organoplatinum(II) hydroxides and alkoxides is the fact that CO inserts into the Pt–O bond more readily than into the Pt–C bond [1]. Thus, complexes containing bidentate ditertiary phosphines, *cis*-Pt(OH)R(L–L) (R $= CH_3$, CF_3, C_6H_9; L–L = dppe, dppp, vdpp) react with CO under ambient conditions to give the corresponding platinum(II) hydroxycarbonyls (metallacarboxylic acids) *cis*-$Pt(CO_2H)$R(L–L) [2–5]; insertion into the Pt–C bond occurs only under more forcing conditions or with longer reaction times, especially when L–L = dppp. Similarly, *trans*-$Pt(OH)(C_6H_5)(PEt_3)_2$ reacts with CO to give *trans*-$Pt(CO_2H)(C_6H_5)(PEt_3)_2$ (**1**), which is a hydrogen-bonded dimer in the solid state but is in equilibrium with the monomer in organic solvents [6]. It would be of interest to know how the structures and properties of the hydroxycarbonyls in the *trans*-series are influenced by the nature of the tertiary phosphine. Unfortunately, attempts to prepare analogues of **1** containing triphenylphosphine or tricyclohexylphosphine by treatment of the appropriate hydroxo-complexes with CO were unsuccessful, apparently owing to competitive displacement of the tertiary phosphine by CO leading to platinum(0) carbonyl clusters.

An obvious way to prevent or slow down this process is to strap the σ-bonded carbon atom and the two trans-tertiary phosphine ligands together in the form of an anionic tridentate ligand. One suitable class of ligand for this purpose seemed to be 2,6-{bis(diorganophosphino)methyl}phenyl, $C_6H_3(CH_2PR_2)_2\text{-}2,6$ (**2**), which in principle could be derived by cyclometallation of 1,3-{bis(diorganophosphino)methyl}benzene (**3**). The preparation of hydroxo- and hydroxycarbonyl-platinum(II) complexes containing **2a** (R = Ph), and

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[*] Dedicated to Professor Gian Paolo Chiusoli in recognition of his important contributions to organometallic chemistry and its applications in organic synthesis.

[**] Abbreviations: COD = 1,5-cyclooctadiene, C_8H_{12}; C_6H_9 = 1-cyclohexenyl; dppe = 1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$; dppp = 1,3-bis(diphenylphosphino)butane; vdpp = *cis*-vinylene-1,2-bis(diphenylphosphine), *cis*-$Ph_2PCH=CHPPh_2$.

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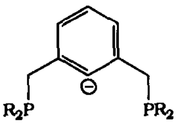
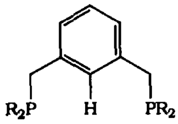
the X-ray structural analysis of the latter complex are described in this paper.



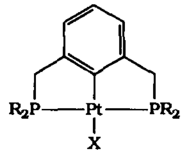
R = Ph : **2a**
R = ${}^tBu$: **2b**



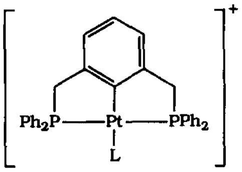
R = Ph : **3a**
R = ${}^tBu$: **3b**

2. Results and discussion

It was first necessary to develop syntheses of halogenoplatinum(II) complexes containing **2a** or **2b** as precursors to the corresponding hydroxides and hydroxycarbonyls. Moulton and Shaw [7] reported that 1,3-{bis(di-t-butylphosphino)methyl}benzene, $1,3\text{-}C_6H_3(CH_2P^tBu_2)_2$ (**3b**) reacts with $PtCl_2(NC^tBu)_2$ in hot 2-methoxyethanol to give the monomeric cyclometallated complex $\overline{PtCl\{C_6H_3(CH_2P}{}^tBu_2)_2\}$ (**4**) in 32% yield, together with a polymeric species, probably *trans*-$[PtCl_2$ (**3b**)$]_n$. We found that **3b** reacted with $PtCl_2(NCPh)_2$ under the same conditions to give the polymer as the predominant product, yields of **4** generally being less than 10%. The monomeric cyclometallated iodo-complex, $\overline{PtI(C_6H_3(CH_2P}{}^tBu_2)_2\}$ (**5**) was, however, obtained in 80% yield as a pale yellow, air-stable solid by heating $PtI_2(COD)$ with **3b** in 2-methoxyethanol. Unfortunately, the iodo group of **5** could not be removed by treatment with $AgBF_4$ or $AgPF_6$, probably because of steric hindrance by the bulky t-butyl groups, so we concentrated on complexes derived from the corresponding diphenylphosphino ligand **2a**.



R = ${}^tBu$; X = Cl (**4**), I (**5**)
R = Ph; X = Cl (**6**), Br (**7**)
I (**9**), OH (**11**)
CO_2H (**12**), CO_2Me (**13**)



L = PPh_3 (**8**), THF (**10**)

Rimml and Venanzi [8,9] showed that 1,3-{bis(diphenylphosphino)methyl}benzene, $1,3\text{-}C_6H_4(CH_2PPh_2)_2$ (**3a**) reacts with anhydrous $PtCl_2$ or $PtBr_2$ in aqueous acetone over 10 d at room temperature to give the cyclometallated complexes $\overline{PtX\{C_6H_3(CH_2P}Ph_2)_2\text{-}2,6\}$ (X = Cl (**6**), Br (**7**)) in about 30% yield; the main products are mixtures of oligomeric species, *cis*-$[PtX_2$-(**2a**)$]_n$. Reaction of *cis*-$PtCl_2(PPh_3)_2$ with **3a** gave the cyclometallated cation $[\overline{Pt(PPh_3)\{C_6H_3(CH_2P}Ph_2)_2\}]^+$ (**8**) in good yield; this reacted with iodide ion to give the cyclometallated iodo-complex **9** and on treatment successively with sulfur (to remove PPh_3) and with KCl gave **6**.

We found that **6** is conveniently obtained in high yield by heating **3a** either with $PtCl(CH_3)(COD)$ in 2-methoxyethanol (eqn. (1)) or with $PtCl_2(COD)$ in mesitylene in the presence of about one equivalent of 2-methylaminoethanol (eqn. (2)).

$$PtCl(CH_3)(COD) + 1,3\text{-}C_6H_4(CH_2PPh_2)_2 \longrightarrow \overline{PtCl\{C_6H_3(CH_2P}Ph_2)_2\text{-}2,6\} + CH_4 \quad (1)$$

$$PtCl_2(COD) + 1,3\text{-}C_6H_4(CH_2PPh_2)_2 \longrightarrow \overline{PtCl\{C_6H_3(CH_2P}Ph_2)_2\text{-}2,6\} + HCl \quad (2)$$

Both reactions may proceed by oxidative addition of the aromatic C–H bond in the 2-position of **3a** and subsequent reductive elimination of CH_4 or HCl; removal of the latter is presumably assisted by the basic alcohol. Similar cleavage of a vinylic C–H bond has been observed in the reaction of $o\text{-}Ph_2PC_6H_4CH{=}CHCHMeC_6H_4PPh_2\text{-}o$ with $PtCl(CH_3)(COD)$ to give $\overline{PtCl(o\text{-}Ph_2PC_6H_4CH{=}C}CHMeC_6H_4PPh_2\text{-}o)$ [10]. Reaction of $PtI_2(COD)$ with **3a** in refluxing 2-methoxyethanol gives the monomeric cyclometallated complex $\overline{PtI\{C_6H_3(CH_2P}Ph_2)_2\}$ (**9**) directly in 90% yield. It has been noted previously that iodo- and bromo-tertiary phosphine complexes undergo cyclometallation more readily than the corresponding chloro-complexes [11].

Analytical and selected IR data for platinum(II) complexes of **2a** and **2b** are summarized in Table 1; NMR data are collected in Table 2. The ^1H NMR spectra of the cyclometallated complexes **5**, **6** and **9** exhibit a characteristic virtual triplet with ^{195}Pt satellites at δ 3–4 ppm due to the benzylic protons, which are coupled with the mutually *trans*-phosphorus atoms ($^2J(P\text{-}H) + {}^4J(P\text{-}H)$ *ca.* 8–9 Hz; $^3J(Pt\text{-}H)$ *ca.* 25 Hz). The $^{31}P\{^1H\}$ NMR spectra correspondingly show a singlet with ^{195}Pt satellites ($^1J(Pt\text{-}P)$ *ca.* 3000 Hz), the magnitude of the coupling constant being typical of mutually *trans* tertiary phosphine ligands in aryl cyclometallated platinum(II) complexes [12]. The IR spectrum of the chloro-complex **6** shows a band of medium intensity at 290 cm^{-1} assignable to $\nu(Pt\text{-}Cl)$ *trans* to a σ-bonded carbon atom [13].

Treatment of **6** with $AgBF_4$ in THF causes precipitation of AgCl, and presumably generates a solvento-cation $[\overline{Pt(THF)\{C_6H_3(CH_2P}Ph_2)_2\text{-}2,6\}]^+$ (**10**), which reacts with KOH to give the pale yellow hydroxo-complex $\overline{Pt(OH)\{C_6H_3(CH_2P}Ph_2)_2\text{-}2,6\}$ (**11**). The IR spectrum of **11** in dichloromethane contains a weak, broad band at 3620 cm^{-1} due to $\nu(OH)$ and the ^1H NMR spectrum shows a triplet with ^{195}Pt satellites at δ 0.21 ($^3J(P\text{-}H)$

TABLE 1. Analytical and IR data for $\overline{\mathrm{PtX\{C_6H_3(CH_2P}}\mathrm{R_2)_2\text{-}2,6\}}$

Compound No.	R	X	Analysis (found (calcd.) (%))			IR (cm^{-1}) [a]
			C	H	P	
5	^tBu	I	40.2(40.3)	6.1(6.1)	8.4(8.7)	
6 [b]	Ph	Cl	53.4(53.2)	4.25(4.05)	8.9(8.6)	290[ν(PtCl)]
11	Ph	OH	56.5(56.1)	4.2(4.1)	8.8(9.0)	3620w[ν(OH)] [c]
12	Ph	CO_2H	55.9(55.5)	4.1(3.95)		2660m[ν(OH)] [d] 1580vs[ν(C=O)] 1030s[ν(C–O)]
13 [e]	Ph	CO_2Me	53.7(53.45)	4.7(4.5)		1620vs[ν(C=O)] 1020vs[ν(C–O)]

[a] In KBr disc, except where stated otherwise. [b] Calcd. for monohydrate. [c] In CD_2Cl_2. [d] IR(CH_2Cl_2) 3610w [ν(OH)], 1620s, 1590m [ν(C=O)]. [e] Calcd. for dihydrate.

5.2 Hz, ^2J(Pt–H) 28.0 Hz). This signal disappears on addition of D_2O, and can therefore be assigned to the hydroxyl proton; the other features of the ^1H and ^{31}P NMR spectra are similar to those of **6** and **9**. Complex **11** represents one of the rare examples of a hydroxobis(tertiary phosphine)platinum(II) complex for which the OH resonance and the accompanying coupling to ^{31}P and ^{195}Pt are readily observed [1]. The magnitude of ^2J(Pt–OH) for **11** is between the values of 21.0 Hz observed for *trans*-Pt(OH)(CF_3)(PPh_3)$_2$ and 35.0 Hz in *trans*-Pt(OH)(CF_3)($PMePh_2$)$_2$ [4].

It is worth noting that the N-donor analogue of **2a**, $C_6H_3(CH_2NMe_2)_2$-2,6, forms a hydroxonickel(II) complex, but the corresponding hydroxopalladium(II) and hydroxoplatinum(II) complexes are unknown [14].

Treatment of the hydroxo-complex **11** in benzene with CO under ambient conditions causes the hydroxycarbonyl complex, $\overline{\mathrm{Pt(CO_2H)\{C_6H_3(P}}\mathrm{Ph_2)_2\text{-}2,6\}}$ (**12**) to precipitate as colourless crystals; the corresponding ^{13}C-labelled complex **12a** is prepared similarly by use of ^{13}CO. The spectroscopic properties of **12** in general resemble those of other platinum(II) hydroxycarbonyls. The IR spectrum in a KBr disk shows a medium-intensity band at 2660 cm^{-1} due to ν(OH); in dichloromethane, this band is absent and is replaced by a band at 3614 cm^{-1}. These observations suggest that **12** contains hydrogen-bonded O–H $\cdots$ O units in the solid state but that it exists mainly as a monomer in CH_2Cl_2. Correspondingly, the intense ν(C=O) band at 1580 cm^{-1} in the solid state IR spectrum shifts to 1620 cm^{-1} in CH_2Cl_2, though it is accompanied by a shoulder at 1590 cm^{-1}. In the ^1H NMR spectrum of **12** in DMSO-d_6, there is a slightly broad resonance at δ 9.0 due to the hydroxyl proton, no coupling to ^{31}P or ^{195}Pt being evident. The signal disappears on addition of D_2O and cannot be located in solvents other than DMSO-d_6, presumably because of self-exchange. The $^{13}C\{^1H\}$ NMR spectrum of **12a** shows a triplet with ^{195}Pt satellites at δ 205 (^1J(Pt–C) 901 Hz, ^2J(P–C) 10 Hz) due to the carboxylate carbon atom. The magnitude of ^1J(Pt–C) in **12a** is less than the values of *ca.* 1300 Hz observed for hydroxycarbonyls such as *cis*-Pt(CO_2H)(C_6H_9)(dppp) [3] and *trans*-PtCl(CO_2H)(PEt_3)$_2$ (**1**) [15], probably reflecting the high *trans*-influence of the σ-aryl group relative to P-donors or chloride. However, the fact that ^1J(Pt–C) in **12a** is significantly larger than that in *trans*-Pt(CO_2H)(C_6H_5)(PEt_3)$_2$ (820 Hz) [6] indicates that the nature of the tertiary phosphine in the *cis*-position may also be important.

Like **1**, complex **12** reacts readily with methanol to give the corresponding methoxycarbonyl complex, Pt(CO_2Me)(**2a**), whose ^1H NMR spectrum shows a singlet at δ 3.67 due to the CO_2Me group that overlaps the resonance due to the CH_2 groups of **2a**. In the IR spectrum there are intense absorptions at 1620 cm^{-1} and 1020 cm^{-1} due to ν(C=O) and ν(C–O) modes. In other respects, however, **1** and **12** differ in their chemistry. Thus, on heating *in vacuo* or in toluene, **12** eliminates CO to give **11** and other unidentified products, whereas **1** gives a dinuclear μ-carbon dioxide complex $\{Pt(C_6H_5)(PEt_3)_2\}_2(\mu\text{-}CO_2)$ [6]. Attempts to form a μ-CO_2 complex of platinum(II) containing **2a** by reaction of **11** with **12** in solution at room temperature were unsuccessful.

X-ray structural analysis of a crystal of **12** $\cdot$ 1.5C_6H_6 shows that it consists of discrete dimers having exact C_i

TABLE 2. NMR Data for $\overline{\mathrm{PtX\{C_6H_3(CH_2P}}\mathrm{R_2)_2\text{-}2,6\}}$

Compound No.	R	X	Solvent	$\delta(CH_2)(N, {}^3J(P\text{–}H))$ [a]	Other	$\delta(P)({}^1J(Pt\text{–}P))$
5	^tBu	I	CD_2Cl_2	2.97 (t, 7.6, 22)		63.0(2833)
6	Ph	Cl	CD_2Cl_2	2.59 (t, 9.6, 26)		34.3(2956)
9	Ph	I	CD_2Cl_2	3.97 (t, 8.8, 26)		36.3(2879)
11	Ph	OH	C_6D_6	3.59 (t, 9.0, 27)	0.21 (t, OH), ^3J(P–H) 5.2, ^2J(Pt–H) 28.0	30.5(3064)
12 [b]	Ph	CO_2H	C_6D_6	3.10 (t, 9.8, 26)	9.1 (s, CO_2H) [c]	35.2(2966)
13	Ph	CO_2Me	C_6D_6	3.70 (t, 8.4, 28)	3.67 (s, OMe)	35.4(2993)

[a] Coupling constants (J) in Hz, $N = {}^2J(P\text{–}H) + {}^4J(P\text{–}H)$. [b] $\delta(^{13}CO_2H)$ in C_6D_6: 205 (t, ^2J(P–C) 10, ^1J(Pt–C) 901). [c] In DMSO-d_6.

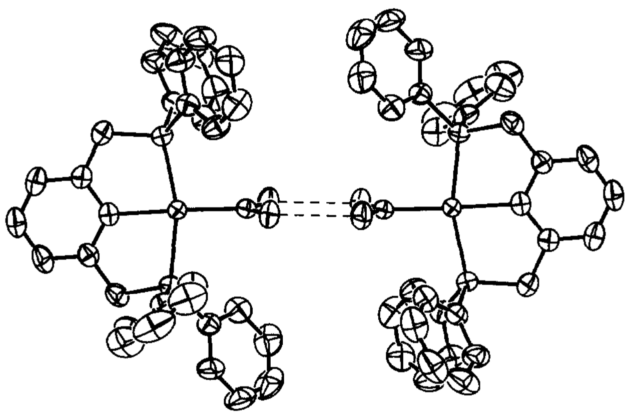


Fig. 1. The hydrogen-bonded dimer unit formed by a pair of centrosymmetrically related $Pt(CO_2H)\{C_6H_3(CH_2PPh_2)_2\text{-}2,6\}$ molecules.

symmetry that contain two $Pt(CO_2H)\{C_6H_3(CH_2PPh_2)_2\text{-}2,6\}$ units held together by closed hydrogen-bonded carboxylate groups, as shown in Fig. 1. The structure of each unit is illustrated in Fig. 2, together with the atom nomenclature.

Coordinates and isotropic thermal parameters for the non-hydrogen atoms are listed in Table 3, selected metrical parameters are in Table 4. The association in **12** is similar to that found in *trans*-$Pt(CO_2H)(C_6H_5)(PEt_3)_2$ (**1**) and in many organic carboxylic acids, but is probably weaker. Thus, the hydrogen-bonded O ··· O separation of 2.750(4) Å is significantly greater than that in **1** [2.695(8)Å] and is also above the range commonly found in organic carboxylic acids [2.63–2.67 Å]. The bond lengths and angles in the carboxylate group [*r*{C(10)–O(11)} 1.302(5) Å, *r*{C(10)–O(12)} 1.282(4) Å, ∡ Pt–C(10)–O(11) 119.2(2)°, ∡ Pt–C(10)–O(12) 123.3(3)°, ∡ O(11)–C(10)–O(12) 117.5(3)°] are close to the corresponding values in **1** and in carboxylic acids. The coordination about each platinum atom is essentially square planar, though some angular distortions are imposed by the tridentate $C_6H_3(PPh_2)_2\text{-}2,6$ ligand. The Pt–C(aryl) and Pt–C(carboxylate) distances [Pt–C(1) 2.066(3) Å; Pt–C(10) 2.058(3) Å] are equal,

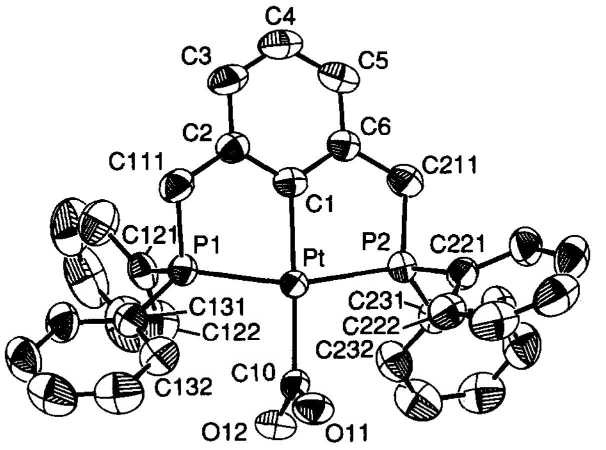


Fig. 2. View of $Pt(CO_2H)\{C_6H_3(CH_2PPh_2)_2\text{-}2,6\}$ (**12**) indicating the labelling of the non-hydrogen atoms (atoms of each phospine phenyl ring are labelled sequentially C(*nml*)–C(*nm*6) in the directions shown). Ellipsoids enclose 50% probability levels; hydrogen atoms have been deleted for clarity.

TABLE 3. Coordinates and isotropic thermal parameters for the non-hydrogen atoms in $[Pt(CO_2H)\{C_6H_3(CH_2PPh_2)_2\text{-}2,6\}\cdot 1.5C_6H_6$-(**12**$\cdot 1.5C_6H_6$) [a]

Atom	*x*	*y*	*z*	U_{eq}
Pt	0.26070(1)	0.12655(1)	0.23826(1)	0.0332(1)
P(1)	0.38574(9)	0.22765(8)	0.28411(6)	0.0377(6)
P(2)	0.1119(1)	0.03108(8)	0.23976(7)	0.0402(7)
C(1)	0.1396(3)	0.2038(3)	0.3549(2)	0.038(2)
C(2)	0.1582(4)	0.2975(3)	0.3984(3)	0.043(3)
C(3)	0.0840(5)	0.3441(4)	0.4802(3)	0.057(3)
C(4)	−0.0131(5)	0.3033(4)	0.5197(3)	0.064(4)
C(5)	−0.0375(4)	0.2143(4)	0.4772(3)	0.056(3)
C(6)	0.0385(4)	0.1641(3)	0.3962(2)	0.041(3)
C(10)	0.3809(4)	0.0586(3)	0.1197(2)	0.043(3)
O(11)	0.3434(3)	0.1045(3)	0.0422(2)	0.059(2)
O(12)	0.4951(3)	−0.0245(3)	0.1180(2)	0.056(2)
C(111)	0.2604(4)	0.3460(3)	0.3520(3)	0.051(3)
C(121)	0.5044(4)	0.1427(3)	0.3610(3)	0.046(3)
C(122)	0.5831(5)	0.0307(4)	0.3346(3)	0.066(4)
C(123)	0.6752(6)	−0.0372(5)	0.3918(5)	0.094(6)
C(124)	0.6867(6)	0.0042(7)	0.4740(5)	0.102(7)
C(125)	0.6096(7)	0.1133(7)	0.5001(4)	0.102(7)
C(126)	0.5181(6)	0.1853(5)	0.4443(4)	0.076(5)
C(131)	0.4807(4)	0.2935(3)	0.2073(3)	0.046(3)
C(132)	0.4482(5)	0.3147(3)	0.1179(3)	0.057(3)
C(133)	0.5203(6)	0.3660(4)	0.0597(4)	0.075(5)
C(134)	0.6197(6)	0.3978(4)	0.0884(4)	0.084(5)
C(135)	0.6517(5)	0.3784(4)	0.1758(4)	0.077(5)
C(136)	0.5841(5)	0.3251(4)	0.2358(3)	0.060(4)
C(211)	0.0186(4)	0.0614(4)	0.3541(3)	0.056(3)
C(221)	−0.0137(4)	0.0761(3)	0.1586(3)	0.047(3)
C(222)	0.0144(4)	0.1310(4)	0.0806(3)	0.056(3)
C(223)	−0.0754(6)	0.1591(5)	0.0143(4)	0.079(5)
C(224)	−0.1890(6)	0.1307(5)	0.0239(4)	0.086(5)
C(225)	−0.2189(5)	0.0793(5)	0.0996(5)	0.085(5)
C(226)	−0.1325(4)	0.0511(4)	0.1687(3)	0.062(4)
C(231)	0.1842(4)	−0.1267(3)	0.2306(3)	0.046(3)
C(232)	0.3239(4)	−0.1806(4)	0.2192(3)	0.058(3)
C(233)	0.3812(5)	−0.2994(4)	0.2094(4)	0.073(4)
C(234)	0.3025(6)	−0.3648(4)	0.2112(4)	0.071(4)
C(235)	0.1629(6)	−0.3135(4)	0.2259(4)	0.075(5)
C(236)	0.1047(5)	−0.1951(4)	0.2349(4)	0.063(4)
C(51)	0.8966(9)	0.5261(9)	0.2672(7)	0.118(9)
C(52)	0.808(1)	0.632(1)	0.2737(6)	0.13(1)
C(53)	0.771(1)	0.6927(9)	0.197(1)	0.15(1)
C(54)	0.820(2)	0.644(2)	0.114(1)	0.22(3)
C(55)	0.908(2)	0.529(2)	0.1166(8)	0.22(2)
C(56)	0.9472(9)	0.4753(9)	0.192(1)	0.15(1)
C(61)	0.5334(7)	0.5345(6)	0.4166(4)	0.087(6)
C(62)	0.4017(6)	0.5746(5)	0.4529(4)	0.082(5)
C(63)	0.3678(6)	0.5403(5)	0.5359(5)	0.084(5)

[a] $U_{eq} = {}^1/_3\Sigma_i\Sigma_j U_{ij} a_i^{\star} a_j^{\star} a_i \cdot a_j$.

TABLE 4. Selected interatomic distances (Å) and angles (°) for $[\overline{\mathrm{Pt(CO_2H)\{C_6H_3(CH_2P}}\mathrm{Ph_2)_2\text{-}2,6\}}$ · $1.5C_6H_6$(**12** · $1.5C_6H_6$) [a]

Pt–P(1)	2.2610(11)	Pt–P(2)	2.2691(12)
Pt–C(1)	2.066(3)	Pt–C(10)	2.058(3)
P(1)–C(111)	1.824(4)	P(1)–C(121)	1.813(4)
P(1)–C(131)	1.807(4)	P(2)–C(211)	1.840(4)
P(2)–C(221)	1.812(4)	P(2)–C(231)	1.827(4)
C(1)–C(2)	1.410(6)	C(1)–C(6)	1.408(6)
C(2)–C(3)	1.386(5)	C(2)–C(111)	1.511(6)
C(3)–C(4)	1.372(8)	C(4)–C(5)	1.384(8)
C(5)–C(6)	1.393(5)	C(6)–C(211)	1.505(7)
C(10)–O(11)	1.302(5)	C(10)–O(12)	1.282(4)
C(121)–C(122)	1.379(6)	C(121)–C(126)	1.383(7)
C(122)–C(123)	1.390(8)	C(123)–C(124)	1.355(11)
C(124)–C(125)	1.346(11)	C(125)–C(126)	1.392(9)
C(131)–C(132)	1.391(6)	C(131)–C(136)	1.385(7)
C(132)–C(133)	1.382(8)	C(133)–C(134)	1.348(10)
C(134)–C(135)	1.360(9)	C(135)–C(136)	1.382(8)
C(221)–C(222)	1.384(6)	C(221)–C(226)	1.389(7)
C(222)–C(223)	1.387(7)	C(223)–C(224)	1.358(10)
C(224)–C(225)	1.339(10)	C(225)–C(226)	1.394(8)
C(231)–C(232)	1.388(6)	C(231)–C(236)	1.379(7)
C(232)–C(233)	1.379(6)	C(233)–C(234)	1.345(9)
C(234)–C(235)	1.385(8)	C(235)–C(236)	1.376(6)
C(51)–C(52)	1.316(13)	C(51)–C(56)	1.26(2)
C(52)–C(53)	1.35(2)	C(53)–C(54)	1.35(2)
C(54)–C(55)	1.40(3)	C(55)–C(56)	1.31(2)
C(61)–C(62)	1.362(9)	C(61)–C(63)′	1.373(8)
C(62)–C(63)	1.344(9)		
P(1)–Pt–P(2)	161.87(4)	P(1)–Pt–C(1)	81.15(12)
P(1)–Pt–C(10)	96.93(13)	P(2)–Pt–C(1)	82.21(12)
P(2)–Pt–C(10)	100.01(13)	C(1)–Pt–C(10)	176.8(2)
Pt–P(1)–C(111)	102.8(2)	Pt–P(1)–C(121)	110.4(2)
Pt–P(1)–C(131)	124.15(15)	C(111)–P(1)–C(121)	106.7(2)
C(111)–P(1)–C(131)	106.0(2)	C(121)–P(1)–C(131)	105.5(2)
Pt–P(2)–C(211)	104.6(2)	Pt–P(2)–C(221)	116.9(2)
Pt–P(2)–C(231)	116.64(15)	C(211)–P(2)–C(221)	106.7(2)
C(211)–P(2)–C(231)	104.7(2)	C(221)–P(2)–C(231)	106.2(2)
Pt–C(1)–C(2)	120.8(3)	Pt–C(1)–C(6)	122.2(3)
C(2)–C(1)–C(6)	117.0(3)	C(1)–C(2)–C(3)	121.0(4)
C(1)–C(2)–C(111)	117.7(3)	C(3)–C(2)–C(111)	121.3(4)
C(2)–C(3)–C(4)	121.0(5)	C(3)–C(4)–C(5)	119.5(4)
C(4)–C(5)–C(6)	120.4(4)	C(1)–C(6)–C(5)	121.1(4)
C(1)–C(6)–C(211)	118.8(3)	C(5)–C(6)–C(211)	120.0(4)
Pt–C(10)–O(11)	119.2(2)	Pt–C(10)–O(12)	123.3(3)
O(11)–C(10)–O(12)	117.5(3)	P(1)–C(111)–C(2)	106.5(3)
P(1)–C(121)–C(122)	117.9(3)	P(1)–C(121)–C(126)	122.8(3)
C(122)–C(121)–C(126)	119.3(4)	C(121)–C(122)–C(123)	119.5(5)
C(122)–C(123)–C(124)	120.9(5)	C(123)–C(124)–C(125)	119.6(6)
C(124)–C(125)–C(126)	121.5(7)	C(121)–C(126)–C(125)	119.0(5)
P(1)–C(131)–C(132)	119.5(4)	P(1)–C(131)–C(136)	121.4(3)
C(132)–C(131)–C(136)	119.2(4)	C(131)–C(132)–C(133)	119.2(5)
C(132)–C(133)–C(134)	121.2(5)	C(133)–C(134)–C(135)	120.2(6)
C(134)–C(135)–C(136)	120.6(6)	C(131)–C(136)–C(135)	119.6(5)
P(2)–C(211)–C(6)	109.3(3)	P(2)–C(221)–C(222)	118.4(3)
P(2)–C(221)–C(226)	122.7(3)	C(222)–C(221)–C(226)	118.8(4)
C(221)–C(222)–C(223)	119.6(5)	C(222)–C(223)–C(224)	120.8(5)
C(223)–C(224)–C(225)	120.4(6)	C(224)–C(225)–C(226)	120.8(6)
C(221)–C(226)–C(225)	119.6(5)	P(2)–C(231)–C(232)	119.3(4)
P(2)–C(231)–C(236)	122.3(3)	C(232)–C(231)–C(236)	118.4(4)
C(231)–C(232)–C(233)	120.6(5)	C(232)–C(233)–C(234)	120.5(4)
C(233)–C(234)–C(235)	120.0(4)	C(234)–C(235)–C(236)	119.9(6)

within experimental error, to their counterparts in **1**, whereas the Pt–P distances [Pt–P(1) 2.261(1) Å, Pt–P(2) 2.269(1) Å] are slightly less than those in **1** [2.279(3) Å, 2.283(3) Å]. The coordination plane and the carboxylate group in **12** are almost orthogonal, the dihedral angle being 79.7(1)°. The corresponding values in **1** and in *trans*-$Pt(CO_2Et)_2(PPh_3)_2$ [16] are 78.0° and 80.8°, respectively. The benzene molecules in the crystal of **12** do not appear to interact significantly with other parts of the structure and simply occupy interstices in the lattice.

We suggest that the weaker association in the solid state between the carboxylate units in **12** relative to those in **1** can be correlated with the greater tendency of **12** to dissociate to monomer in CH_2Cl_2, as judged by IR spectroscopy. The difference may be a consequence of steric crowding induced by the bulky PPh_2 groups and by the somewhat shorter Pt–P distances, although obviously electronic effects may also play a role.

3. Experimental details

All reactions were performed under nitrogen by use of standard Schlenk techniques, although the isolated complexes were air-stable in the solid state. Most hydrocarbon and ether solvents were dried by distillation from sodium benzophenone ketyl/tetraglyme. Mesitylene and 2-methoxyethanol were dried over 3 Å molecular sieves and nitrogen gas was bubbled through them for 30–50 min. The following instruments were used for spectroscopic measurements: Jeol FX-200 (^1H NMR, 200 MHz; ^{13}C NMR, 50.1 MHz), Varian XL-200 (^1H NMR, 200 MHz; ^{13}C NMR, 50.3 MHz; ^{31}P NMR, 81.0 MHz), Jeol FX-60 (^{31}P NMR, 24.2 MHz), and Perkin Elmer 683 and FT 1800 (IR). Elemental analyses were performed in-house. The compounds PtX_2-(COD) (X = Cl [17], I [18]), $PtCl(CH_3)(COD)$ [18] and 1,3-$C_6H_4(CH_2P^tBu_2)_2$ [7] were prepared by literature methods. The ligand 1,3-$C_6H_4(CH_2PPh_2)_2$ was made in *ca.* 60% yield by the reaction of 1,3-$C_6H_4(CH_2Br)_2$ with $NaPPh_2$ in liquid ammonia according to Rimml [9]. Analytical and selected IR data are in Table 1, NMR data are in Table 2.

3.1. Preparations

3.1.1. 2,6-({Di-t-butylphosphino)methyl]methyl}phenyl)iodoplatinum(II), $\overline{PtI\{C_6H_3(CH_2P}{}^tBu_2)_2$-2,6} (5)

A mixture of $PtI_2(COD)$ (1.7 g, 3.1 mmol) and 1,3-$C_6H_4(CH_2P^tBu_2)_2$ (**3b**) (1.26 g, 3.2 mmol) in 2-methoxyethanol (40 ml) was stirred and heated under reflux overnight. The solution was evaporated to dryness under reduced pressure and the orange-red solid residue was dissolved in dichloromethane (*ca.* 15 ml). The solution was treated with ethanol until solid just began to precipitate and then set aside at −5°C overnight. The cream crystalline solid that separated (1.14 g) was removed by filtration and more solid (0.48 g) was obtained by addition of water to the red filtrate. The total yield of **5** was 70%. The product did not melt below 230°C.

3.1.2. 2,6-({(Diphenylphosphino)methyl}phenylplatinum(II) complexes

3.1.2.1. $\overline{PtCl\{C_6H_3(CH_2P}Ph_2)_2$-2,6} *(6).* (a) A slurry of $PtCl(CH_3)(COD)$ (60 mg, 0.17 mmol) in 2-methoxyethanol (5 ml) was treated with a solution of 1,3-$C_6H_4(CH_2PPh_2)_2$ (**3a**) (80 mg, 0.17 mmol) in 2-methoxyethanol (10 ml) and the mixture was heated under reflux overnight. The solution was allowed to cool to room temperature and the volume was reduced to *ca.* 10 ml under reduced pressure. The colourless solid that separated was separated by filtration, washed successively with ethanol, water and again with ethanol, and dried in a vacuum to give **6** (100 mg, 83%).

(b) A suspension of $PtCl_2(COD)$ (1.6 g, 4.2 mmol) and **3a** (2.0 g, 4.2 mmol) in mesitylene (250 ml) was heated to reflux and 2-(methylamino)ethanol (0.5 ml) was added carefully. The mixture was stirred vigorously under reflux overnight. The pale brown solution was allowed to cool to room temperature and filtered through Celite to remove a small amount of black solid. The filtrate was evaporate to dryness and the brown, sticky residue was treated with ethanol (2 × 20 ml). The resulting cream solid was dried in a vacuum to give 2.1 g (72%) of **6**, the NMR and IR spectra of which were identical with that obtained in (a).

TABLE 4 (continued)

C(231)–C(236)–C(235)	120.6(4)	C(52)–C(51)–C(56)	122.8(10)
C(51)–C(52)–C(53)	120.0(9)	C(52)–C(53)–C(54)	120.6(11)
C(53)–C(54)–C(55)	113.8(14)	C(54)–C(55)–C(56)	123.7(14)
C(51)–C(56)–C(55)	119.0(11)	C(63)′–C(61)–C(62)	120.7(6)
C(61)–C(62)–C(63)	119.8(5)	C(62)–C(63)–C(61)′	119.6(5)

[a] Primes indicate atoms transformed by the symmetry operation (1 − x, 1 − y, 1 − z).

3.1.2.2. $\overline{Pt(OH)\{C_6H_3(CH_2P}Ph_2)_2\text{-}2,6\}$ *(11).* A solution of **6** (200 mg, 0.28 mmol) in THF (25 ml) was treated with a solution of $AgBF_4$ (60 mg, 0.31 mmol) in THF (2 ml) at room temperature for 3 h. The precipitate of AgCl was removed by centrifugation and the pale yellow filtrate was treated with a solution of KOH (20 mg, 0.36 mmol) in water (1 ml). The solution was stirred overnight, filtered to remove a small amount of black solid, and evaporated to dryness under reduced pressure. The residue was recrystallized from THF/ether to give **11** as a pale yellow powder, m.p. 128–134°C (120 mg, 63%).

3.1.2.3. $\overline{Pt(CO_2H)\{C_6H_3(CH_2P}Ph_2)_2\text{-}2,6\}$ *(12).* A solution of **11** (60 mg, 0.09 mmol) in benzene (10 ml) in a 100 ml Schlenk flask was treated with CO (100 mm Hg) overnight. The colourless crystals that precipitated were filtered off, washed with benzene/ether (1:1), and dried in a vacuum. The yield of **12** was 60 mg (93%). X-ray crystallography (see below) showed that, before being dried in a vacuum, the crystals contained 1.5 mol of C_6H_6 per mol of **12**.

3.1.2.4. $\overline{Pt(CO_2Me)\{C_6H_3(CH_2P}Ph_2)_2\text{-}2,6\}$ *(13).* A solution of **12** (60 mg, 0.08 mmol) in benzene (20 ml) was treated with methanol (3 ml) and the mixture was stirred overnight. Evaporation to dryness gave a pale yellow solid, which was washed with ether and dried in a vacuum to give **13** (50 mg, 86%) as a colourless solid.

4. Crystallography

A crystal of **12**, obtained directly from the reaction (3) above, was coated with a thin film of epoxy resin and sealed in a thin-walled glass capillary. X-ray photographs showed the crystal to be of good quality. The crystal was transferred to a Philips PW1100/20 diffractometer equipped with Mo Kα radiation and unit cell dimensions were determined by least squares analysis of the setting angles of the α_1 peaks of 25 reflections (39° < 2θ < 46°), which were accurately centred on the counter [$\lambda(\alpha_1) = 0.70930$ Å]. Crystal data are given in Table 5. The intensities of reflections $\pm h$, $\pm k$, l were collected as outlined in Table 6. Three standards measured every 90 min showed a small decrease in intensity during data collection (*ca.* 1%) and data were corrected accordingly [19]. Data were also corrected for absorption; A^* ranged from 2.030 to 1.660 [20–22].

The SHELXS-86 computer program [23] was used to solve the structure by direct methods in space group $P\bar{1}$, and XTAL2.4 [20] was used for subsequent calculations. Successful refinement confirmed the selection of $P\bar{1}$ as the space group. The non-hydrogen atoms were refined initially with isotropic and then with anisotropic thermal parameters. Hydrogen atoms (with the exception of the one on the carboxylate group) were included at their calculated positions [r(C–H) = 0.95 Å]. Careful examination of a difference electron-density map [24,25] showed two discrete maxima along the vector between O(11) and O(12) of an adjacent molecule to which it is apparently hydrogen-bonded (Fig. 1), suggesting that the hydrogen atom is disordered over two sites. The fact that the C(10)–O distances are almost equal confirms that the hydrogen atom is not exclusively bound to O(11) or O(12) (Fig. 1), so hydrogen atoms of occupancy 0.5 were placed at each site. Hydrogen atom parameters were not refined but their coordinates were calculated periodically during the refinement.

TABLE 5. Crystal data for $\overline{Pt(CO_2H)\{C_6H_3(CH_2P}Ph_2)_2\text{-}2,6\}\cdot 1.5C_6H_6$ ($\mathbf{12}\cdot 1.5C_6H_6$) [a]

Formula	$C_{42}H_{37}O_2P_2Pt$
FW	830.78
Cryst. system	triclinic
Space group	$P\bar{1}$
a (Å)	10.582(1)
b (Å)	12.326(2)
c (Å)	14.733(2)
α (°)	89.10(2)
β (°)	84.32(2)
γ (°)	69.62(2)
V (Å)	1792.2
Z	2
ρ_{calc} (g cm^{-3})	1.539
μ (cm^{-1})	40.7 [b]

[a] Ambient temperature 24(±2)°C. [b] Mo Kα radiation.

TABLE 6. Data collection and refinement for $\overline{Pt(CO_2H)\{C_6H_3(CH_2P}Ph_2)_2\text{-}2,6\}\cdot 1.5C_6H_6$ ($\mathbf{12}\cdot 1.5C_6H_6$)

Diffractometer	Philips PW1100/20
Radiation	Mo Kα, graphite monochromator
λ of radiation (Å)	0.71069 ($\bar{\alpha}$)
Scan mode	θ–2θ
θ scan width (°)	0.80 + 0.346 tan θ
θ scan speed (° min^{-1})	2
Background	stationary counts of 6s at each side of every scan
Crystal size (mm)	0.33 × 0.23 × 0.18
2θ range (°)	4–54
No. unique reflns	7865
Obs. reflns [a]	6623
No. variables	424
Final R_F [b]	0.025 [c]
Final R_{wF} [d]	0.030 [c]
Final s [e]	1.03 [c]

[a] Reflections with $I > 3\sigma(I)$. [b] $R_F = \Sigma \| F_o | - | F_c \| / | F_o |$. [c] Observed reflections only. [d] $R_{wF} = [\Sigma_w(| F_o | - | F_c |)^2 / \Sigma w | F_o |^2]^{1/2}$. [e] $s = [\Sigma w(| F_o | - | F_c |)^2 / (\text{No. obs} - \text{no. var})]^{1/2}$.

Least-squares refinement was continued until shift/error ratios for all parameters were less than 0.1. The largest features in a final difference electron-density map were close to the platinum atom. The function minimized in least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$. Block-diagonal refinement (unit weights) was used in the early stages and full-matrix ($w = 1/((\sigma(F))^2 + 0.0004(F)^2)$) in the final cycles. Computer programs were run on a VAX 8700 computer. Neutral-atom scattering factors with anomalous dispersion corrections were used throughout [22]. Diagrams were drawn with the aid of ORTEP [26].

Hydrogen atom parameters, temperature factors for the non-hydrogen atoms, selected least-squares planes, torsion angles, additional distances and angles and structure factor amplitudes are available from the authors.

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