

Coordination modes of 1,2,3,4-tetrahydro-1,4-diphenyl-1,4-benzodiphosphinine (*bedip*) to Pt and Pd metal ions: Synthesis and structural characterization of mono- and bi-nuclear complexes

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Abstract

Within this study, coordination properties of the cyclic diphosphine 1,2,3,4-tetrahydro-1,4-diphenyl-1,4-benzodiphosphinine (*bedip*) are investigated, through the preparation of neutral and cationic Pt(II), Pt(IV) and Pd(II) complexes. The diphosphine acts as bridging ligand in the neutral Pt(II) and Pd(II) complexes, affording $[MX(CH_3)(\mu\text{-}bedip)]_2$ ($X = Cl, Br, I, CH_3$) species. Chelation is observed in all the remaining complexes. The molecular structures of $[PtX(CH_3)(\mu\text{-}bedip)]_2$ ($X = Br, I$) and $[PtI(CH_3)_3(\textit{bedip})]$ are also determined.

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1. Introduction

Bidentate phosphines are widely used in the stabilization of metal complexes. Their steric, electronic and chiral properties can be easily modified by changing the substituents on the phosphorus atoms and the backbone chain, often giving rise to effective metal catalyst [1]. While diphosphines with the two phosphorus atoms linked by a flexible hydrocarbon chain are important chelating ligands [2], minor attention has been directed towards diphosphines with the phosphorus atoms belonging to a cycle. In this case, steric restrictions are expected to afford a higher control on the two phosphorus lone pairs, thus affecting coordination ability. Significant differences between open chain and cyclic species are expected also on the basis of previous

theoretical [3] and experimental [4] studies. Besides, we recall that substantially distinct behaviour is observed [5] in case of comparable bidentate nitrogen donors.

Among cyclic diphosphines, those having a $-P(-C-C-)_2P-$ skeleton and two phosphorus lone pairs in *cis* configuration, attract particular interest due to a versatile coordination behaviour involving a binucleating versus chelating ability. In fact, this kind of phosphorus ligands can bridge two metal centres, so providing binuclear complexes, or chelate a single metal centre.

For the reasons above, we have recently focused our studies on the coordination modes of this class of ligands and the properties of related complexes. A previous investigation [6] has disclosed that *cis-P,P'*-diphenyl-1,4-diphosphino-cyclohexane (*dpdpc*, Fig. 1a) [7] acts as a versatile ligand, its hapticity being dependent on the metal charge. We have found a neat preference of *dpdpc* for chelating mode in cationic group 10 complexes, while binucleation has been observed in neutral species. Further evidences,

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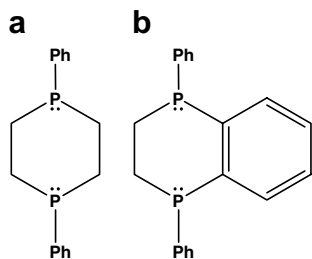


Fig. 1. Structure of (a) *dpdp* ligand and (b) *bedip* ligand.

more structural informations and extension of the study to rhodium complexes have been added by Helm et al. [8,9].

In this work, we report on the extension of our studies to the analogous 1,2,3,4-tetrahydro-1,4-diphenyl-1,4-benzodiphosphinine (*bedip*, Fig. 1b). *bedip* is a six-membered cyclic diphosphine, with two different bridges linking the phosphorus atoms: an aliphatic one and an unsaturated one, the latter belonging to an aromatic ring. The resulting heterocyclic ring is formally analogous [10] to cyclohexene since it contains two sp^2 -hybridized carbon atoms. This feature affords a more rigid structure compared with the previously studied *dpdp* [3]. Moreover, unlike *dpdp*, in a square-planar environment, chelating *bedip* affords a different steric hindrance below and above the coordination plane with a possible influence in catalysis. Finally, although the unsubstituted cyclic diphosphine here considered is not asymmetric since the two equivalent prochiral phosphorus atoms have opposite configuration, chiral species can be obtained by introduction of a substituent in one methylene group.

Although the stereoselective synthesis of the *cis*-isomer of *bedip*, in principle suitable not only to act as a bridge by binding two metal centres, but also to chelate one metal atom, was attained many years ago [11], at the best of our knowledge, it has never used as ligand in coordination compounds.

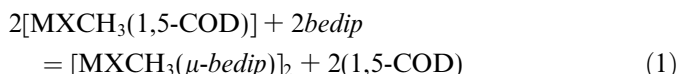
In this paper, we report the synthesis and the characterization of neutral and cationic *bedip* complexes of Pt(II), Pt(IV) and Pd(II). Molecular and crystal structures of

$[\text{PtX}(\text{CH}_3)(\mu\text{-bedip})]_2$ ($\text{X} = \text{Br}, \text{I}$) and $[\text{PtI}(\text{CH}_3)_3(\text{bedip})]$ are also reported. Finally, preliminary investigation about the reactivity of *bedip* complexes has been performed.

2. Results and discussion

2.1. Synthesis and NMR characterization of neutral Pt(II) and Pd(II) complexes (1a–e)

The synthesis of the neutral complexes $[\text{MXCH}_3(\mu\text{-bedip})]_2$ (1a–e) (Fig. 2) has been carried out by reaction at room temperature of the appropriate precursor $[\text{MXCH}_3(1,5\text{-COD})]$ (1,5-COD = 1,5-cyclooctadiene) with a stoichiometric amount of *bedip*, according to Eq. (1). The complexes have been obtained as pure microcrystalline solids by adding diethyl ether to the concentrated solution of the crude products



Analysis of the ^1H and ^{31}P NMR spectra suggests for all the complexes a polynuclear structure in solution. More precisely, ^1H NMR spectra [12] of 1a, 1b and 1c show a very similar pattern, which discloses the presence of two species in 3:1 ratio, namely, respectively, as **M** (major product) and **m** (minor product) (Fig. 3).

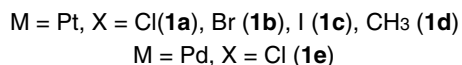
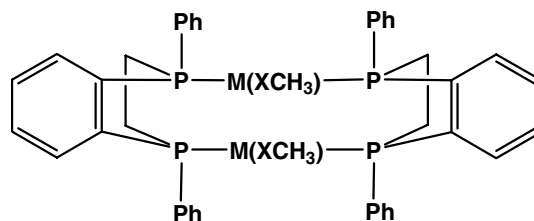


Fig. 2. Neutral Pt(II) and Pd(II) complexes (1a–e).

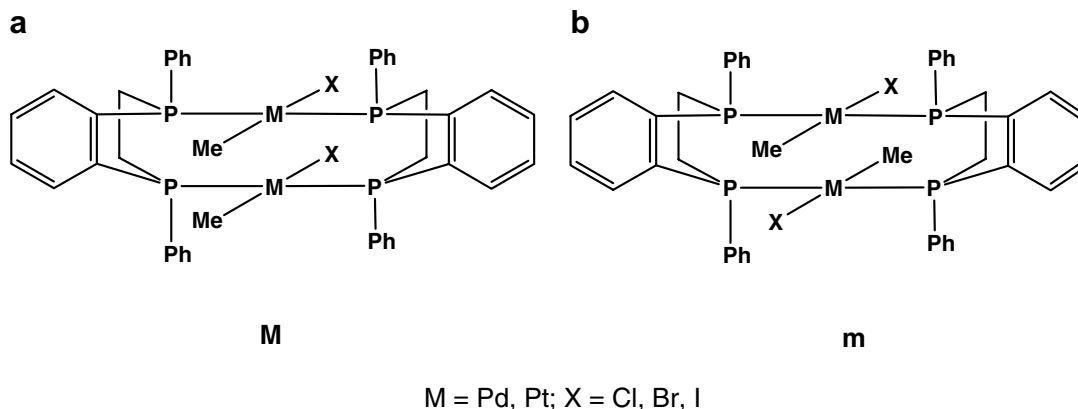


Fig. 3. (a) Major **M** and (b) minor **m** products of type 1 complexes.

Despite several attempts, we have failed to separate the two products by fractional crystallization and chromatographic techniques. In addition, in all fractions collected we have found the same 3:1 ratio of the two starting products.

In the ^{31}P NMR spectra, a unique signal, coincident for **M** and **m** isomers, discloses the equivalence of the two phosphorus atoms and the polynuclear nature of these complexes, the range $0 < \delta < 15$ being characteristic [13] of non-chelate diphosphines. Furthermore, values of the Pt–P coupling constants >3000 Hz are diagnostic [14] of two phosphorus atoms *trans* to each other.

In **M**, the equivalent Pt–CH₃ ^1H NMR resonances are at low frequency ($\delta < 0$), while in **m** the two methyl groups are not equivalent and a large difference in their chemical shifts is found: $0.98 < \delta_1 < 1.18$ and $-0.30 < \delta_2 < -0.15$.

When single crystals of **1b** and **1c** are grown, only one isomer is found in the solid state. The X-ray molecular structure discloses the binuclear nature of these compounds (Figs. 4 and 5).

According to the just mentioned NMR equivalence of the methyl groups, the structure found in the solid state is attributed to **M** isomer (Fig. 3a), while the alternative geometry showed in Fig. 3b is proposed for **m**. When a sample of crystals is dissolved and immediately analyzed in solution by ^1H NMR, again the 3:1 mixture is found. All the experimental evidences suggest that in solution there is equilibrium between the two isomers. The K_{eq} con-

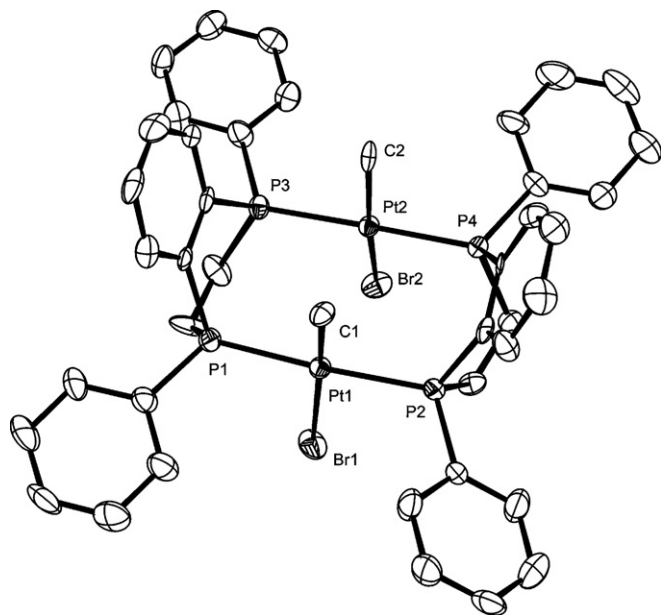


Fig. 4. ORTEP view of **M1b**. Thermal ellipsoids are shown at 50% probability level. All the hydrogen atoms and two chloroform solvent molecules are not shown for clarity. Selected bond distances (Å) and angles (°): Pt1–C1 = 2.087(6), Pt1–P1 = 2.280(2), Pt1–P2 = 2.293(2), Pt1–Br1 = 2.545(1), Pt2–C2 = 2.135(7), Pt2–P4 = 2.287(2), Pt2–P3 = 2.302(2), Pt2–Br2 = 2.552(9), C1–Pt1–P1 = 91.1(2), C1–Pt1–P2 = 90.0(2), P1–Pt1–P2 = 175.41(7), C1–Pt1–Br1 = 170.5(2), P1–Pt1–Br1 = 89.2(6), P2–Pt1–Br1 = 90.4(6), C2–Pt2–P4 = 88.0(2), C2–Pt2–P3 = 88.7(2), P4–Pt2–P3 = 174.9(7), C2–Pt2–Br2 = 169.0(2), P4–Pt2–Br2 = 91.4(6), P3–Pt2–Br2 = 92.6(5).

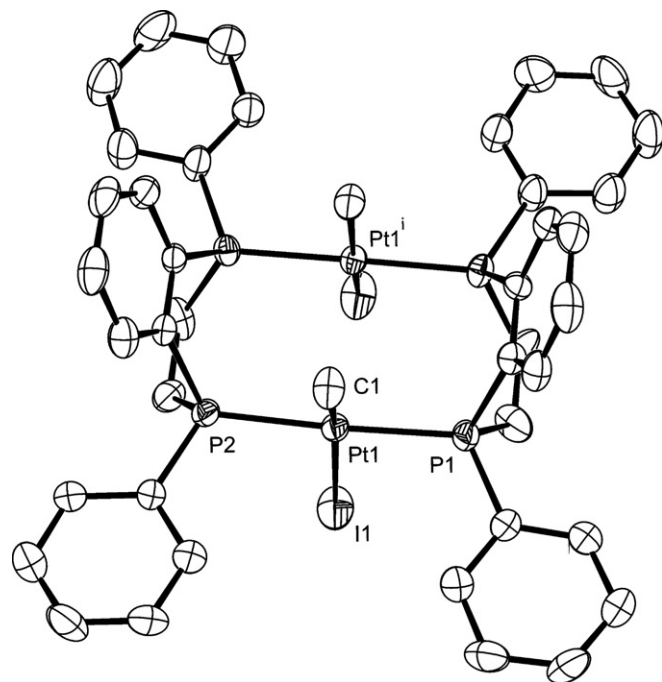


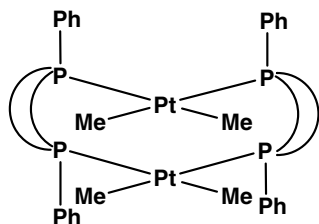
Fig. 5. ORTEP view of **M1c**. Thermal ellipsoids are shown at 30% probability level. All the hydrogen atoms are not shown for clarity. Symmetry transformation used to generate equivalent atoms: *i*: $x, -y + 1/2, z$ (the molecule has C_s symmetry as it lies on a crystallographic mirror plane bisecting *bedip* ligands). Selected bond distances (Å) and angles (°): Pt1–C1 = 2.071(8), Pt1–P1 = 2.289(3), Pt1–P2 = 2.288(3), Pt1–I1 = 2.703(9), C1–Pt1–P1 = 89.8(3), C1–Pt1–P2 = 87.3(3), P1–Pt1–P2 = 176.4(9), C1–Pt1–I1 = 165.3(3), P1–Pt1–I1 = 91.72(7), P2–Pt1–I1 = 91.63(7).

stant of **M/m** isomerization has been evaluated by integrating suitable separated peaks ($K_{\text{eq}} = 0.30$ at 298 K). By monitoring the isomerization at different temperatures (293–358 K), it is also estimated $\Delta H = 2.9 \pm 0.1$ kcal mol⁻¹ and $\Delta S = 7.2 \pm 0.3$ cal mol⁻¹ K⁻¹.

The ^1H NMR spectrum of **1d** discloses the presence of only one species in solution with equivalent methyl groups resonating at $\delta = 0.45$. The chemical shift ($\delta = 13.57$) of the single signal in the ^{31}P NMR spectrum is characteristic of the non-chelate diphosphines and the Pt–P coupling constant ($^1J_{\text{Pt-P}} = 1925$) is typical of a phosphorus atom *trans* to a methyl group [13].

Thus, for this compound we assume again a binuclear structure though with two phosphorus atoms of two *bedip* moieties *cis* to each other (Fig. 6). This geometry is plausibly adopted in order to avoid two methyl groups being *trans*. Due to the possibility to obtain several different isomers and lacking single crystal suitable for diffractometric analysis, the stereochemistry at phosphorous atoms cannot be univocally established.

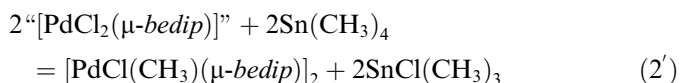
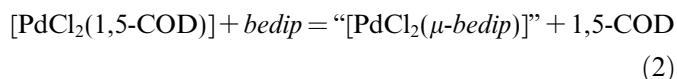
The ^1H NMR spectrum of **1e** discloses the presence of three species in solution. Also in this case, the presence of a unique signal in the ^{31}P NMR spectrum in the diagnostic region [13] for non-chelate diphosphines ($\delta = 12.40$) indicates for all the complexes a polynuclear structure. Based on the analogy for both the resonance values and the signal

Fig. 6. Neutral dimethyl Pt(II) complex (**1d**).

shapes in the ^1H NMR spectrum, we recognize the presence of the **M** and **m** isomers, in a ratio close to 1:1.

As for the third less abundant species (**mm**), additional relevant NMR features for structure assignment are the following ones: (i) the presence of a single signal for the equivalent methyl groups, similar to that observed for the **M** product; (ii) its resonance ($\delta = 0.43$) is a mean value between the lower frequency ($\delta = -0.40$) observed for the methyl groups pointing toward the aromatic bridges (**M** product) and the higher frequency ($\delta = 1.04$) assigned to the methyl groups oriented toward the aliphatic bridges (**m** product). Due to these observations, we infer a binuclear structure with the methyl groups in “*sin*”-type arrangement, experimenting both the aliphatic and the aromatic bridges (Fig. 7).

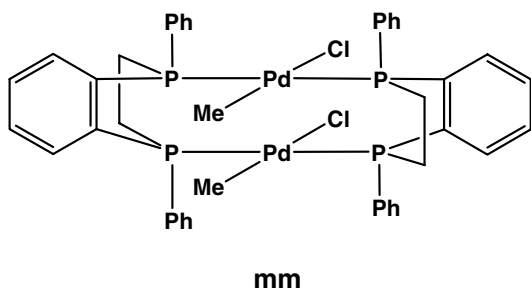
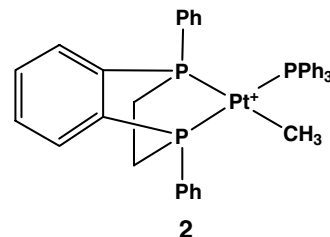
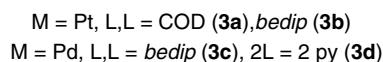
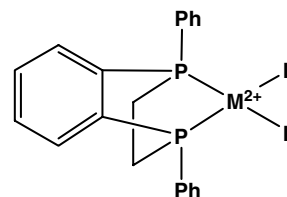
Complex **1e** is also obtained by a different procedure in two steps, according to Eqs. (2) and (2’):



“ $[\text{PdCl}_2(\mu\text{-bedip})]$ ” is poorly soluble and its structure, probably polynuclear, cannot be unambiguously determined. The subsequent reaction with $\text{Sn}(\text{CH}_3)_4$ affords the **1e** mixture disclosing the same ratio for the three isomers. We assume this fact as a further proof of an equilibrium in solution among the isomers that are formed in the reactions.

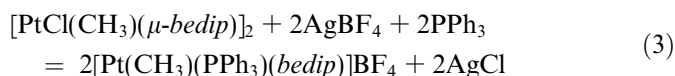
2.2. Synthesis and NMR characterization of cationic Pt(II) and Pd(II) complexes (**2**; **3a–d**)

A cationic monopositive Pt(II) (**2**) and several dipositive Pt(II) and Pd(II) (**3a–d**) *bedip* complexes (Figs. 8 and 9)

Fig. 7. **mm** isomer of neutral Pd(II) complex (**1e**).Fig. 8. Cationic mono-positive Pt(II) complex (**2**).Fig. 9. Cationic bipoisitive Pt(II) and Pd(II) complexes (**3a–d**).

have been synthesized and isolated as microcrystalline solids, tetrafluoroborate salts. Attempts to isolate the corresponding mono-positive Pd(II) complex, which displays fluxional behaviour in solution, have failed. All these complexes have been characterized by ^1H and ^{31}P NMR spectroscopy and conductivity measurements. In these cases, a single crystal suitable for X-ray analysis has not obtained. Nevertheless, the NMR spectra give useful information for the structures assignment. In particular, the chemical shift of the ^{31}P resonances ($50 < \delta < 70$) indicates for all the prepared cationic complexes a mononuclear structure with *bedip* chelating one metal centre. This spectroscopic evidence is in accordance with conductivity measurements [15] and elemental analyses.

The complex of formula $[\text{PtCH}_3(\text{PPh}_3)(\text{bedip})]\text{BF}_4$ (**2**) has been synthesized by reaction of the neutral dinuclear **1a** with silver tetrafluoroborate in presence of triphenylphosphine, according to Eq. (3). Running of the reaction for 24 h at r.t. and subsequent crystallization from diethyl ether allows to isolate the pure complex.

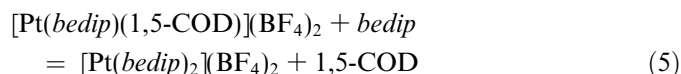
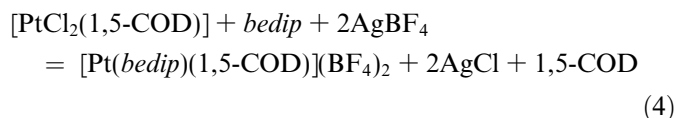


In the ^{31}P NMR spectrum, three signals relative to the three non-equivalent phosphorus atoms are found. Two resonances lie in a diagnostic region for chelate diphosphine, thus we assign to this complex the mononuclear structure showed in Fig. 8. As for the two phosphorus atoms belonging to *bedip*, the first one is *trans* to the methyl group and the other one *trans* to the phosphorus atom of PPh_3 . In fact, due to the too small *cis* $J_{\text{P-P}}$, the first one appears as a singlet at 45.2 ppm and shows a low value of $^1J_{\text{Pt-P}}$ (2106 Hz), characteristic [13] of a phosphorus atom *trans* to a methyl group; the second one is a doublet

at 49.6 ppm for the significant coupling with the *trans* phosphorus atom of PPh_3 ($^2J_{\text{P-P}(trans)} = 389$ Hz, $^1J_{\text{Pt-P}} = 2592$ Hz). Finally, the third signal in the spectrum, a doublet at 33.2 ppm with $^1J_{\text{Pt-P}} = 2948$ Hz, is assigned to PPh_3 . Complex **2** is poorly stable in solution and the ^1H NMR spectrum shows the disappearance of the methyl signal after 24 h.

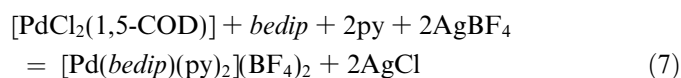
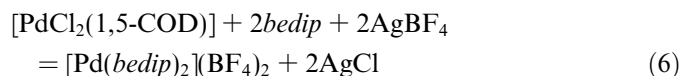
Cationic dipositive Pt(II) and Pd(II) complexes (**3a–d**) have been prepared from the appropriate precursors and have been isolated in nearly quantitative yield upon crystallization in diethyl ether.

$[\text{Pt}(bedip)(1,5\text{-COD})](\text{BF}_4)_2$ (**3a**) and $[\text{Pt}(bedip)_2](\text{BF}_4)_2$ (**3b**) have been obtained according to the following equations:



Relevant feature in the ^{31}P NMR spectrum for the structure assignment is the presence of a unique signal, respectively, at 53.34 ppm ($^1J_{\text{Pt-P}} = 2970$ Hz) for **3a** and at 51.08 ppm ($^1J_{\text{Pt-P}} = 2337$ Hz) for **3b** that support the mononuclear structure given above.

$[\text{Pd}(bedip)_2](\text{BF}_4)_2$ (**3c**) and $[\text{Pd}(bedip)(py)_2](\text{BF}_4)_2$ (**3d**), $py = \text{pyridine}$, has been prepared according to the following equations:

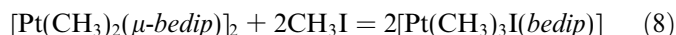


Also in these cases, ^{31}P NMR spectra show only one signal, respectively, at 60.19 ppm for **3c** and at 64.99 ppm for **3d**. Both Pt(II) and Pd(II) cationic dipositive complexes display a good stability in solution, being their spectra unchanged after standing several days at room temperature.

2.3. Reactivity

A preliminary investigation on the reactivity of the *bedip* complexes has involved both a stoichiometric and a catalytic process.

As for the former type, the binuclear Pt(II) dimethyl derivative **1d** has been chosen for the oxidative addition of methyl iodide, according to the following equation:



The oxidative addition product **4** has been obtained in the presence of a strong excess of CH_3I and after running the reaction for several hours.

The NMR spectrum discloses the presence of only one isomer, whose mononuclear octahedral structure has been

confirmed by single crystal X-ray analysis (Fig. 10). By assuming that the phosphorus atoms define the equatorial plane, the iodide is in axial position and faces the aliphatic bridge of the diphosphine. In the ^1H NMR spectrum, the signals at 1.43 (6H) and 0.62 (3H) ppm are relative to the equatorial and axial methyl groups, respectively.

The lack of the isomer showing the iodine versus the aromatic bridge is not immediately explainable, while the alternative possibility that two methyl groups were in axial positions can be reasonably excluded on the grounds of their high *trans*-influence.

An interesting feature of the reaction is the formation of a mono-nuclear addition product starting from a binuclear species. In analogy with what found in the cationic Pt(II) compounds, this may reflect the preference of *bedip* towards chelation in the presence of a hard metal centre.

On aging in chloroform solution, complex **4** slowly eliminates ethane with formation of the bi-nuclear Pt(II) compound **1c**. Its formation has been inferred by comparing the spectrum of the elimination reaction with that of **1c** prepared as previously described.

The Heck reaction has been selected for the catalytic test [16]. In particular, iodobenzene has been coupled with two olefins, styrene (i) and ethyl acrylate (ii), affording, respectively, *trans*-stilbene and *trans*-ethylcinnamate (Scheme 1).

In order to investigate the effect of the cyclic and unsymmetrical *core* of *bedip*, its influence has been compared with the linear non-cyclic *dppe* (1,2-bis(diphenylphosphino)ethane) and the cyclic symmetrical *dpdpc* (*cis*-*P,P'*-diphenyl-1,4-diphospha-cyclohexane).

A comparison of their activities was made by determining the yields of the reactions after 1, 3 and 4 h. The results summarized in Table 1 show that *bedip* promotes the higher conversion with both the olefins.

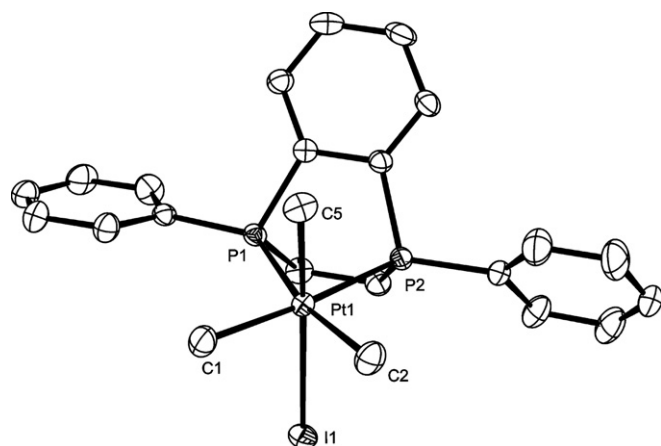
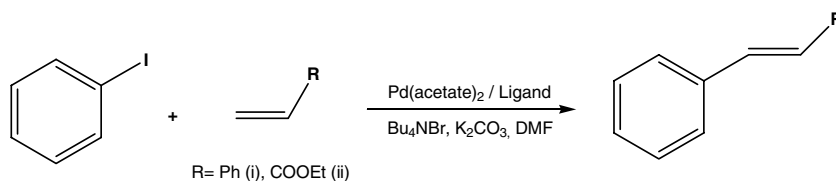
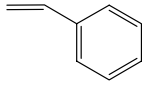
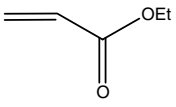


Fig. 10. ORTEP view of **4**. Thermal ellipsoids are shown at 50% probability level. All the hydrogen atoms are not shown for clarity. Selected bond distances (Å) and angles (°): Pt1–C2 = 2.078(6), Pt1–C5 = 2.082(6), Pt1–C1 = 2.094(6), Pt1–P2 = 2.366(1), Pt1–P1 = 2.394(1), Pt1–I1 = 2.770(7), C2–Pt1–C1 = 88.0(3), C2–Pt1–P2 = 97.8(2), C1–Pt1–P1 = 103.0(2), P2–Pt1–P1 = 71.1(5), C5–Pt1–I1 = 172.1(2).



Scheme 1. C–C coupling of iodobenzene Pd-catalyzed.

Table 1
Catalytic results (% conversion) for palladium-catalyzed Heck reaction of iodobenzene with styrene and ethyl acrylate^a

<i>t</i> (h)						
	<i>dppe</i> (%)	<i>dpdpc</i> (%)	<i>bedip</i> (%)	<i>dppe</i> (%)	<i>dpdpc</i> (%)	<i>bedip</i> (%)
1	20	11	31	37	26	44
3	25	18	66	50	34	59
4	30	23	73	56	37	66

^a Conditions: catalyst = Pd(OAc)₂/diphosphine = 1/1, catalyst/substrate (mol) = 3%, solvent = DMF, *T* = 333 K.

The electronic properties of the alkene decisively influence the activity of the catalysts based on *dppe* and *dpdpc*, i.e. the reaction proceeds faster with the electron-deficient ethyl acrylate than with styrene. No such an effect has been observed in the case of *bedip*.

In the whole, these preliminary results reveal a positive and interesting influence of the unsymmetrical cyclic *core* in *bedip*, worthy of further investigations.

2.4. X-ray molecular structures

The molecular structures of **M1b**, **M1c** and **4** are reported in Figs. 4, 5 and 10.

As can be observed from Figs. 4 and 5, the complexes **M1b** and **M1c** exhibit a very similar molecular structure. In **M1b** the molecule shows a local mirror symmetry, while in **M1c** the molecule lies on a crystallographic mirror plane bisecting the two *bedip*. Molecules show a dimeric structure with two *trans* Pt(CH₃)X (X = Br, I) fragments bridged by two mutually *trans bedip* ligands in a face to face arrangement. A “*syn*” arrangement of halogens as well as methyl groups is adopted, with the halogen atoms pointing toward the aliphatic moiety of *bedip*. The geometry at metal centres is typical square planar, even if a slight deviation from the regular coordination is observed, probably due to steric hindrance between the facing halogen atoms (Br1–Pt1–C1 = 170.5(2)°; Br2–Pt2–C2 = 169.0(2)°; I1–Pt1–C1 = 165.3(3)°). It should be noted that the four phosphorus atoms are coplanar with the two platinum centres and that the coordination planes are mutually eclipsed and normal to Pt₂P₄ plane (dihedral angles are 80.5(1)° and 85.8(1)° for **M1b** and exactly 90° for **M1c**). The presence of the bridging ligands on two

metal centres imposes a metal to metal distance not compatible with any intermetallic bonding interactions (3.272(8) Å and 3.380(7) Å, for **M1b** and **M1c**, respectively). The phenyl groups not involved in the bridge of each *bedip* are almost coplanar in **M1c**, while deviation from coplanarity is observed in **M1b**, probably due to packing interactions (angle between the mean planes of the phenyl groups bonded to P1, P3 and to P2, P4 is 12.2(8)° and 30.7(7)°, respectively).

The molecular structure of **4** shows an octahedral coordination around the metal centre, slightly distorted due to the constraints imposed by the chelation of the *bedip* (major deviation is P1–Pt1–P2 = 71.09(5)°). The two phenyl groups of *bedip* bound to P1 and P2 are tilted (angle between their mean planes is 48.5(7)°). This arrangement produces in the crystal packing favourable face to edge interactions between phenyl groups of different molecules.

3. Conclusions

This study discloses the versatile coordination properties of *bedip*, which is able to coordinate both in chelating and bridging mode, depending on the formal metal charge. X-ray molecular structures of representative complexes have pointed out relevant coordination parameters.

In comparison with known chelating diphosphines, *bedip* based catalyst shows highest activity in the coupling of iodobenzene with both styrene and ethyl acrylate, which stimulates further studies for understanding the positive influence of the unsymmetrical metal environment.

4. Experimental

All the reactions were carried out under a nitrogen atmosphere by using Schlenk techniques. Solvents were dried with standard procedures before use. ¹H NMR spectra [17] were recorded at 298 K with a Gemini 300 MHz spectrometer. CDCl₃, CD₂Cl₂ and CD₃NO₂ were used as solvents, and CHCl₃ (δ = 7.26 ppm), CHDCl₂ (δ = 5.31 ppm) and CHD₂NO₂ (δ = 4.33 ppm) as internal standards. ³¹P NMR spectra were recorded at 298 K on an AM 400-MHz Bruker spectrometer and referenced to an external standard of PPh₃. The following abbreviations were used for describing NMR multiplicities: s, singlet; d, doublet; t, triplet; app. q, apparent quartet; m, multiplet; br, broad signal; ax, axial; eq, equatorial. The coupling constants, when measurable, are reported in Hz. Conductivity measurements were

performed on a Crison Conductimeter, model microCM 2200. The complexes [PtCl₂(1,5-COD)] [18], [PtCl(CH₃)-(1,5-COD)] [18], [Pt(CH₃)₂(1,5-COD)] [18], [PdCl(CH₃)-(1,5-COD)] [19] and [PdCl₂(1,5-COD)] [20] were obtained by known methods.

Particular care was employed in excluding moisture or air in the synthesis of *bedip*, which was obtained as previously reported [11].

4.1. Synthesis of [PtX(CH₃)(μ-*bedip*)]₂ (X = Cl, Br, I) (**1a-c**)

A solution of *bedip* (36 mg, 0.11 mmol) in chloroform (1 mL) of was added to a stirred solution of [PtX(CH₃)-(1,5-COD)] (0.11 mmol) in the same solvent (1 mL). After 1 h, the solution was passed on a small Celite bed and the solvent was removed in vacuo. The crude product was dissolved in a minimum amount of chloroform and diethyl ether was added to crystallize the product as a yellow (X = Cl, Br) or yellow-orange (X = I) microcrystalline solid. The solid was washed with diethyl ether and dried in vacuo. Yield: 85–90%.

Compound 1a: Anal. Calc. for C₄₂H₄₂Cl₂P₄Pt₂: C, 44.58; H, 3.74. Found: C, 44.28; H, 3.60%.

¹H NMR relevant resonances (CD₂Cl₂) δ: (**M** isomer) 4.2 (br, 2H, CH₂P); 2.6 (br, 2H, CH₂P); -0.45 (m, 3H, ²J_{Pt-H} = 61); (**m** isomer) 3.4 (br, 2H, CH₂P); 2.0 (br, 2H, CH₂P); 0.98 (t, 3H, ³J_{P-H} = 7.2); -0.30 (t, 3H, ³J_{P-H} = 7.2); ³¹P NMR resonance (CD₂Cl₂) δ = 5.75 (s, ¹J_{Pt-P} = 3174).

Compound 1b: Anal. Calc. for C₄₂H₄₂Br₂P₄Pt₂: C, 41.33; H, 3.47. Found: C, 41.52; H, 3.37%.

¹H NMR relevant resonances (CD₂Cl₂) δ: (**M** isomer) 4.3 (br, 2H, CH₂P); 2.8 (br, 2H, CH₂P); -0.45 (m, 3H, ²J_{Pt-H} = 80); (**m** isomer) 3.4 (br, 2H, CH₂P); 2.4 (br, 2H, CH₂P); 1.18 (t, 3H, ³J_{P-H} = 6.0); -0.22 (t, 3H, ³J_{P-H} = 6.0); ³¹P NMR resonance (CD₂Cl₂) δ = 7.7 (s, ¹J_{Pt-P} = 3098).

Compound 1c: Anal. Calc. for C₄₂H₄₂I₂P₄Pt₂: C, 38.38; H, 3.22. Found: C, 38.45; H, 3.60%.

¹H NMR relevant resonances (CD₂Cl₂) δ: (**M** isomer) 4.4 (br, 2H, CH₂P); 2.9 (br, 2H, CH₂P); -0.45 (m, 3H, ²J_{Pt-H} = 77); (**m** isomer) 3.5 (br, 2H, CH₂P); 1.12 (t, 3H, ³J_{P-H} = 6.7); -0.15 (t, 3H, ³J_{P-H} = 6.7); ³¹P NMR resonance (CD₂Cl₂) δ = 5.4 (s, ¹J_{Pt-P} = 3057).

4.2. Synthesis of [Pt(CH₃)₂(μ-*bedip*)]₂ (**1d**)

A solution of *bedip* (58 mg, 0.18 mmol) in tetrahydrofuran (1 mL) was added to a stirred solution of [Pt(CH₃)₂-(1,5-COD)] (60 mg, 0.18 mmol) in the same solvent (1 mL). After 2.5 h the yellow solution was passed on a small Celite bed and the solvent was removed in vacuo. The crude product was dissolved in a minimum amount of tetrahydrofuran and diethyl ether was added to crystallize the product as a white solid. The solid was washed with diethyl ether and dried in vacuo. Yield: 75%.

Anal. Calc. for C₄₄H₄₈P₄Pt₂: C, 48.45; H, 4.44. Found: C, 48.21; H, 4.56%.

¹H NMR relevant resonances (CD₂Cl₂) δ: 3.2 (br, 2H, CH₂P); 2.5 (br, 2H, CH₂P); 0.45 (m, 6H, ²J_{Pt-H} = 74); ³¹P NMR resonance (CD₂Cl₂) δ = 13.57 (s, ¹J_{Pt-P} = 1925).

4.3. Synthesis of [PdCl(CH₃)(μ-*bedip*)]₂ (**1e**)

Two alternative procedures were used to prepare **1e**:

- A solution of *bedip* (48 mg, 0.15 mmol) in dichloromethane (1 mL) was added to a stirred solution of [PdCl(CH₃)(1,5-COD)] (40 mg, 0.15 mmol) in the same solvent (2 mL). After 2 h the orange solution was passed on a small Celite bed and concentrated to a small volume. Addition of diethyl ether prompted the precipitation of the yellow product. Yield: 85%.
- A solution of *bedip* (48 mg, 0.15 mmol) in dichloromethane (1 mL) was added to a stirred solution of [PdCl₂(1,5-COD)] (43 mg, 0.15 mmol) in the same solvent (2 mL). After 24 h the yellow solid was recovered by filtration, suspended in dichloromethane (1 mL) and Sn(CH₃)₄ (25 mg, 0.14 mmol) was added. After 24 h of stirring the resulting orange solution was passed on a small Celite bed and concentrated to a small volume. Addition of diethyl ether prompted the precipitation of the yellow product. Yield: 75%.

Anal. Calc. for C₄₂H₄₂Cl₂P₄Pd₂: C, 52.86; H, 4.44. Found: C, 52.60; H, 4.37%.

¹H NMR relevant resonances (CD₂Cl₂) δ: (**M** isomer) 4.15 (br, 2H, CH₂P); 2.5 (br, 2H, CH₂P); -0.40 (m, 3H); (**m** isomer) 1.04 (t, 3H, ³J_{P-H} = 4.9); -0.16 (t, 3H, ³J_{P-H} = 4.9); (**mm** isomer) 0.43 (m, 3H); ³¹P NMR resonance (CD₂Cl₂) δ = 12.4 (s).

4.4. Synthesis of [Pt(CH₃)(PPh₃)(*bedip*)]BF₄ (**2**)

To a stirred solution of [PtCl(CH₃)(μ-*bedip*)]₂ (96 mg, 0.085 mmol) in a minimum amount of a dichloromethane/nitromethane (1:1), a solution of AgBF₄ (33 mg, 0.17 mmol) and PPh₃ (44 mg, 0.17 mmol) in nitromethane (0.5 mL) was added and the stirring was continued for 24 h at r.t. The solvent was removed in vacuo and the residue was extracted with chloroform (3 × 1 mL). The solution was concentrated to a small volume and passed on a small Celite bed. Addition of diethyl ether prompted the precipitation of the white product. Yield: 80%.

Anal. Calc. for C₃₉H₃₆BF₄P₃Pt: C, 53.26; H, 4.13. Found: C, 53.15; H, 4.51%.

¹H NMR relevant resonances (CD₃NO₂) δ: 3.3 (br, 2H, CH₂P); 2.4 (br, 2H, CH₂P); 0.44 (app q, 3H, ²J_{Pt-H} = 65, ³J_{P-H} = 6.7); ³¹P NMR resonances (CD₃NO₂) δ = 33.2 (d, ¹J_{Pt-P} = 2948, ²J_{P-P(trans)} = 389); 45.2 (s, ¹J_{Pt-P} = 2106); 49.6 (d, ¹J_{Pt-P} = 2592).

Conductivity in nitromethane at 293 K: 66.3 S mol⁻¹ cm⁻¹.

4.5. Synthesis of [Pt(*bedip*)(1,5-COD)](BF₄)₂ (**3a**)

To a stirred solution of [PtCl₂(1,5-COD)] (42 mg, 0.11 mmol) in chloroform (1 mL), a solution of AgBF₄ (21 mg, 0.11 mmol) in nitromethane (0.27 mL) and *bedip* (36 mg, 0.11 mmol) in chloroform (1 mL) were added. After 1 h, the resulting mixture was passed on a small Celite bed and solvents were removed in vacuo. The crude product was dissolved in a minimum amount of chloroform and diethyl ether was added to crystallize the product as a pale-yellow microcrystalline solid. The solid was washed with diethyl ether and dried in vacuo. Yield: 90%.

Anal. Calc. for C₂₈H₃₀B₂F₈P₂Pt: C, 42.19; H, 3.79. Found: C, 42.48; H, 3.90%.

¹H NMR relevant resonances (CD₃NO₂) δ: 6.1 (br, 2H, ²J_{Pt-H} = 47, CH = CH-COD); 5.9 (br, 2H, ²J_{Pt-H} = 54, CH = CH-COD); 3.85 (dd, 2H, ²J_{H-H} = 11, ²J_{P-H} = 3.0, PCHHCHHP); 2.98 (dd, 2H, ²J_{P-H} = 3.0, PCHHCHHP); 3.0–2.4 (br, 8H, CH₂-COD); ³¹P NMR resonances (CD₃NO₂) δ = 53.3 (s, ¹J_{Pt-P} = 2970).

Conductivity in nitromethane at 293 K: 132 S mol⁻¹ cm⁻¹.

4.6. Synthesis of [Pt(*bedip*)₂](BF₄)₂ (**3b**)

Solid *bedip* (36 mg, 0.11 mmol) was added to a stirred solution of **3a** (88 mg, 0.11 mmol) in chloroform (2 mL). After 1.5 h the white microcrystalline precipitate was recovered by filtration. The solid was washed with diethyl ether and dried in vacuo. Yield: 95%.

Anal. Calc. for C₄₀H₃₆B₂F₈P₄Pt: C, 47.60; H, 3.60. Found: C, 47.16; H, 3.73%.

¹H NMR relevant resonances (CD₃NO₂) δ: 3.58 (d, 2H, ²J_{H-H} = 10, PCHHCHHP); 2.47 (m, 2H, PCHHCHHP); ³¹P NMR resonance (CD₃NO₂) δ: 51.08 (s, ¹J_{Pt-P} = 2337).

Conductivity in nitromethane at 293 K: 112 S mol⁻¹ cm⁻¹.

4.7. Synthesis of [Pd(*bedip*)₂](BF₄)₂ (**3c**)

A solution of *bedip* (48 mg, 0.15 mmol) in dichloromethane (1 mL) was added to a stirred solution of [PdCl₂(1,5-COD)] (43 mg, 0.15 mmol) in the same solvent (2 mL). After 24 h, the white solid was recovered by filtration. To a stirred suspension of isolated product “[PdCl₂(*bedip*)]” (30 mg, 0.060 mmol) in dichloromethane (0.5 mL), a solution of *bedip* (19 mg, 0.060 mmol) in the same solvent (0.5 mL) and AgBF₄ (23 mg, 0.12 mmol) in nitromethane (0.27 mL) were added. After stirring for 24 h, the white precipitate was removed by filtration on a small Celite bed and the resulting yellow solution was dried in vacuo. The product was recovered as a pale-yellow solid. Yield: 90%.

Anal. Calc. for C₄₀H₃₆B₂F₈P₄Pd: C, 52.19; H, 3.94. Found: C, 51.93; H, 3.70%.

¹H NMR relevant resonances (CD₃NO₂) δ: 3.50 (d, 2H, ²J_{H-H} = 9.5, PCHHCHHP); 2.8 (br, 2H, PCHHCHHP); ³¹P NMR resonance (CD₃NO₂) δ: 60.2 (s).

Conductivity in nitromethane at 293 K: 124 S mol⁻¹ cm⁻¹.

4.8. Synthesis of [Pd(*bedip*)(*py*)₂](BF₄)₂ (**3d**)

A solution of *bedip* (48 mg, 0.15 mmol) in 1 mL of dichloromethane was added to a stirred solution of [PdCl₂(1,5-COD)] (43 mg, 0.15 mmol) in the same solvent (2 mL). After 24 h the white solid was recovered by filtration. To a stirred suspension of isolated product “[PdCl₂(μ-*bedip*)]” (30 mg, 0.06 mmol) and pyridine (9.5 mg, 0.12 mmol) in dichloromethane (2 mL), AgBF₄ (23 mg, 0.12 mmol) in nitromethane (0.275 mL) was added. After 24 h, the white precipitate was removed by filtration on a small Celite bed and the resulting yellow solution was dried in vacuo. The product was recovered as a pale-yellow solid. Yield: 90%.

Anal. Calc. for C₃₀H₂₈B₂F₈N₂P₂Pd: C, 47.50; H, 3.72. Found: C, 47.22; H, 3.68%.

¹H NMR relevant resonances (CD₃NO₂) δ: 8.65 (d, 2H, ³J_{H-H} = 4.0, CH=N-py); 3.82 (m, 2H, PCHHCHHP); 2.78 (t, 2H, ²J_{H-H} = 10, PCHHCHHP); ³¹P NMR resonance (CD₃NO₂) δ: 65.0 (s).

Conductivity in nitromethane at 293 K: 130 S mol⁻¹ cm⁻¹.

4.9. Synthesis of [PtI(CH₃)₃(*bedip*)] (**4**)

To a stirred solution of **1d** (50 mg, 0.046 mmol) in dichloromethane (1 mL), an excess of CH₃I (0.46 mmol) was added and the stirring was continued for 8 h at r.t. Addition of diethyl ether prompted the precipitation of the white product. Yield: 80%.

Anal. Calc. for C₂₃H₂₇IP₂Pt: C, 40.19; H, 3.96. Found: C, 40.31; H, 3.88%.

¹H NMR relevant resonances (CD₂Cl₂) δ: 3.50 (d, 2H, ²J_{H-H} = 10, PCHHCHHP); 2.55 (br, 2H, PCHHCHHP); 1.43 (s, 6H, ²J_{Pt-H} = 62, 2CH₃ eq), δ = 0.64 (t, 3H, ²J_{Pt-H} = 69, ³J_{P-H} = 6.2, CH₃ ax).

4.10. Catalytic tests

In a typical experiment iodobenzene (1.0 mmol), olefin (1.0 mmol), K₂CO₃ (1.0 mmol), Bu₄NBr (1.0 mmol), Pd(OAc)₂ (0.030 mmol) and the appropriate ligand (0.030 mmol) are placed simultaneously in *N,N*-dimethylformamide (2 mL).

The mixture is placed in an oil bath at 333 K and kept under stirring. After times indicated in Table 1, little amounts are collected from the mixture reaction, quenched by water and then analyzed by ¹H NMR spectroscopy in chloroform solution.

4.11. Structures determination

Single crystals suitable for X-ray analysis were obtained, at room temperature, by slow diffusion of diethyl ether into a solution of the complexes in chloroform for **M1b** and **M1c**, and by slow evaporation from a methylene chloride solution for **4**.

Data collection was performed in flowing N₂ at 173 K for **M1b** and at room temperature for **M1c** and **4** on a Bruker-Nonius kappaCCD diffractometer (Mo K α radiation, CCD rotation images, thick slices, φ scans + ω scans to fill the asymmetric unit). Cell parameters were determined from 186 reflections in the range $3.24^\circ \leq \theta \leq 20.98^\circ$, 369 reflections in the range $3.28^\circ \leq \theta \leq 22.46^\circ$, and 139 reflec-

tions in the range $3.11^\circ \leq \theta \leq 21.31^\circ$ for **M1b**, **M1c** and **4**, respectively. Semiempirical absorption correction (multi-scan SADABS) [21] was applied. The structures were solved by direct methods (SIR-97 package) [22] and refined by the full-matrix least-squares method (SHELXL program of SHELX-97 package) [23] on F^2 against all independent measured reflections, using anisotropic thermal parameters for all non-hydrogen atoms. H atoms were placed in calculated positions with U_{eq} equal to those of the carrier atom and refined by the riding method. Crystal data and details of the data collection for all the structures are reported in Table 2.

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Appendix A. Supplementary material

CCDC 628741, 628742 and 628743 contain the supplementary crystallographic data for **M1b**, **M1c** and **4**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.08.003.

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Table 2
Crystal data and experimental details for **M1b**, **M1c** and **4**

Compound	M1b	M1c	4
Chemical formula	C ₄₂ H ₄₂ Br ₂ P ₄ Pt ₂ · 2CHCl ₃	C ₄₂ H ₄₂ I ₂ P ₄ Pt ₂	C ₂₃ H ₂₇ IP ₂ Pt
Crystal size (mm)	0.15 × 0.25 × 0.2	0.3 × 0.3 × 0.2	0.4 × 0.3 × 0.3
Crystal habitus, colour	Prism, yellow	Prism, orange	Prism, white
Formula weight	1459.37	1314.60	687.38
Temperature (K)	173	293	293
λ (Å)	0.71069	0.71069	0.71069
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	<i>Pbca</i>	<i>Pnma</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	14.309(3)	14.896(2)	9.343(2)
<i>b</i> (Å)	21.834(4)	21.635(1)	9.585(1)
<i>c</i> (Å)	31.531(4)	12.683(4)	13.972(2)
α (°)	90	90	96.79(1)
β (°)	90	90	104.74(1)
γ (°)	90	90	104.52(1)
Volume (Å ³)	9851(3)	4087(2)	1149.0(3)
<i>Z</i>	8	4	2
<i>D</i> _{calc} (g cm ⁻³)	1.968	2.136	1.987
μ (mm ⁻¹)	7.783	8.534	7.595
θ Range (°)	3.04–27.50	3.17–27.51	3.01–27.50
Reflections collected	52973	29329	21462
Unique observed reflections (<i>R</i> _{int})	11295 (0.0981)	4785 (0.0849)	5173 (0.0595)
Data/parameters	11295/523	4785/227	5173/247
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0503, 0.0787	0.0500, 0.1124	0.0340, 0.0778
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (all data)	0.1143, 0.0914	0.0960, 0.1369	0.0539, 0.0869
Largest difference in peak and hole (e Å ⁻³)	1.237 and -1.327	1.488 and -2.564	0.825 and -2.003

^a $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$.

^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

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