

SOME PALLADIUM(II) AND PLATINUM(II) LEAD BONDED COMPLEXES

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SUMMARY

Complexes of the type $M(PPh_3)_2(PbPh_3)_2$ [$M = Pd$, (Ia) and Pt , (Ib)] have been prepared by oxidative addition of hexaphenyldilead to $M(PPh_3)_4$. The compound $Pt(PPh_3)_2(PbPh_3)_2$, (Ib), slowly decomposes in dichloromethane to give *cis*- $Pt(PPh_3)_2(PbPh_3)Ph$, (II), which can also be obtained by treating (Ib) with the stoichiometric amount of $LiPh$. Reaction of $Pt(PPh_3)_4$ with hexamethyldilead gives the complex $Pt(PPh_3)_2(PbMe_3)Me$ directly.

The $M-Pb$ bonds are easily cleaved by bromine, iodine and hydrogen bromide. The X-ray structure of (II) has been determined using three-dimensional counter data and refined by the least-squares method ($R=0.07$). The crystals are monoclinic $a=22.501$, $b=10.502$, $c=24.120$ Å, $\beta=113.43^\circ$, space group $P2_1/c$ with $Z=4$. The complex exhibits a *cis* configuration, with the coordination around the platinum atom essentially square-planar: the $Pt-Pb$ and $Pt-C$ (phenyl) bond lengths are 2.698(1) and 2.055(3) Å, respectively.

INTRODUCTION

In the last few years the chemistry of complexes containing direct bonds between a transition metal and a Group IVB element has been much studied, attention being directed to the nature and reactivity of the metal-metal bond, and to the use of the complexes as catalysts in homogeneous hydrogenations.

Complexes of the type $M(PEt_3)_2(PbPh_3)_2$ ($M = Pd$ and Pt) were prepared in our laboratory by treating *trans*- $M(PEt_3)_2Cl_2$ with $LiPbPh_3$ ^{1,2}. However, all attempts to obtain the corresponding triphenylphosphine derivatives through such nucleophilic substitution was unsuccessful, probably owing to the low solubility of $M(PPh_3)_2Cl_2$ in ether. These compounds, $Pd(PPh_3)_2(PbPh_3)_2$, (Ia), and $Pt(PPh_3)_2(PbPh_3)_2$, (Ib), have now been prepared by oxidative addition of hexaphenyldilead to $M(PPh_3)_4$, following the approach successfully employed by Akhtar and Clark³ for the prepara-

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tion of some Pt-Sn bonded complexes, and the properties and reactions of (Ia) and (Ib) are described below. Of special interest is that from the compound (Ib) another interesting derivative, *cis*-Pt(PPh₃)₂(PbPh₃)Ph, (II), can be obtained. The crystal and molecular structures of (II) have been investigated by X-ray analysis in order to confirm the presence of the Pt-Pb bond, and to determine its length. To the best of our knowledge, this is the first X-ray structural investigation on a platinum-lead complex.

EXPERIMENTAL

Pd(PPh₃)₄ and Pt(PPh₃)₄ were prepared by established methods^{4a}. Commercial hexaphenyldilead was purified by recrystallization from a benzene/ethanol mixture. Hexamethyldilead was prepared by the method of Calingaert and Soroos⁵. All other chemicals were of commercial grade.

I. Reactions of M(PPh₃)₄ (M = Pd or Pt) with Pb₂R₆ (R = Ph or Me)

(a). Pd(PPh₃)₄ (1.150 g, 1 mmole) was dissolved in anhydrous benzene (ca. 50 ml) under nitrogen and a suspension of Pb₂Ph₆ (0.80 g, 1 mmole) in anhydrous benzene was gradually added with stirring. The mixture, which immediately became orange, was allowed to stand at room temperature for 15 min. After treatment with charcoal and filtration, ligroin was added to the clear solution until some precipitate formed. Partial removal of the solvent under vacuum gave a further crop of precipitate as a yellow-greenish powder. It can be purified by reprecipitation from the same solvents (yields 0.6–0.7 g, 40–50%). This compound was identified as Pd(PPh₃)₂(PbPh₃)₂. (Found: C, 57.5; H, 4.10; Pb, 27.0. C₇₂H₆₀P₂PdPb₂ calcd.: C, 57.34; H, 4.01; Pb, 27.48%). M.p.: 90–95° (dec.).

(b). Pt(PPh₃)₄ (1.250 g, 1 mmole) was treated with Pb₂Ph₆ (0.880 g, 1 mmole) in anhydrous benzene under nitrogen as above. After 30 min at room temperature the reaction mixture was treated with charcoal and filtered. The clear filtrate was concentrated to half its volume under reduced pressure, and diluted with ether until a precipitate began to form. After 24 h in the refrigerator, precipitation was completed by adding light petroleum (40–70°). A yellowish microcrystalline compound, identified as Pt(PPh₃)₂(PbPh₃)₂, was obtained (yield 0.8 g, ca. 50%). (Found: C, 53.9; H, 3.80; Pb, 25.4. C₇₂H₆₀P₂PtPb₂ calcd.: C, 54.16; H, 3.79; Pb, 25.95%). Mol. wt. in 1,2-dichloroethane solution at 37°; found 1130; calcd. 1596. M.p.: 155–160° (dec.).

(c). Pt(PPh₃)₄ (1.250 g, 1 mmole) was treated with Pb₂Me₆ (0.510 g, 1 mmole) in anhydrous benzene under nitrogen as above. The reaction mixture was stirred for 15 min, during which time the colour turned from yellow-orange to deep red and finally to black. After treatment with charcoal and filtration, the resulting yellow solution was concentrated to a small volume under vacuum. Addition of 1/1 ether/light petroleum (40–70°) gave a pale-yellow microcrystalline precipitate, which was purified by recrystallization from the same solvents (yield 0.75 g, 75%). Analysis, IR spectra and chemical reactivity proved this compound to be Pt(PPh₃)₂(PbMe₃)Me. (Found: C, 49.3; H, 4.21; Pb, 20.4. C₄₀H₄₂P₂PtPb calcd.: C, 48.67; H, 4.29; Pb, 20.99%). M.p.: 130–132° (dec.).

II. Preparation of *cis*-Pt(PPh₃)₂(PbPh₃)Ph

Pt(PPh₃)₂(PbPh₃)₂ (0.800 g, 0.5 mmoles) suspended in anhydrous benzene was

treated with LiPh (0.5 mmoles) under nitrogen. A fine yellow precipitate (probably LiPbPh₃) immediately appeared. After 1 h of stirring at room temperature, the reaction mixture was taken to dryness under vacuum, and the crude product was treated with methanol (2 ml) and dichloromethane (70 ml). Addition of charcoal and filtration gave a pale yellow solution, which was concentrated to small volume, and treated with a 1/1 ether/light petroleum (40–70°) mixture, to produce an off-white crystalline product. This was purified by reprecipitation from the same solvents (yield 0.85 g, 70%), and identified as *cis*-Pt(PPh₃)₂(PbPh₃)Ph by analysis, molecular weight measurement, and X-ray structural investigation. (Found: C, 58.5; H, 4.1; Pb, 16.5. C₆₀H₅₀P₂PtPb calcd.: C, 58.34; H, 4.08; Pb, 16.77%). Mol. wt. in 1,2-dichloroethane at 37°; found 1190; calcd. 1234. M.p.: 168° (dec.). The same compound was also produced by decomposition of Pt(PPh₃)₂(PbPh₃)₂ in a dichloromethane/ether solution which had been allowed to stand for three weeks in the refrigerator.

III. Reaction with I₂, Br₂ and HBr

(a). The complex Pd(PPh₃)₂(PbPh₃)₂ (0.3 mmoles) suspended in anhydrous benzene was treated with iodine (0.6 mmoles) with stirring. Reaction took place immediately, as indicated by the disappearance of the iodine colour. After 20 min the mixture was treated with charcoal and filtered, and the clear filtrate taken to low volume under vacuum. Addition of ether gave orange crystals, identified as *trans*-Pd(PPh₃)₂I₂ by comparison of the melting point and IR spectrum with those of an authentic sample. The yield was almost quantitative.

(b). The complex *cis*-Pt(PPh₃)₂(PbPh₃)Ph (0.3 mmoles) was suspended in anhydrous benzene and treated dropwise with bromine (0.3 mmoles in CCl₄). The mixture was worked up as in (a), to give pale yellow crystals which were identified as Pt(PPh₃)₂PhBr from the elemental analysis and IR spectrum. (Found: C, 57.4; H, 4.0; Br, 9.3. C₄₂H₃₅P₂BrPt calcd.: C, 57.54; H, 4.02; Br, 9.12%). Yield ca. 90%.

An analogous reaction took place with Pt(PPh₃)₂(PbMe₃)Me to give the pale yellow microcrystalline complex, Pt(PPh₃)₂MeBr, as confirmed by the analysis and IR spectrum. (Found: C, 54.1; H, 4.1; Br, 10.0. C₃₇H₃₃P₂BrPt calcd.: C, 54.55; H, 4.08; Br, 9.81%).

(c). To a benzene suspension of *cis*-Pt(PPh₃)₂(PbPh₃)Ph (0.3 mmoles) HBr (0.3 mmoles in methanol) was added dropwise. The reaction mixture was stirred for 1 h and worked up as described above to give pale yellow crystals of Pt(PPh₃)₂PhBr, which was characterized as in (b). Yield ca. 80%.

(d). The complex Pt(PPh₃)₂(PbMe₃)Me (350 mg, ca. 0.35 mmoles) suspended in CHCl₃ was treated with an excess of bromine (2.2 mmoles in CCl₄). The mixture was refluxed for 4 h and then taken to dryness. The solid was washed 3–4 times with boiling water and filtered off. The aqueous solution, containing PbBr₂, was used for the quantitative determination of lead as PbSO₄. The product, which was insoluble in water, was washed with ether and dried under vacuum. The analysis, melting point, and IR spectrum showed it to be Pt(PPh₃)₂Br₂. Yield ca. 80%.

Spectra and molecular weights

Infrared spectra were recorded with a Perkin-Elmer 621 spectrophotometer in the region 4000–250 cm⁻¹, and with a Beckmann IR 11 in the region 300–140 cm⁻¹. Hexachlorobutadiene (4000–1300 cm⁻¹) and Nujol mulls (1700–140 cm⁻¹) were used.

Molecular weights were measured with a Mechrolab thermoelectric apparatus at 37°.

X-ray analysis

Crystallization from CH₂Cl₂ at room temperature gave long, transparent, pale yellow needles with a rectangular cross-section. The crystals were initially examined in Weissenberg and precession cameras with the oscillation axis parallel to the needle (*b*) axis, and showed systematic absences characteristic of space group *P*2₁/*c* (*C*_{2h}⁵). Accurate lattice and orientation parameters were obtained by a least-squares treatment. Crystal data: *a* = 22.501(6), *b* = 10.502(4), *c* = 24.120(6) Å, β = 113.43° (5), *d*₀ = 1.54, *d*_c = 1.57 g · cm⁻³ for 4 molecules per unit cell.

X-ray intensity data were collected at room temperature on a Siemens-AED-automated four circle diffractometer, with a Cu-target tube (λ 1.54178 Å for Kα) at take-off angle 4.5° equipped with an Na(Tl)I scintillation counter. The maximum sin θ/λ was 0.562 Å⁻¹. Any reflection with intensity, after correction for background, greater than twice its statistical standard deviation, was considered "observed". On this basis 5698 reflections were regarded as observed, and 1997 unobserved.

The position of the lead and platinum atoms, derived from a three-dimensional unsharpened Patterson synthesis, gave a first residual error index *R* = 0.23. Least-squares refinement followed by a difference map gave the missing atoms, and the structure was refined with individual isotropic temperature factors to an *R* factor (calculated on observed reflections only) 0.11. Introduction of anisotropic temperature factors (for the heavy atoms) followed by five cycles of refinement reduced the *R* index to 0.073. A difference map, calculated after the refinement, was essentially featureless. A table of measured and calculated structure factors is available from the authors, along with the atomic and thermal parameters. The scattering factors curves employed were those derived by Cromer and Waber⁶ and in the case of the lead and platinum atoms were corrected to the real part of the anomalous dispersion⁶.

All computations were carried out on the Consorzio Interuniversitario Italia Nord-Orientale, Casalecchio (Bologna), CDC 6600 computer, using the *X-ray* 70 programs.

RESULTS AND DISCUSSION

The complexes M(PPh₃)₄ (M = Pd or Pt) react with hexaphenyldilead, under mild conditions, to give products of the type M(PPh₃)₂(PbPh₃)₂, containing Pd–Pb or Pt–Pb bonds:



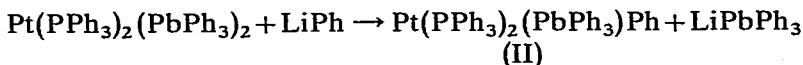
These compounds have been characterized by elemental analysis, molecular weight measurements, IR spectra, and X-ray powder photographs, and by cleavage reactions of the metal–metal bonds. The IR spectra show, in addition to the bands of the phosphine, the characteristic absorptions of the PbPh₃ grouping^{1,2,7}, consisting of a sharp band at 1570–1560 cm⁻¹, attributed to a C=C stretching vibration of the phenyl groups, and of multiplets in the ranges 460–430 and 230–200 cm⁻¹. The X-ray powder patterns, by comparison with those of the starting materials, Pb₂Ph₆ and M(PPh₃)₄, confirm that (Ia) and (Ib) are definite new compounds. Molecular weight

measurements of (Ib) in 1,2-dichloroethane gave a value of 1130 (calcd. mol. wt., 1596) the difference between the observed and calculated values probably being due to the decomposition of metal-metal derivatives in halogenated solvents^{8,9}.

The Pd-Pb bonds of (Ia) are easily cleaved by iodine to give *trans*-Pd(PPh₃)₂I₂ quantitatively.

Reaction (1) does not occur in the case of Pt(P(OMe)₃)₄^{4b}, even under more severe conditions (in refluxing benzene for several hours). This behaviour parallels that of (fluorophosphine)platinum(0) towards alkyl halides¹⁰, and is probably related to the lack of dissociation of PtL₄ when L is a strong π-acceptor ligand such as fluorophosphines or, in our case, trimethyl phosphite. Further study of the reaction (1) is now in progress starting from PtL₄ species with different π-accepting ligands L.

The complex (Ib) decomposes slowly in halogenated solvents to give *cis*-Pt-(PPh₃)₂(PbPh₃)Ph. This probably occurs via the migration of a phenyl group from the coordinated PbPh₃ moiety, by the mechanism proposed by Baird for the disproportionation of the compounds Pt(PPh₃)₂(MPh₃)Cl (M = Sn, Pb) into Pt(PPh₃)₂-PhCl in polar solvents¹¹. The complex (II) can also be prepared by the following metathetical reaction:

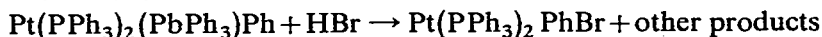


The analysis and molecular weight of (II) are in good agreement with the proposed formulation. The X-ray investigation (see later) shows that it has a *cis* configuration. Its IR spectrum is characterized by the typical bands of the PbPh₃ ligand (1567 m, 452 s, 435 ms; 219 m, 208 m cm⁻¹^{1,2,7}). Because of the presence of other ligands containing phenyl groups, no clear absorption attributable to the Pt-Ph system could be found.

The analogous methyl derivative, Pt(PPh₃)₂(PbMe₃)Me, is the main product of the reaction between Pt(PPh₃)₄ and hexamethyldilead. This was a rather surprising result, since we expected to isolate the compound Pt(PPh₃)₂(PbMe₃)₂, by analogy with Akhtar and Clark's preparation of the di-tin complex, *trans*-Pt(PPh₃)₂(SnMe₃)₂. Probably the di-lead derivative is first formed according to reaction (1)*, but then undergoes fast disproportionation to give Pt(PPh₃)₂(PbMe₃)Me (III), analogously to the formation of (II) from (Ib). The greater ease of disproportionation of Pt-Pb compounds than of the corresponding Pt-Sn derivatives has already been observed by Baird¹¹.

The IR spectrum of (III) shows characteristic bands at 2972 mw, 2942 w, 2908 m, 2877 mw cm⁻¹, arising from the C-H stretching frequencies of the methyl groups. A very strong band at 437, with a shoulder at 445 cm⁻¹, is attributed to ν-(Pb-C) of the PbMe₃ group¹². No IR spectrum of (III) could be recorded because of the low solubility of the complex in the suitable deuterated solvents.

The complexes (II) and (III) were also characterized by their reactions with bromine and hydrogen bromide at room temperature:



* Pb₂Me₆ would be expected to undergo reaction (1) more easily than Sn₂Me₆, since the Pb-Pb bond is usually weaker than the corresponding Sn-Sn bond. For instance, the metal-metal stretching force constants are 0.83 for Pb₂Me₆ and 0.99 mdyne/Å for Sn₂Me₆ (see ref. 12).

Such reactions (1/1 molar ratio) probably proceed via an oxidative addition-elimination process, in which a hexa-coordinate platinum(IV) species is formed, by electrophilic attack on platinum(II)^{1,3,13}. The complex $\text{Pt}(\text{PPh}_3)_2\text{PhBr}$, formed in the reaction of (II) with Br_2 or HBr , has a *trans* configuration as suggested by the position of the $\nu(\text{Pt}-\text{Pr})$ band at 182 cm^{-1} [$\nu(\text{Pt}-\text{Br})$ 184 cm^{-1} for *trans*- $\text{Pt}(\text{PET}_3)_2\text{PhBr}$ ¹⁴]. In contrast, a *cis* structure is tentatively assigned to $\text{Pt}(\text{PPh}_3)_2\text{MeBr}$ on the basis of its far IR spectrum [$\nu(\text{Pt}-\text{Br})$ 196 cm^{-1} , while in *trans*- $\text{Pt}(\text{PET}_3)_2\text{CD}_3\text{Br}$ the $\text{Pt}-\text{Br}$ stretching vibration occurs at $<180\text{ cm}^{-1}$ ¹⁴], and of its limited solubility, which prevented any NMR investigation. The ^1H NMR spectrum of *trans*- $\text{Pt}(\text{PPh}_3)_2\text{MeBr}$ in CDCl_3 has been reported by Cook and Wan¹⁵. It is interesting to observe that in the above reactions, only the $\text{Pt}-\text{Pb}$ bond is easily broken, whilst the $\text{Pt}-\text{C}$ bond is not appreciably attacked, thus indicating a lower stability of the metal-metal bond towards electrophilic agents. In this connection it is noteworthy that the reaction of (III) with an excess of bromine (1/6 molar ratio in refluxing benzene leads to the cleavage of all the $\text{Pt}-\text{Pb}$, $\text{Pt}-\text{Me}$ and $\text{Pb}-\text{Me}$ bonds, and formation of PbBr_2 and $\text{Pt}(\text{PPh}_3)_2\text{Br}_2$. The latter compound is probably obtained as a mixture of *trans* and *cis* isomers, as shown by its IR spectrum: $\nu(\text{Pt}-\text{Br})$ 254 cm^{-1} (*trans* isomer)¹⁶; $\nu(\text{Pt}-\text{Br})$ $220, 205\text{ cm}^{-1}$ (*cis* isomer)¹⁶.

Since the metal-lead compounds described above are not suitable for a structural investigation by means of IR or NMR spectroscopy we decided to carry out an X-ray analysis on the complex $\text{Pt}(\text{PPh}_3)_2(\sigma\text{-Ph})\text{Pt}(\text{PbPh}_3)\text{Ph}$, in which both the $\text{Pt}-\text{Pb}$ and

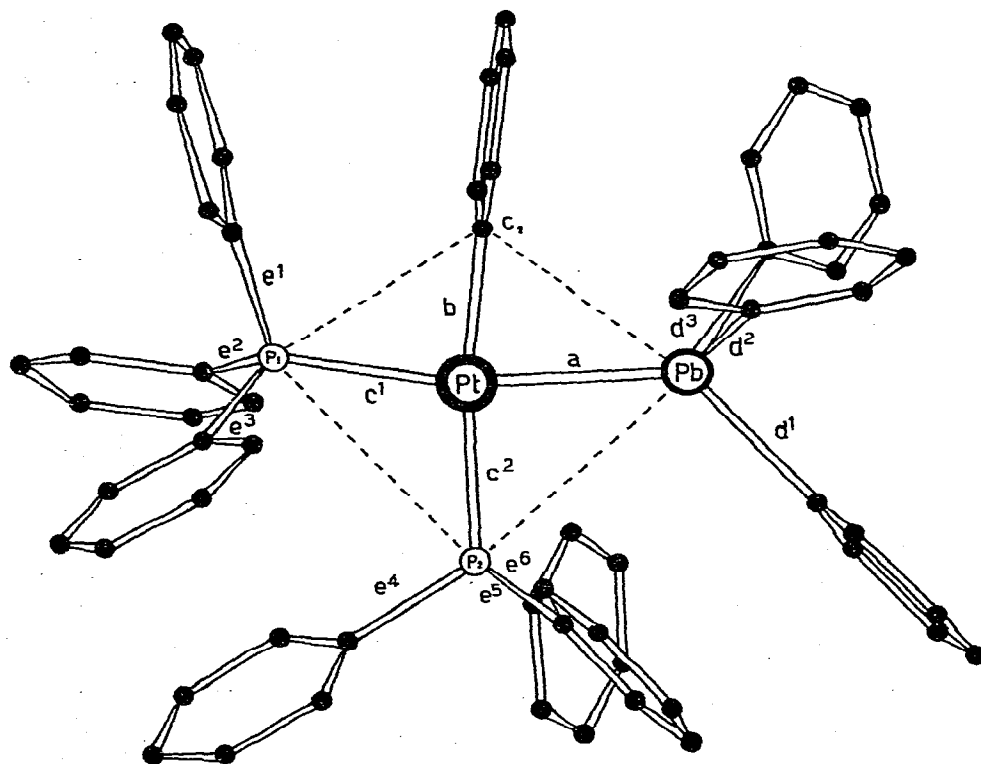


Fig. 1. Projection of the *cis*- $(\text{Ph}_3\text{P})_2(\sigma\text{-Ph})\text{Pt}(\text{PbPh}_3)$ complex on to the mean plane of coordination.

TABLE 1

INTERATOMIC DISTANCES (Å) AND ANGLES (DEGREES)^a

a	2.698	∠ a b	81.2	∠ c ² e ⁴	121.5
b	2.055	∠ a c ¹	165.8	∠ c ² e ⁵	111.7
c ¹	2.307	∠ a c ²	90.8	∠ c ² e ⁶	114.7
c ²	2.330	∠ a d ¹	127.8	∠ d ¹ d ²	96.9
d ¹	2.288	∠ a d ²	112.1	∠ d ¹ d ³	101.5
d ²	2.275	∠ a d ³	116.1	∠ d ² d ³	96.9
d ³	2.248	∠ b c ¹	87.5	∠ e ¹ e ²	102.4
e ¹	1.86	∠ b c ²	168.6	∠ e ¹ e ³	101.9
e ²	1.82	∠ c ¹ c ²	101.6	∠ e ² e ³	108.0
e ³	1.86	∠ c ¹ e ¹	116.1	∠ e ⁴ e ⁵	101.6
e ⁴	1.86	∠ c ¹ e ²	114.1	∠ e ⁴ e ⁶	98.8
e ⁵	1.84	∠ c ¹ e ³	113.1	∠ e ⁵ e ⁶	106.5
e ⁶	1.84				

^a Letters refer to those of Fig. 1. Estimated standard deviations in bond lengths average 0.03 Å (0.01 for Pt–Pb and 0.02 Å for Pt–P); the e.s.d.'s in angles are ca. 2°. The bond lengths and angles in the benzene rings are all normal, and the rings are planar within 0.02 Å.

Pt–Pb bonds are present. The salient features of the structure are given in Fig. 1, and the most significant bond lengths and angles are listed in Table 1.

The structure of (Ph₃P)₂(σ-Ph)PtPbPh₃ shows a number of features:

(i). The co-ordination about the platinum atom is virtually planar, although far from square-planar.

(ii). The deviations from the best least-square plane through P1, C₁, Pb, P2 calculated according to the procedure described by Schomaker¹⁷, are P1+0.16, C₁-0.18, Pb+0.15, P2-0.12 and Pt-0.01 Å. An examination of all intermolecular distances suggests no explanation for this lack of planarity in terms of packing distortions (in fact all the intermolecular contacts appear to be normal, and hence are not reported). Thus, the angle between the planes C₁, Pt, Pb and P1, Pt, P2 is 108°.

(iii). The platinum-lead bond length is 2.698 ± 0.008 Å, and this is the first unequivocal structural evidence for such a bond. The covalent radii quoted by Pauling¹⁸ for square-planar platinum and tetrahedral lead are 1.31 and 1.46 Å respectively. Thus, the value of 2.698 for the Pt–Pb bond is ca. 0.07 Å shorter than the sum of the covalent radii. It seems that in addition to the σ-bond there is some π-contribution to the Pt–Pb bond involving unoccupied 6d orbitals of lead and the filled non-bonding 5d orbitals of the platinum atom.

(iv). The Pt–P distances, are equal within experimental error (2.307 and 2.330 Å), indicating that the *trans*-influence of the phenyl group is similar to that of the PbPh₃ group agreeing with observations on the related compound (Et₃P)₂(σ-Ph)PtGePh₂(OH)¹⁹. Furthermore, these distances are longer than most quoted Pt–P distances in square-planar complexes containing two triphenylphosphine groups²⁰. In these last complexes there is some variation in the Pt–P distances [from 2.24 in Pt(CO₃)-(PPh₃)₂²¹ to 2.35 Å in Pt(CS₂)(PPh₃)₂²²] due to the different properties of the ligands. All these distances are shorter than the distance of 2.41 Å which would be expected for a single covalent Pt–P bond from Pauling's covalent radii. It seems that, besides the pure Pt–P σ-bond, there is some degree of π-bonding, presumably by overlap of filled d_π orbitals on the metal with empty d_π orbitals on the phosphorus^{19,20}.

(v). The Pt-C₁ distance of 2.055 Å is similar to the Pt-alkyl carbon distances of 2.03 and 2.07 Å in Pt(Me₃)OH²³ and Pt(OMe)(dicyclopentadiene)²⁴, respectively, and very similar to the value of 2.043 Å in (Et₃P)₂(σ-Ph)PtGePh₂(OH)¹⁹. This distance is in very good agreement with the expected value for a single covalent bond between a square-planar platinum and a trigonal carbon atom. Moreover, it is noteworthy that the plane of the phenyl ring is nearly perpendicular (87.5°) to the plane containing the four platinum bonds, and the Pt-C₁ bond distance indicates that overlap between the platinum orbitals and the ring system is negligible, again as observed in (Et₃P)₂(σ-Ph)PtGePh₂(OH)¹⁹.

(vi). The bonds about the phosphorus atoms are at almost tetrahedral angles. The P-C distances vary from 1.82 to 1.86 Å, and thus do not differ from the mean value of 1.844 Å, close to the sum of the covalent radii.

(viii). The lead coordination may be described as distorted tetrahedral, with the three Pt-Pb-C angles of 127.8, 112.1 and 116.1°. The mean Pb-C distance of 2.27 Å is in good agreement with the sum of Pauling's covalent radii (2.23 Å).

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