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Halo-carbonyl complexes of platinum(II) and palladium(II)

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Abstract

The mononuclear and binuclear square-planar complexes of palladium(II) and platinum(II) *cis*-$PtCl_2(CO)_2$ (**1**), *trans*-$Pt_2Cl_4(CO)_2$ (**2**), *cis*-$PtBr_2(CO)_2$ (**3**), and *cis*-$Pd_2Cl_4(CO)_2$ (**4**), have been prepared by new synthetic procedures and some of them (**2**, **3**, and **4**) structurally characterised by X-ray diffraction methods. In the mononuclear platinum derivatives, *cis*-$PtX_2(CO)_2$, X = Cl, Br, the molecules are arranged in columns, the Pt···Pt separation being 3.378 Å (X = Cl) or 3.65 Å (av., X = Br). The chloride-bridged dinuclear chloro-carbonyl complexes $M_2Cl_4(CO)_2$, M = Pd, Pt, contain terminal chloride and carbonyl groups, *trans* for the platinum derivative **2**, but, unexpectedly, *cis* for the corresponding palladium compound **4**. Packing is based on intermolecular C···X or Pt···Pt interactions, as a function of the nature of the halide. The carbonylation at atmospheric pressure and room temperature of the tetrahalo complexes of platinum(II) in the presence of AlX_3 as halide scavenger leads to $[PtX_3(CO)]^-$ or $PtX_2(CO)_2$, depending on the Pt/AlX_3 molar ratio. The crystal and molecular structural data of $[NBu_4][PtBr_3(CO)]$ (**5**), show the anion to have substantially identical Pt–Br bond distances, the CO ligand performing no trans influence. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Palladium; Platinum; Carbonyls; Structures

1. Introduction

Halo-carbonyl complexes of palladium(II) and platinum(II) have been studied extensively [1], for their unusual properties [2], for their importance in catalysis [3] and, last but not least, for historical reasons, *cis*-$PtCl_2(CO)_2$ being the first metal carbonyl derivative ever reported in the literature [4]. On the other hand, several spectroscopic and structural features are still unexplored, mainly because of the experimental difficulties connected with the isolation and handling of these compounds. The neutral complexes *cis*-$PtX_2(CO)_2$ [1a,c,j] and *trans*-$PtX_2(CO)_2$ [1f, 2], $Pt_2X_4(CO)_2$ (X = Cl, Br, I) [1a,g,2] and $Pd_2X_4(CO)_2$ (X = Cl, Br) [1d,e,h] are known and the reactions between the metal halides and carbon monoxide to give the corresponding carbonyl derivatives have been studied. Interestingly, the mononuclear carbonyl derivatives of platinum(II) are thermodynamically stable at room temperature, see Eqs. (1a) and (1b), with respect to the corresponding anhydrous metal halides and CO, as previously reported for $PtCl_2$ [1j] and PtI_2 [1g] and observed in the course of this work for $PtBr_2$. The direct carbonylation of the three halides is therefore a viable process at room temperature. On the other hand, the mononuclear halo-carbonyl derivatives of palladium(II) are unknown and the dinuclear ones (X = Cl, Br) are in equilibrium with CO and PdX_2 [1e,g,5], see Eq. (2); in the case of X = Cl, the hexanuclear β-$PdCl_2$ [5] was established to be the crystalline phase involved in the equilibrium.

In spite of the considerable interest for palladium(II) and platinum(II) carbonyl derivatives in several fields, the preparative procedures to these compounds still

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required further improvement and, moreover, structural information about unsubstituted halo-carbonyl derivatives of palladium and platinum is limited. As a matter of fact, the crystal and molecular structures of $Pt_2I_4(CO)_2$ [1g] and *cis*-$PtCl_2(CO)_2$ [1j] only have been published.

This paper reports new facile preparative methods to *cis*-$PtX_2(CO)_2$ (X = Cl, Br) and to $M_2Cl_4(CO)_2$ (M = Pd, Pt) by operating at atmospheric pressure of carbon monoxide and describes the crystal and molecular structures of *cis*-$PtBr_2(CO)_2$, *trans*-$Pt_2Cl_4(CO)_2$ and *cis*-$Pd_2Cl_4(CO)_2$.

$$PtX_2 + 2CO \rightarrow PtX_2(CO)_2 \ (X = Cl, Br) \qquad (1a)$$

$$2PtI_2 + 2CO \rightarrow Pt_2I_4(CO)_2 \overset{CO}{\rightleftarrows} 2PtI_2(CO)_2 \qquad (1b)$$

$$2PdX_2 + 2CO \rightleftarrows Pd_2X_4(CO)_2 \ (X = Cl, Br) \qquad (2)$$

2. Results and discussion

2.1. Halide substitutions on platinum precursors

The starting materials to bromocarbonyl platinum complexes were obtained by chloride/bromide substitution. For instance, the preparation of $[NBu_4]_2[PtBr_4]$ was accomplished by two alternative methods: (a) from aqueous K_2PtCl_4 by halide substitution with KBr, see Eq. (3), and extracting the resulting $[Pt_2Br_6]^{2-}$ into CH_2Cl_2 using $[NBu_4]Br$ as a phase-transfer agent; (b) in chlorinated solvents from $[NBu_4]_2[PtCl_4]$ by reaction with RBr (R = H, ^{t}Bu).

Method (a) requires an excess of KBr. As a matter of fact, using a Br^-/Pt molar ratio of 4.5 at room temperature, a mixture of the species $[PtCl_nBr_{4-n}]^{2-}$ (n = 0–3) resulting from partial substitution was obtained, see Equilibria (3a)–(3d). The different complex anions can be detected by ^{195}Pt-NMR [6] as follows: $[PtCl_3Br]^{2-}$, δ −1846 ppm; $[PtCl_2Br_2]^{2-}$, two resonances at δ −2087 and −2098 ppm, due to the *trans*- and *cis*-isomer, respectively; $[PtClBr_3]^{2-}$, δ −2366 ppm and $[PtBr_4]^{2-}$, δ −2662 ppm. On the basis of the relative peak intensities the prevailing species is $[PtClBr_3]^{2-}$. For complete substitution, a saturated solution of KBr was used, corresponding to a nominal Br^-/Pt molar ratio ≥ 20.

$$[PtCl_4]^{2-} + 4Br^- \rightleftarrows [PtBr_4]^{2-} + 4Cl^- \qquad (3)$$

$$[PtCl_4]^{2-} + Br^- \rightleftarrows [PtBrCl_3]^{2-} + Cl^- \qquad (3a)$$

$$[PtBrCl_3]^{2-} + Br^- \rightleftarrows [PtBr_2Cl_2]^{2-} + Cl^- \qquad (3b)$$

$$[PtBr_2Cl_2]^{2-} + Br^- \rightleftarrows [PtBr_3Cl]^{2-} + Cl^- \qquad (3c)$$

$$[PtBr_3Cl]^{2-} + Br^- \rightleftarrows [PtBr_4]^{2-} + Cl^- \qquad (3d)$$

Thermodynamic data about substitution reactions of this type are not numerous: a paper by Leden and Chatt [7] reports $\Delta G° = -0.7$ kcal mol^{-1} for reaction (4) in aqueous solution. Thus,

$$[PtCl_3(C_2H_4)]^- + Br^- \rightleftarrows [PtCl_2Br(C_2H_4)]^- + Cl^- \qquad (4)$$

the hydration free energy [8,9] of Cl^- (−74.8 kcal mol^{-1}) with respect to that of Br^- (−67.9 kcal mol^{-1}) is mainly responsible for the observed exchange.

As far as point (b) is concerned, when the preparation of $[NBu_4]_2[PtBr_4]$ was carried out by treating $[NBu_4]_2[PtCl_4]$ with ^{t}BuBr in $CDCl_3$, see Eq. (5), a mixture of the chloride and bromide derivatives was also obtained. By ^{195}Pt-NMR and using a ^{t}BuBr/Pt molar ratio of 5.5 it was established that at room temperature in 7 days the platinum complexes $[PtBr_3Cl]^{2-}$ (δ −2270 ppm), $[Pt_2Br_6]^{2-}$ (δ −2318 ppm) and $[PtBr_4]^{2-}$ (δ −2559 ppm) are present in equilibrium with relative intensities 1:3:4. Using a large excess of ^{t}BuBr it was possible to convert this mixture to $[Pt_2Br_6]^{-2-}$ and $[PtBr_4]^{2-}$.

$$[NBu_4]_2[PtCl_4] + 4{}^tBuBr \rightarrow [NBu_4]_2[PtBr_4] + 4{}^tBuCl \qquad (5)$$

If $[NBu_4]_2[PtCl_4]$ was treated with the stoichiometric amount of anhydrous HBr in CH_2Cl_2 a fast reaction was observed leading to $[NBu_4]_2[Pt_2Br_6]$ exclusively, see Eq. (6).

$$\begin{aligned}&2[NBu_4]_2[PtCl_4] + 8HBr\\ &\rightarrow [NBu_4]_2[PtBr_6] + 8HCl + 2[NBu_4]Br \qquad (6)\end{aligned}$$

The $\Delta G_f°$ of ^{t}BuCl, ^{t}BuBr, HCl, HBr are −16.0, −7.9, −22.8 and −12.8 kcal mol^{-1}, respectively [10]. The contributions to $\Delta G°$ due to the bromide exchange are −6.9, −8.1 and −10.0 kcal mol^{-1} for $Br^-_{(aq.)}$, ^{t}BuBr and HBr, respectively, thus justifying the observed exchange increasing in the sequence $Br^-_{(aq.)} < {}^tBuBr <$ HBr.

2.2. Syntheses of platinum and palladium halocarbonyls

Relevant to the thermodynamics of these systems is the early preparation [4] of *cis*-$PtCl_2(CO)_2$: Schützenberger first converted [4b] a platinum sponge into a platinum chloride with chlorine at 250°C, further reaction at lower temperature with CO giving the colourless *cis*-$PtCl_2(CO)_2$ and $Pt_2Cl_4(CO)_2$.

We had shown earlier that the dinuclear $Pt_2Cl_4(CO)_2$ undergoes carbonylation to *cis*-$PtCl_2(CO)_2$ through the intermediacy of *trans*-$PtCl_2(CO)_2$ [1f]. We have now established that $PtCl_2$ suspended in CH_2Cl_2 or $SOCl_2$ reacts at moderate rate with CO at room temperature and atmospheric pressure producing *cis*-$PtCl_2(CO)_2$ (**1**), 1 mmol of platinum chloride being converted completely in about 3 days.

Compound **1** can be readily prepared also by carbonylation of $[PtCl_4]^{2-}$ in the presence of $AlCl_3$ as halide scavenger in chlorinated solvents, the tetrachloroplatinate(II) anion, as the tetrabutylammonium derivative, being obtained by solvent-extraction from aqueous solution, see Eq. (7).

$$[PtCl_4]^{2-}_{(aq.)} + 2NBu_4Cl_{(CH_2Cl_2)} \rightarrow [NBu_4]_2[PtCl_4]_{(CH_2Cl_2)} + 2Cl^-_{(aq.)} \quad (7)$$

$$[NBu_4]_2[PtCl_4] + AlCl_3 + CO \rightarrow [NBu_4][PtCl_3(CO)] + [NBu_4][AlCl_4] \quad (8)$$

$$[PtCl_4]^{2-} + CO \rightleftarrows [PtCl_3(CO)^- + Cl^- \quad (9)$$

$$[NBu_4][PtCl_3(CO)]^- + AlCl_3 + CO \rightarrow [NBu_4][AlCl_4] + trans\text{-}PtCl_2(CO)_2 \quad (10a)$$

$$trans\text{-}PtCl_2(CO)_2 \rightarrow cis\text{-}PtCl_2(CO)_2 \quad (10b)$$

$$[NBu_4][PtCl_3(CO)] + AlCl_3 \rightarrow [NBu_4][AlCl_4] + 1/2trans\text{-}Pt_2Cl_4(CO)_2 \quad (11)$$

The reaction sequence was followed spectroscopically by IR and NMR, and by gas-volumetric measurements of the CO uptake. In order to avoid the intermediate precipitation of $PtCl_2$, which subsequently would react slowly with CO to yield **1**, the carbonylation is best carried out by adding the first equivalent of $AlCl_3$, and allowing the system to form the monocarbonylated product of Eq. (8). It is interesting to note that $[NBu_4]_2[PtCl_4]$ itself (i.e. even in the absence of $AlCl_3$) reacts with CO producing the $[PtCl_3(CO)]^-$ anion: in about 40 h at 21°C, a 1.3×10^{-2} M solution of $[NBu_4]_2[PtCl_4]$ in *sym*-$C_2H_4Cl_2$ absorbed CO up to a CO/Pt molar ratio of 0.65, as for Equilibrium 9.

Only after the addition of one equivalent of $AlCl_3$, the equilibrium was displaced to the right upon subtraction of Cl^- and further carbon monoxide was rapidly absorbed up to a CO/Pt molar ratio of 1. Under these conditions, the IR spectrum is characterized by a band at 2098 cm^{-1}, due to $[PtCl_3(CO)]^-$. The addition of a second equivalent of $AlCl_3$ was followed by the rapid uptake of further CO forming *trans*- and then *cis*-$PtCl_2(CO)_2$, see reactions (10a) and (10b), as evidenced by the band at 2098 cm^{-1} being replaced by bands at 2150 cm^{-1} (*trans*-isomer) and 2138, 2178 cm^{-1} (*cis*-isomer). These experiments show that the *trans*-isomer is the primary product of the reaction, in agreement with the strong *trans* effect of ligated CO, followed by isomerization to **1**. *trans*-$PtCl_2(CO)_2$ was also found to be the primary product of the carbonylation of the dinuclear *trans*-$Pt_2Cl_4(CO)_2$ [1f]: if the *trans* geometry of the dimer (as effectively found in the solid state, vide infra) is assumed, the strong *trans* effect of coordinated CO can be again considered to be responsible for this observation.

When the treatment with $AlCl_3$ of the intermediate $[PtCl_3(CO)]^-$ was carried out under dinitrogen rather than under carbon monoxide, the dinuclear complex *trans*-$Pt_2Cl_4(CO)_2$ (**2**) was obtained exclusively, see Eq. (11). This methodology can therefore be directed towards the formation of the mononuclear- or the dinuclear compound simply by a change of the operating procedure in the final step.

The preparation of *cis*-$PtBr_2(CO)_2$ (**3**) was performed from $[NBu_4]_2[PtBr_4]$ and CO by using $AlBr_3$ as bromide scavenger. The reaction, monitored by gasvolumetry and IR spectroscopy, shows similar features to the corresponding chloride system.

$$[NBu_4]_2[PtBr_4] + CO + AlBr_3 \rightarrow [NBu_4][PtBr_3(CO)] + [NBu_4][AlBr_4] \quad (12)$$

$$[NBu_4][PtBr_3(CO)] + CO + AlBr_3 \rightarrow trans\text{-}PtBr_2(CO)_2 + [NBu_4][AlBr_4] \quad (13)$$

$$trans\text{-}PtBr_2(CO)_2 \rightarrow cis\text{-}PtBr_2(CO)_2 \quad (14)$$

Compound **3** has been prepared alternatively by reacting **1** with RBr (R = ^{t}Bu, ^{s}Bu), see Eq. (15).

$$cis\text{-}PtCl_2(CO)_2 + 2RBr \rightarrow cis\text{-}PtBr_2(CO)_2 + 2RCl \quad (15)$$

By using a slight excess of ^{t}BuBr in CH_2Cl_2 as solvent, the high-yielding reaction is over in a few minutes. When the reaction was carried out in CCl_4, the conversion, monitored by ^{1}H-NMR, was about 75% after 30 min. With ^{s}BuBr the reaction proceeded more slowly, a conversion of about 33% being observed in 48 h. These data suggest that the cleavage of the Br–C bond is probably the rate-determining step.

Another method of preparation of *cis*-$PtBr_2(CO)_2$ consists of treating a suspension of $PtBr_2$ in a chlorinated hydrocarbon with CO at room temperature and atmospheric pressure (under these conditions the reaction is very slow), or under a moderate CO pressure (about 6 atm).

Dehalogenation of $[Pd_2Cl_6]^{2-}$ as the tetrabutylammonium derivative with $AlCl_3$ in the presence of CO led to the dinuclear *cis*-$Pd_2Cl_4(CO)_2$ (**4**), see Eq. (16).

$$[NBu_4]_2[Pd_2Cl_6] + 2AlCl_3 + 2CO \rightarrow Pd_2Cl_4(CO)_2 + 2NBu_4[AlCl_4] \quad (16)$$

The IR data of the neutral platinum(II) and palladium(II) carbonyl derivatives are reported in Table 1, which can be used, with some precaution, for structural information. Although some of these compounds have been known for many years, structural information in the solid state is still rather limited. We therefore decided to carry out an extended study of their solid-state structures. As we shall see later, the IR spectra, suggesting a similar molecular arrangement for the dinuclear chloro-carbonyl derivatives of platinum(II) and palladium(II), were misleading as these compounds were found to have different solid-state molecular structures.

2.3. Crystal structure determinations

The molecular structure of **2**, *trans*-$Pt_2Cl_4(CO)_2$, is shown in Fig. 1. Bond distances and angles are listed in Table 2.

Table 1
IR spectra (ν_{CO}, cm^{-1}) of some carbonyl derivatives of platinum(II) and palladium(II)

	Nujol	*sym*-$C_2H_2Cl_4$	Heptane
cis-$PtCl_2(CO)_2$ (**1**)	2187, 2152 [a]	2179, 2136 [1c]	2167, 2120 [1g]
trans-$Pt_2Cl_4(CO)_2$ (**2**)	2146 [1d] 2146 [a,b]	2138 [a,c]	2130 [1g]
cis-$PtBr_2(CO)_2$ (**3**)	2167, 2122 [a]	2170, 2130 [1g]	2156, 2115 [1g]
$Pt_2Br_4(CO)_2$	2129 [a,b]	2127 [1g]	2122 [1g]
cis-$Pd_2Cl_4(CO)_2$ (**4**)	2167 [1d]	2166 [c] [1h]	2159 [d] [1d]

[a] This work.
[b] PCTFE (polychlorotrifluoroethylene).
[c] CH_2Cl_2.
[d] Cyclohexane.

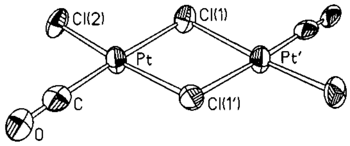

Fig. 1. The molecular structure of *trans*-$Pt_2Cl_4(CO)_2$ (**2**). The apex in the labels have the same meaning as in Table 2. Thermal ellipsoids are at 30% probability.

Table 2
Bond lengths (Å) and angles (°) for *trans*-Pt_2 $Cl_4(CO)_2$ (**2**) [a]

Pt–C	1.86(5)	Pt–Cl(1′)	2.396(12)
Pt–Cl(2)	2.127(8)	C–O	1.08(5)
Pt–Cl(1)	2.287(13)		
C–Pt–Cl(2)	89.4(17)	Cl(2)–Pt–Cl(1′)	173.7(7)
C–Pt–Cl(1)	176.6(18)	Cl(1)–Pt–Cl(1′)	85.2(2)
Cl(2)–Pt–Cl(1)	93.8(4)	Pt–Cl(1)–Pt′	94.5(2)
C–Pt–Cl(1′)	91.5(18)	O–C–Pt	176(4)

[a] Symmetry transformations used to generate equivalent atoms: $' = -x+2, -y+1, z$.

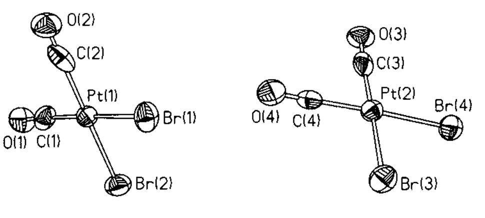

Fig. 2. The molecular structure of the two independent molecules in the crystal of *cis*-$PtBr_2(CO)_2$ (**3**). Thermal ellipsoids are at 30% probability.

Table 3
Main bond lengths (Å) and angles (°) of *cis*-$PtBr_2(CO)_2$ (**3**)

Pt(1)–C(1)	1.86(4)	Pt(2)–C(4)	1.88(3)
Pt(1)–C(2)	1.96(6)	Pt(2)–C(3)	1.89(5)
Pt(1)–Br(1)	2.411(4)	Pt(2)–Br(3)	2.416(4)
Pt(1)–Br(2)	2.417(4)	Pt(2)–Br(4)	2.417(4)
C(1)–O(1)	1.12(4)	C(3)–O(3)	1.17(5)
C(2)–O(2)	1.06(5)	C(4)–O(4)	1.12(4)
C(1)–Pt(1)–C(2)	93.8(17)	C(4)–Pt(2)–C(3)	95.0(14)
C(1)–Pt(1)–Br(1)	178.3(12)	C(4)–Pt(2)–Br(4)	176.0(9)
C(2)–Pt(1)–Br(1)	87.7(12)	C(3)–Pt(2)–Br(4)	89.0(10)
C(1)–Pt(1)–Br(2)	87.1(12)	C(4)–Pt(2)–Br(3)	85.0(9)
C(2)–Pt(1)–Br(2)	179.0(12)	C(3)–Pt(2)–Br(3)	178.8(9)
Br(1)–Pt(1)–Br(2)	91.35(17)	Br(3)–Pt(2)–Br(4)	91.08(14)
O(1)–C(1)–Pt(1)	177(4)	O(3)–C(3)–Pt(2)	176(3)
O(2)–C(2)–Pt(1)	178(4)	O(4)–C(4)–Pt(2)	179(3)

Compound **2** is constituted by two $\{PtCl_3(CO)\}$ squares joined by two bridging chlorides. The squares deviate somewhat from coplanarity, the point symmetry of the molecule being C_2, rather than C_{2h}. For each $\{PtCl_3(CO)\}$ system, the Pt, Cl(1), Cl(1′), C and O atoms are coplanar within 0.029 Å, while the Cl(2) atom is 0.228 Å out of this plane. Moreover, the dihedral angle at the bridging chlorides Pt–Cl(1)···Cl(1′)–Pt′ is 171.8° and the Pt–Cl(1) and Pt–Cl(1′) distances differ by 0.11 Å. The Pt–Cl_t (Cl_t = terminal chloride) and Pt–CO distances are similar to those observed in *cis*-$PtCl_2(CO)_2$, whereas the Pt–Cl_b (Cl_b = bridging chloride) distances are, as expected, longer by 0.16 and 0.27 Å, respectively. The molecules are stacked on each other, with completely eclipsed atoms, the separation being 3.525 Å (**c** translation). Different from **3** (vide infra) and *cis*-$PtCl_2(CO)_2$ [1j], where the shortest contacts are between the halide and the carbonyl carbon, the shortest contact is between the platinum atoms.

The molecular structure of *cis*-$PtBr_2(CO)_2$, **3**, is shown in Fig. 2. Bond distances and angles are listed in Table 3.

The molecular structure consists of a square-planar disposition of two bromines and two carbonyl groups around platinum.

The geometry is similar to that of *cis*-$PtCl_2(CO)_2$ [1j]. However, two independent molecules of *cis*-$PtBr_2(CO)_2$ are present in the asymmetric unit. As in the crystal of *cis*-$PtCl_2(CO)_2$, the molecules are stacked with the bromide facing the carbonyl carbon of the nearest molecules, the C···Br distances being: C(1)···Br(1), 3.599; C(2)···Br(2), 3.581; C(3)···Br(3), 3.603; C(4)···Br(4), 3.665 Å. The two independent molecules form stacks along the **a** and **b** directions, respectively. The Pt···Pt distances within the stacks are 3.615 and 3.656 Å and 3.640 and 3.702 Å, respectively, whereas the Pt···Pt···Pt angles are 157 and 170°, respectively. The wider stacking of the bromide derivative with respect to *cis*-$PtCl_2(CO)_2$ is due to the larger size of the bromide.

The molecular structure of **4**, *cis*-$Pd_2Cl_4(CO)_2$, is shown in Fig. 3 and Table 4 lists the bond distances and angles.

In **4** the CO groups are in *cis* positions. The two {Pd Cl_3(CO)} squares are almost exactly planar (maximum deviation, 0.019 Å) and share the Cl(2)···Cl(3) edge at a dihedral angle of 174.9°. The inversion centres present in the crystal structure produce pairs of molecules, whose centroids are 3.75 Å apart, with the carbonyl groups of the two molecules within each pair pointing out in opposite directions. The Pd···Pd non-bonding contact within each pair is 3.624 Å. The shortest non-bonding contacts are, however, between atoms belonging to molecules of different pairs, namely 3.388 Å for Cl(4)···Pd(2′), 3.262 Å for Cl(1)···O(1″) and 3.358 Å for Cl(1)···C(1‴) ($' = -1/2-x,\ -1/2+y,\ 1/2-z$; $'' = x,\ -1+y,\ z$; $''' = 1/2-x,\ -1/2+y,\ 1/2-z$).

The expected square-planar coordination around platinum(II) was found for the ionic compound **5** $[NBu_4][PtBr_3(CO)]$. The structural parameters [C(1)–Pt, 1.85(2), Br(1)–Pt, 2.427(2); Br(2)–Pt, 2.423(2); Br(3)–Pt, 2.428 Å; C(1)–Pt–Br(2) 177.4°] correspond to practically identical Pt–Br distances, in agreement with the earlier findings for the corresponding chloride derivative $[NBu_4][PtCl_3(CO)]$ [11],which has a Pt–Cl distance *trans* to the CO ligand of 2.289(3) Å. In other words, as noted earlier also for $[NBu_4][PdX_3(CO)]$ [1h], X = Cl, Br, the CO ligand has no appreciable *trans* influence in these three cases. Moreover, the C(1)–Pd distance is 1.87(1) Å, i.e. practically the same as the C–Pt distance of the corresponding platinum complex, in agreement with the substantially identical ionic radii of platinum(II) (0.60 Å) and palladium(II) (0.64 Å) [12].

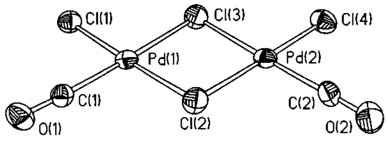

Fig. 3. The molecular structure of *cis*-$Pd_2Cl_4(CO)_2$ (**4**). Thermal ellipsoids are at 30% probability.

Table 4
Bond lengths (Å) and angles (°) of *cis*-$Pd_2Cl_4(CO)_2$ (**4**)

Pd(1)–C(1)	1.891(13)	Pd(2)–C(2)	1.879(15)
Pd(1)–Cl(1)	2.260(3)	Pd(2)–Cl(4)	2.260(3)
Pd(1)–Cl(3)	2.327(3)	Pd(2)–Cl(3)	2.328(3)
Pd(1)–Cl(2)	2.331(3)	Pd(2)–Cl(2)	2.336(3)
C(1)–O(1)	1.105(13)	C(2)–O(2)	1.112(14)
C(1)–Pd(1)–Cl(1)	86.1(3)	C(2)–Pd(2)–Cl(4)	87.0(4)
C(1)–Pd(1)–Cl(3)	177.6(3)	C(2)–Pd(2)–Cl(3)	178.5(4)
Cl(1)–Pd(1)–Cl(3)	91.55(12)	Cl(4)–Pd(2)–Cl(3)	91.62(12)
C(1)–Pd(1)–Cl(2)	95.5(3)	C(2)–Pd(2)–Cl(2)	94.7(4)
Cl(1)–Pd(1)–Cl(2)	177.93(11)	Cl(4)–Pd(2)–Cl(2)	178.18(13)
Cl(3)–Pd(1)–Cl(2)	86.84(11)	Cl(3)–Pd(2)–Cl(2)	86.70(11)
Pd(1)–Cl(2)–Pd(2)	92.91(11)	Pd(1)–Cl(3)–Pd(2)	93.23(11)
O(1)–C(1)–Pd(1)	177.4(11)	O(2)–C(2)–Pd(2)	178.4(11)

3. Conclusions

This paper, which is believed to be relevant for people interested in carbonyl derivatives of platinum(II) and palladium(II), has produced some new observations.

1. The dinuclear platinum(II) and palladium(II) chloro-carbonyl complexes $M_2Cl_4(CO)_2$ are not isostructural and have a different arrangement of the ligands. In fact, while the platinum(II) derivative **2** has the *trans* structure, the palladium(II) compound **4** has been shown to prefer a *cis* arrangement of the ligands in the solid state. This was unexpected in view of the similarity of the IR spectra, see Table 1, in Nujol as medium or in solution (*sym*-$C_2H_2Cl_4$ or heptane), once the shift of the CO stretching vibrations towards high wavenumbers for palladium(II), vide infra, is taken into consideration. It is interesting to note that the *cis* structure **4** was considered as a possibility for the uncharged chlorocarbonyl of palladium(II) [13], although a less likely one on the basis of the '*uneven distribution of electron density in the molecule and uneven strengths of bonds linking similar atoms*'. The presence of only one ν_{CO} for the palladium(II) derivative was taken initially as evidence [1d,h] for a *trans* arrangement. This structural assignment must now be revised. Assuming that the *cis* structure persists in solution too, the IR observation is to be attributed to the fact that the two fragments of the molecule are not vibrationally coupled.
2. The IR data of Table 1 confirm the earlier notion [1d,h] that palladium(II) carbonyl derivatives have ν_{CO}s higher than those of the corresponding platinum(II) derivatives. This has been attributed [2] to the presumably negligible π–back bond component within the Pd–CO bond. Other interpretations of the experimental observations concerning the high ν_{CO}s for carbonyl derivatives of late transition metals [Pd(II), Pt(II), Ag(I), Au(I)] in their *usual* oxidation states, both neutral and cationic, have been proposed [14a,b]. However, we still prefer to maintain the earlier suggestion [2], corroborated by further experimental data by Strauss and coworkers [15a,b] and by Aubke and coworkers [15c–e] that π–backbonding should not be heavily involved in a satisfactory description of these metal complexes.
3. In the $[MX_3(CO)]^-$ anions of platinum(II) and palladium(II), for which three structural determina-

tions are now available [1h,11] with the same countercation, no elongation of the halide ligand *trans* to the carbonyl group has been observed.

4. In conjunction with the structural data reported earlier for *trans*-$Pt_2I_4(CO)_2$ [1g] this paper shows that within the dinuclear units, the non-bonding Pt···Pt distance increases from 3.441 Å in *trans*-$Pt_2Cl_4(CO)_2$ (**2**), to 3.846 Å in *trans*-$Pt_2I_4(CO)_2$. It is interesting to note that the intramolecular Pd···Pd distance in the dinuclear *cis*-$Pd_2Cl_4(CO)_2$ (**4**) is 3.383 Å, i.e. similar to the corresponding contact in the platinum(II) complex, in agreement again with the similar ionic radii, as noted above. The intramolecular nonbonding distance (3.525 Å) is comparable to the *interlayer* Pt···Pt distance of *trans*-$Pt_2Cl_4(CO)_2$.
5. In view of the high reactivity of these systems of platinum(II) and palladium(II) towards nucleophilic reagents, some of the compounds reported in this paper have been [16] and will be further used for the chemical deposition under mild conditions of the corresponding metals on metal oxide surfaces.

4. Experimental

4.1. General

All manipulations were performed under an atmosphere of prepurified *dry* dinitrogen or carbon monoxide. Solvents were carefully dried by conventional methods prior to use. IR spectra were recorded with Perkin–Elmer spectrophotometers (mod. 283 B or 1725X FT-IR) in solution or as Nujol or polychlorotrifluoroethylene (PCTFE) mulls prepared under rigorous exclusion of moisture. ^1H-, ^{13}C-, ^{31}P- and ^{195}Pt-NMR spectra were recorded with a Varian Gemini 200 BB spectrometer, chemical shifts being reported in ppm versus $SiMe_4$ for ^1H and ^{13}C, versus 85% H_3PO_4 and H_2PtCl_6 in D_2O for ^{31}P and ^{195}Pt, respectively.

Commercial aqueous solutions of K_2PtCl_4 (Chimet S.p.A., Badia al Pino, Arezzo, Italy) were used. The halides $AlCl_3$ and $AlBr_3$ (Aldrich) were sublimed in vacuo and stored under N_2, while *cis*-$Pd_2Cl_4(CO)_2$ was prepared according to the literature [1d,e] or from $[NBu_4]_2[Pd_2Cl_6]$, as described below.

4.2. $[NBu_4]_2[PtCl_4]$ by solvent extraction

An aqueous solution of K_2PtCl_4 (0.154 M, 90 ml, 13.9 mmol) was shaken in a separatory funnel with a solution of NBu_4Cl (7.72 g, 27.8 mmol) in CH_2Cl_2 (130 ml). The organic layer immediately became red, while the aqueous solution discoloured. The CH_2Cl_2 layer was separated, concentrated to a small volume by gentle warming at atmospheric pressure and then evaporated to dryness in vacuo. The red product was dried over P_4O_{10} in vacuo for 3 h (9.35 g, 81.8% yield). Anal. Calc for $C_{32}H_{72}Cl_4N_2Pt$: Cl, 17.2; Pt, 23.7. Found: Cl, 16.9; Pt, 23.1%. ^1H-NMR ($CDCl_3$, 298 K): δ 3.65 (2 H, t, NCH_2); 1.78 (2 H, m, NCH_2CH_2); 1.56 (2 H, sext,CH_2CH_3); 0.99 (3 H, t, CH_3) ppm. ^{195}Pt-NMR ($CDCl_3$, 298 K): δ −1574 ppm.

4.3. Halide exchange

4.3.1. From aqueous $K_2[PtCl_4]$

An aqueous solution of K_2PtCl_4 (0.154 M, 17 ml, 2.62 mmol) was saturated with KBr. The orange solution became red-brown and was shaken with a solution of NBu_4Br (1.71 g, 5.30 mmol) in CH_2Cl_2 (40 ml) in a separatory funnel. The organic layer immediately became red-brown, and the aqueous phase discoloured. The CH_2Cl_2 solution was separated and evaporated to dryness under reduced pressure. The oily residue was treated in vacuo at 50°C for 2 h. The product thus obtained was dried over P_4O_{10} for 3 h in vacuo (2.11 g, 80.6% yield). Anal. Calc for $[NBu_4]_2[PtBr_4]$, $C_{32}H_{72}Br_4N_2Pt$: Br, 32.0; Pt, 19.5. Found: Br, 32.5; Pt, 18.9%. ^1H-NMR ($CDCl_3$, 298 K): δ 3.63 (2 H, t, NCH_2); 1.75 (2 H, m, NCH_2CH_2); 1.54 (2 H, sext,CH_2CH_3); 0.98 (3 H, t, CH_3) ppm. ^{195}Pt-NMR ($CDCl_3$, 298 K): δ −2560 ppm. After 15 d at room temperature (r.t.) a new resonance of low intensity at δ −2318 ppm was detected due to $[Pt_2Br_6]^{2-}$ (vide infra).

In an experiment, KBr (49.5 mg, 0.416 mmol) and 1.1 ml of water were added to 0.720 g of an aqueous solution of K_2PtCl_4 (2.47% platinum; 1.78×10^{-2} g of Pt; 9.11×10^{-2} mol). The resulting solution was transferred into a NMR tube containing 0.3 ml of D_2O for ^{195}Pt-NMR monitoring. After 18 h the spectrum showed resonances at −1846 {$[PtBrCl_3]^{2-}$}, −2087 and −2098 {*trans*- and *cis*-$[PtBr_2Cl_2]^{2-}$}, −2366 {$[PtBr_3Cl]^{2-}$} and −2662 ppm {$[PtBr_4]^{2-}$}, the most intense peak being that at −2366 ppm. Spectra recorded after several days showed no change.

In another experiment, K_2PtCl_4 (9.20×10^{-2} mol) was treated with KBr (77.5 mg, 0.651 mmol) in $H_2O + D_2O$ (0.6 ml + 0.3 ml). After 90 min, a ^{195}Pt-NMR spectrum showed resonances at −1625 {$[PtCl_4]^{2-}$}, −1846 {$[PtBrCl_3]^{2-}$}, −2087 {*trans*-$[PtBr_2Cl_2]^{2-}$}, −2366 {$[PtBr_3Cl]^{2-}$} and −2662 ppm {$[PtBr_4]^{2-}$}, the most intense being the first one. After 24 h, the last two resonances only were observed. After addition of more KBr (138 mg, 1.16 mmol), a spectrum recorded 18 h later showed the resonances due to $[PtBr_3Cl]^{2-}$ and $[PtBr_4]^{2-}$, the latter being predominant.

4.3.2. From $[NBu_4]_2[PtCl_4]$ in $CDCl_3$

4.3.2.1. With ^{t}BuBr. A solution in $CDCl_3$ (1 ml) of ^{t}BuBr (0.1 ml, $d = 1.189$ g ml^{-1}, 0.868 mmol) and $[NBu_4]_2[PtCl_4]$ (129 mg, 0.157 mmol) was prepared in a

NMR tube. After 20 h a ^{195}Pt-NMR spectrum of the solution showed three peaks at −2004 {$[PtBr_2Cl_2]^{2-}$}, −2270 {$[PtBr_3Cl]^{2-}$}, and −2560 ppm {$[PtBr_4]^{2-}$}. After 48 h the spectrum showed a new peak of low intensity at −2318 ppm {$[Pt_2Br_6]^{2-}$}. After 72 h the intensities of the peaks at −2004 and −2270 ppm decreased, while increased the peak at −2318 ppm. After 6 days at r.t. and three days at 40°C, the intensity of the peaks at −2318 and −2560 ppm increased. Addition of an excess of ^{t}BuBr (1.00 ml, 8.68 mmol) caused the disappearance of the lower field resonances, and the peaks at −2318 and −2560 ppm had an intensity ratio of 1.25.

4.3.2.2. With HBr. In a 100 ml flask, equipped with a silicone-rubber stopper, CH_2Cl_2 (20 ml) and $[NBu_4]_2[PtCl_4]$ (0.420 g, 0.511 mmol) were introduced under N_2. After evacuation, gaseous HBr (50 ml, about 2 mmol) was added through the plug by syringe. A ^{195}Pt-NMR spectrum recorded after 15 h showed the peak at −2297 ppm due to $[Pt_2Br_6]^{2-}$ only. The assignment was confirmed in the following manner. To a suspension of $PtBr_2$ (0.240 g, 0.676 mmol) in CH_2Cl_2 (20 ml) NBu_4Br (0.230 g, 0.713 mmol) was added, giving a red–brown solution. The solid residue obtained by evaporating the solvent under reduced pressure was collected (0.37 g, 77% yield). Anal. Calc. for $[NBu_4]_2[Pt_2Br_6]$, $C_{32}H_{72}Br_6N_2Pt_2$: Br, 35.4; Pt, 28.8. Found: Br, 34.6; Pt, 27.9%. ^{195}Pt-NMR (CH_2Cl_2), δ −2297 ppm.

4.4. $[NBu_4]_2[Pd_2Cl_6]$

An aqueous acidic (for hydrochloric acid) solution (33 ml) of $PdCl_2$ (4.70 mmol) was treated in a separatory funnel with a solution of NBu_4Cl (1.303 g, 4.69 mmol) in *sym*-$C_2H_2Cl_4$ (50 ml). The aqueous layer immediately discoloured and the organic layer became red–orange: the latter one was transferred to a flask and evaporated to dryness under reduced pressure. The red residue was treated with heptane (30 ml). The suspension was filtered and the solid dried in vacuo (90% yield). Anal. Calc. for $[NBu_4]_2[Pd_2Cl_6]$, $C_{32}H_{72}Cl_6N_2Pd_2$: C, 42.2; H, 8.0; N, 3.1. Found: C, 42.0; H, 7.9; N, 2.6%.

4.5. *cis*-$PtCl_2(CO)_2$ (**1**)

4.5.1. From $[NBu_4]_2PtCl_4$

Solid $[NBu_4]_2PtCl_4$, obtained from an aqueous solution of K_2PtCl_4 (6.70 mmol) as for the above description, was dissolved in CH_2Cl_2 (50 ml). The solution was saturated with CO and 0.850 g (6.37 mmol) of $AlCl_3$ were added. After stirring for 20 h, an IR spectrum showed an intense band at 2098 cm^{-1} due to $[NBu_4][PtCl_3(CO)]$. A second equivalent of $AlCl_3$ (0.900 g, 6.75 mmol) was introduced and the mixture was stirred under CO for 6 h at atmospheric pressure at r.t. [carbonyl bands at 2178 and 2138 cm^{-1} due to *cis*-$PtCl_2(CO)_2$]. The suspension was filtered and the filtrate was evaporated to dryness. The colourless residue was extracted with CCl_4 (100 ml) in a Soxhlet for 5 h. The analytically and spectroscopically pure product was recovered by filtration of the extract and dried in vacuo (1.28 g, 60.6% yield).

In a gas-volumetric experiment carried out in 1,2-dichloroethane (20 ml) at 21.4°C, 213 mg (0.259 mmol) of $[NBu_4]_2[PtCl_4]$ absorbed CO up to a CO/Pt molar ratio of 0.65 in 40 h. By addition of $AlCl_3$ (37.5 mg, 0.281 mmol) further CO was absorbed in 2 h (final CO/Pt molar ratio of 0.97). Additional $AlCl_3$ (44.8 mg, 0.336 mmol) gave new CO uptake (1.5 h) corresponding to a total CO/Pt molar ratio of 1.90. The IR spectrum of the solution showed bands at 2178 and 2138 cm^{-1} [*cis*-$PtCl_2(CO)_2$] and at 2150 cm^{-1} [*trans*-$PtCl_2(CO)_2$]. After 15 h under CO, only the bands due to the *cis*-isomer were observed.

4.5.2. From $PtCl_2$

A suspension of $PtCl_2$ (280 mg, 1.05 mmol) in CH_2Cl_2 (30 ml) was stirred under CO at r.t. for 3 days. The resulting colourless solution, which showed the IR bands of *cis*-$PtCl_2(CO)_2$, was added of heptane (100 ml) and stored at −30°C for 3 days. The product was collected by filtration and dried in vacuo (284 mg, 84% yield). Analogous results were obtained by operating in $SOCl_2$. In a gas-volumetric experiment carried out in *sym*-$C_2H_2Cl_4$ (25 ml) 215 mg (0.81 mmol) of $PtCl_2$ absorbed CO at 18.6°C up to a CO/Pt molar ratio of 1.92 in 3 days.

4.6. *trans*-$Pt_2Cl_4(CO)_2$ (**2**)

By operating under CO, solid $[NBu_4]_2PtCl_4$ obtained from an aqueous solution of K_2PtCl_4 (6.60 mmol) was dissolved in 1,2-$C_2H_4Cl_2$ (50 ml), and the resulting solution was added of 0.890 g (6.67 mmol) of $AlCl_3$. After 18 h stirring, an IR spectrum showed the band at 2098 cm^{-1} due to $[NBu_4][PtCl_3(CO)]$. The solution was degassed and saturated with N_2. A second equivalent of $AlCl_3$ (0.88 g, 6.60 mmol) was added and the solution turned orange. After 1 h, an IR spectrum showed the band at 2138 cm^{-1} due to *trans*-$Pt_2Cl_4(CO)_2$. After filtration, the solution was stored at 0°C for 2 days. Orange crystals, suitable for an X-ray diffraction study, separated out, which were filtered and dried in vacuo (0.69 g, 35.6% yield).

4.7. *cis*-$PtBr_2(CO)_2$ (**3**)

4.7.1. From $[NBu_4]_2[PtBr_4]$

Compound **3** was obtained from $[NBu_4]_2[PtBr_4]$ and CO, using $AlBr_3$ as halide scavenger in two separate steps (22.5% yield after extraction with CCl_4). In a gas-volumetric experiment, the CO uptake by $[NBu_4]_2[PtBr_4]$ in dichloroethane at 16.6°C was measured, corresponding to a CO/Pt molar ratio of 0.99 (in 2 h) and 1.9 (in 0.5 h, after addition of the second equivalent of $AlBr_3$). The IR spectrum of the solution showed a band at 2142 cm^{-1} due to *trans*-$PtBr_2(CO)_2$. After 24 h under CO, this band had disappeared, being substituted by bands at 2170 and 2130 cm^{-1} of the *cis*-isomer.

4.7.2. From cis-$PtCl_2(CO)_2$

To a suspension of *cis*-$PtCl_2(CO)_2$ (0.580 g, 1.80 mmol) in CCl_4 (10 ml), ^tBuBr (0.50 ml, 4.34 mmol) was added. After 30 min a ^1H-NMR spectrum showed the peaks at 1.62 ppm (^tBuBr) and at 1.45 ppm (^tBuCl) in the 1:2.6 ratio. After 24 h stirring the suspension was filtered and the solid was dried in vacuo (0.46 g, 62% yield). Found: Br, 38.6; Pt, 46.6. $C_2Br_2O_2Pt$ requires: Br, 38.9; Pt, 47.5%. IR (Nujol): 2167 and 2122 cm^{-1}. ^{195}Pt-NMR (CH_2Cl_2): δ −4243 ppm. In another experiment carried out in CH_2Cl_2 and using a $^tBuBr/Pt$ molar ratio of 2.7 at r.t., a 0.13 M solution of *cis*-$PtCl_2(CO)_2$ was rapidly (about 10 min) converted into the corresponding bromide, the latter being recovered by precipitation with heptane (75.5% yield).

4.7.3. From $PtBr_2$

A suspension of $PtBr_2$ (0.81 g, 2.28 mmol) in *sym*-$C_2H_4Cl_2$ (75 ml) was pressurized in a glass autoclave with CO (6 atm). After 1 h stirring at r.t. the solid had disappeared. The mixture was heated at 60°C for 3 h and a yellow solution was obtained which was siphoned into a flask under N_2 and concentrated under reduced pressure. An IR spectrum of the solution showed the bands at 2170 and 2130 cm^{-1} due to *cis*-$PtBr_2(CO)_2$. The solution was treated with heptane (100 ml) and the pale yellow product precipitated out. The suspension was stored at −30°C for 2 days and then filtered. The solid was dried in vacuo (0.70 g, 74.7% yield). The filtrate was evaporated to dryness and the residue, after addition of heptane (5 ml), was recovered by filtration and dried in vacuo (0.16 g, 91.7% total yield). The product had correct elemental analysis (Br, Pt) and IR.

The same reaction carried out in CH_2Cl_2 at r.t. and $p_{CO} \sim 0.5$ atm proceeded very slowly.

4.8. cis-$Pd_2Cl_4(CO)_2$ (**4**)

A solution of $[NBu_4]_2[Pd_2Cl_6]$ (752 mg, 0.83 mmol) in 30 ml of CH_2Cl_2, prepared as described above, was treated under CO with $AlCl_3$ (219 mg, 1.64 mmol). After 2 days stirring at r.t. the IR spectrum of the solution showed an intense band at 2166 cm^{-1} due to *cis*-$Pd_2Cl_4(CO)_2$. The solution was treated with heptane (120 ml) and cooled down to −30°C. The orange compound was filtered and dried for a short time under a CO flux (76% yield). The product had correct elemental analysis (Cl, Pd) and IR [1d].

4.9. Crystal structure determinations

Due to the extreme sensitivity to moisture of the compounds, single crystals were selected under a protecting atmosphere of an accurately dried gas. The X-ray diffraction measurements were carried out by means of an ENRAF-Nonius-CAD4 diffractometer equipped with a graphite-monochromated Ag–K_α radiation ($\lambda = 0.56087$ Å) for compound **2** at 203 K and with a Siemens P4 diffractometer equipped with a graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å) for compounds **3**, **4**, and **5** at r.t. ($T = 293$ K). The samples were sealed in glass capillaries under an inert atmosphere. The $\omega/2\theta$ scan mode was used for intensity data collection, a redundant set of data allowing diffraction symmetry and reliability of the absorption correction procedure to be checked. Three standard reflections were measured every 97 measurements to check sample decay. The intensities were corrected for Lorentz and polarisation effects and for absorption by means of a ψ-scan method [17]. The intensities of compound **3** were also corrected for decay [18]. The structure solutions were obtained by means of the Patterson method and the refinements, based on full-matrix least-squares on F^2, were done by means of the SHELX-97 programme [19].

4.9.1. Crystal structure of **2**

Orange needle-like single crystals were obtained by cooling (0°C) a solution of **2** in dichloroethane. Several crystals were tested, the best results being obtained with a sample of dimensions 0.52 × 0.04 × 0.04 mm. The cell parameters were calculated from the setting angles of 25 reflections having $6.0° < \theta < 10.0°$. They are listed, together with some other structural parameters in Table 5. A total of 811 independent reflections were measured ($1.4° < \theta < 21.0°$). The structure solution was obtained in the space group $P4_2$, see Table 5.

4.9.2. Crystal structure of **3**

Colourless prismatic crystals of **3**, obtained by sublimation under reduced pressure (about 10^{-2} mmHg) in a sealed ampoule in the temperature gradient 100–30°C, were mounted in glass capillaries under an argon atmosphere. The crystal used for structure solution had dimensions 0.23 × 0.18 × 0.06 mm. The cell parameters, calculated from the setting angles of 25 reflections having $5.0° < \theta < 12.0°$, are listed in Table 5, together with some other structural details. A total of 2292 independent reflections were measured between $2.9° < \theta < 25.0°$. During data collection, a 15% decay of the standard reflections was observed, while the crystal

Table 5
Crystal data and structure refinement[a]

Compound	**2**	**3**	**4**	**5**
Empirical formula	$C_2Cl_4O_2Pt_2$	$C_2Br_2O_2Pt$	$C_2Cl_4O_2Pd_2$	$C_{17}H_{36}Br_3NOPt$
Formula weight	588.01	410.93	410.67	705.29
Temperature (K)	203(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.56087	0.71073	0.71073	0.71073
Crystal system, space group	Tetragonal, $P4_2$ (no. 77)	Triclinic, $P\bar{1}$ (no. 2)	Monoclinic, $P2_1/n$ (no. 14)	Monoclinic, $P2_1/n$ (no. 14)
Unit cell dimensions				
a (Å)	11.183(3)	7.126(1)	10.451(1)	14.992(2)
b (Å)	11.183(3)	7.315(1)	6.649(1)	9.158(1)
c (Å)	3.525(2)	13.525(3)	13.032(1)	18.642(2)
α (°)	–	75.31(1)	–	–
β (°)	–	78.12(1)	97.83(1)	106.93(1)
γ (°)	–	75.04(1)	–	–
Volume (Å^3)	440.8(3)	651.4(2)	897.1(2)	2448.6(5)
Z	2	4	4	4
ρ_{calc} (Mg m^{-3})	4.430	4.190	3.040	1.913
μ (mm^{-1})	17.864	33.706	4.532	10.630
Data/restraints/parameters	811/33/47	2292/0/128	1908/0/91	4267/0/209
$R(F_o)$ [a] $[I>2\sigma(I)]$	0.0368	0.0738	0.0468	0.0529
$Rw(F_o^2)$ [a] $[I>2\sigma(I)]$	0.0462	0.1611	0.0850	0.1078

[a] $R(F_o) = \Sigma \| F_o| - |F_c \| / \Sigma | F_o |$; $Rw(F_o^2) = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (AQ)^2 + BQ]$ where $Q = [\max(F_o^2, 0) + 2F_c^2]/3$.

became yellow–orange. Three collections on three different specimens gave the same results. The structure solution was obtained in the space group $P\bar{1}$. The final refinement cycles gave the reliability factors listed in Table 5.

4.9.3. Crystal structure of **4**

Red–orange needle-like single crystals were obtained by cooling (−40°C) a solution of **4** in thionyl chloride/heptane (1:3). One of them, of dimensions 0.51 × 0.10 × 0.05 mm was mounted on the diffractometer and the cell parameters were calculated from the setting angles of 23 reflections having $5.3° < \theta < 12.5°$. Other structural details are in Table 5. The intensities of 1908 independent reflections with $2.35° < \theta < 30.0°$ were collected. The structure solution was obtained in the space group $P2_1$. The final refinement cycles gave the reliability factors listed in Table 5.

4.9.4. Crystal structure of **5**

A fragment of a yellow needle-like crystal of **5** of dimensions 0.88 × 0.18 × 0.08 mm was mounted on the diffractometer and the cell parameters were calculated from the setting angles of 27 reflections having $5.4° < \theta < 12.45°$. The lattice parameters, together with some other structural details, are listed in Table 5. The intensities of 4267 independent reflections with $2.07° < \theta < 25.01°$ were collected. The structure solution was obtained in the space group $P2_1/n$. The final refinement cycles gave the reliability factors listed in Table 5.

5. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 151361 for compound **2**, CCDC no. 151362 for compound **3**, CCDC no. 151363 for compound **4** and CCDC no. 151364 for compound **5**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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