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Organoplatinum complexes with an ester substituted bipyridine ligand: Oxidative addition and supramolecular chemistry

Muhieddine Safa, Richard J. Puddephatt*

Department of Chemistry, University of Western Ontario, London, Canada N6A 5B7

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ABSTRACT

The synthesis and chemistry of the complex [$PtMe_2$(bebipy)], **1**, where bebipy = 4,4′-bis(ethoxycarbonyl)-2,2′-bipyridine, are described. Complex **1** reacted with HCl to give [PtClMe(bebipy)] and [$PtCl_2$(bebipy)], and all of these platinum(II) complexes gave π-stacking in the solid state. Complex **1** reacted with X_2 by *trans* oxidative addition to give [PtX_2Me_2(bebipy)], X = Br, I, OH, and the complex with X = I is characterized by structure determination as [PtI_2Me_2(bebipy)].1.5I_2. Complex **1** usually reacted with RX by *trans* oxidative addition, to give [PtXRMe$_2$(bebipy)], R = Me, X = I; R = CO_2Et, X = Cl; R = CH_2CO_2H, X = Br; R = CH_2-4-C_6H_4-CO_2H, X = Br; R = CH_2-4-C_6H_4-CH_2CO_2H, X = Br; R = $CH_2CONHC_6H_5$, X = Br; R = CH_2CONH-4-C_6H_4-*t*-Bu, X = Br; R = CH_2-3-C_6H_4-CH_2OH, X = Br. However, acetyl chloride reacted to give a mixture of compounds formed by *cis* and *trans* oxidative addition, and it is suggested that the reaction occurs by initial nucleophilic attack by platinum(II) at the carbonyl group with formation of a tetrahedral intermediate [Pt^+Me_2($CMeClO^-$)(bebipy)]. The platinum(IV) complexes with hydrogen bonding groups formed supramolecular dimers or polymers in the crystalline state, but the ester groups of the bebipy ligands did not participate in the hydrogen bonding.

1. Introduction

The complexes of formula [$PtMe_2$(NN)], where NN is a chelating nitrogen donor ligand such as 2,2′-bipyridine [1,2], react with alkyl halides, RX, to give platinum(IV) complexes [$PtXMe_2R$(NN)] by oxidative addition [3,4,5]. These reactions have been used to prepare a wide range of functional organoplatinum(IV) complexes [3,6,7,8,9,10,11,12,13,14,15,16,17], and several of them have served as paradigms for understanding reactivity and mechanism in oxidative addition reactions [3,18,19,20,21,22,23]. Several substituted derivatives of 2,2′-bipyridine have been studied, most commonly by introducing alkyl groups to increase solubility of the complexes [$PtMe_2$(NN)], such as in ***A*** (Chart 1) [3,24]. However, functional groups have also been used as in complexes ***B*** and ***C*** (Chart 1) to allow formation of polymers or oligomers through either covalent bond formation with ***B*** or hydrogen bond formation with ***C*** [15,17,24,25].

This article describes the synthesis and chemistry of the complex [$PtMe_2$(bebipy)], **1** (Chart 1), where bebipy = 4,4′-bis(ethoxycarbonyl)-2,2′-bipyridine [26]. The ligand 2,2′-bipyridine-4,4′-dicarboxylic acid has often been used to anchor transition metal catalysts to oxide supports, and complexes of its ester derivatives have been studied as sensitizers for electron transfer or as catalysts [26,27,28,29,30]. Complex **1** was expected to be less electron rich, and so less reactive in oxidative addition, than [$PtMe_2$(bipy)], because the ethoxycarbonyl groups are electron withdrawing substituents, but there is potential for the ester groups to participate in some reactions. For example, they can act as hydrogen bond acceptors [8,26,27,28,29,30].

2. Results and discussion

2.1. Synthesis and structure of square planar complexes

Three square planar platinum(II) complexes with the ligand bebipy were prepared according to Scheme 1. Complex **1** was prepared as a purple solid by reaction of the ligand bebipy with [Pt_2Me_4(μ-SMe_2)$_2$] with displacement of the weakly bound dimethylsulfide ligands. In the ^{1}H NMR spectrum of complex **1**, the methylplatinum resonance occurred at δ = 1.14, with coupling $^2J_{PtH}$ = 86 Hz, while the *ortho* pyridyl protons occurred at δ = 9.42, with coupling $^3J_{PtH}$ = 28 Hz. Only one set of pyridyl and ethyl resonances was observed as expected for a complex with effective C_{2v} symmetry. The reaction of complex **1** with HCl gave complexes **2** and **3**, with loss of methane in each step. The ^{1}H NMR spectrum of complex **3** contained no methylplatinum resonance and the *ortho* pyridyl protons occurred at δ = 9.97, with coupling $^3J_{PtH}$ = 48 Hz.

* Corresponding author. Fax: +519 661 3022.
E-mail address: pudd@uwo.ca (R.J. Puddephatt).

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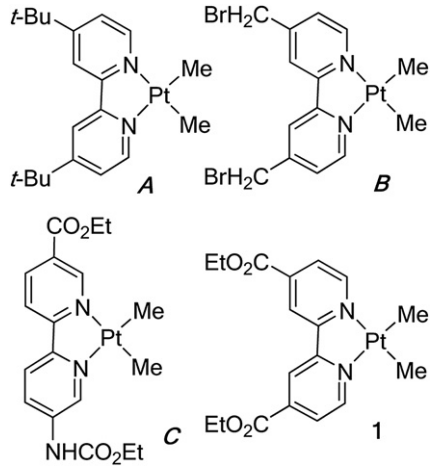
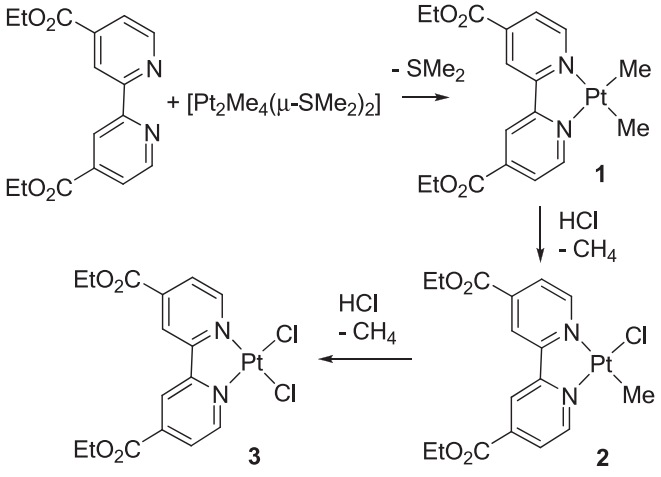


Chart 1. Some derivatives of [$PtMe_2$(bipy)].

The higher coupling constant compared to that in **1** is a result of the lower *trans* influence of the chloride ligands in **3** compared to the methyl ligands in **1**.

The molecular structures of complexes **1**–**3** were determined and are shown in Fig. 1. In each case, there are two non-equivalent molecules in the unit cell and, for the unsymmetrical complex **2** there is also disorder of the methyl and chloride ligands which caused the refinement of the structure to be difficult. The Pt(1) and Pt(2) molecules in **2** were refined to have 85:15 and 60:40 occupation respectively, and only the major components are shown in Fig. 1. The coordination geometries of the complexes are similar, with the mean Pt–N distance in **1** being slightly higher and the NPtN angle slightly lower in **1** compared to **3** [mean Pt–N = 2.08 Å in **1**, 2.04 Å in **3**; mean N–Pt–N = 78.1° in **1**, 79.9° in **3**], as a result of the higher *trans* influence of methyl compared to chloride.

One notable feature of the structures is that the conformations of the ester groups are varied (Fig. 1). The CO_2 unit of each ester group tends to be roughly coplanar with the attached pyridyl group, presumably because this allows a higher degree of conjugation. The carbonyl group may be directed towards (*endo* conformation) or away (*exo* conformation) from the plane which bisects the two pyridyl groups. In complex **1** the two ester groups for the Pt(1) and Pt(2) molecules are in the *endo,endo* and *endo,exo* conformation respectively, while in complex **3** the two ester groups for both the Pt(1) and Pt(2) molecules are in the *exo,exo* conformation (Fig. 1). The Pt(1) and Pt(2) molecules of the unsymmetrical complex **2** have



Scheme 1. Synthesis of platinum(II) complexes.

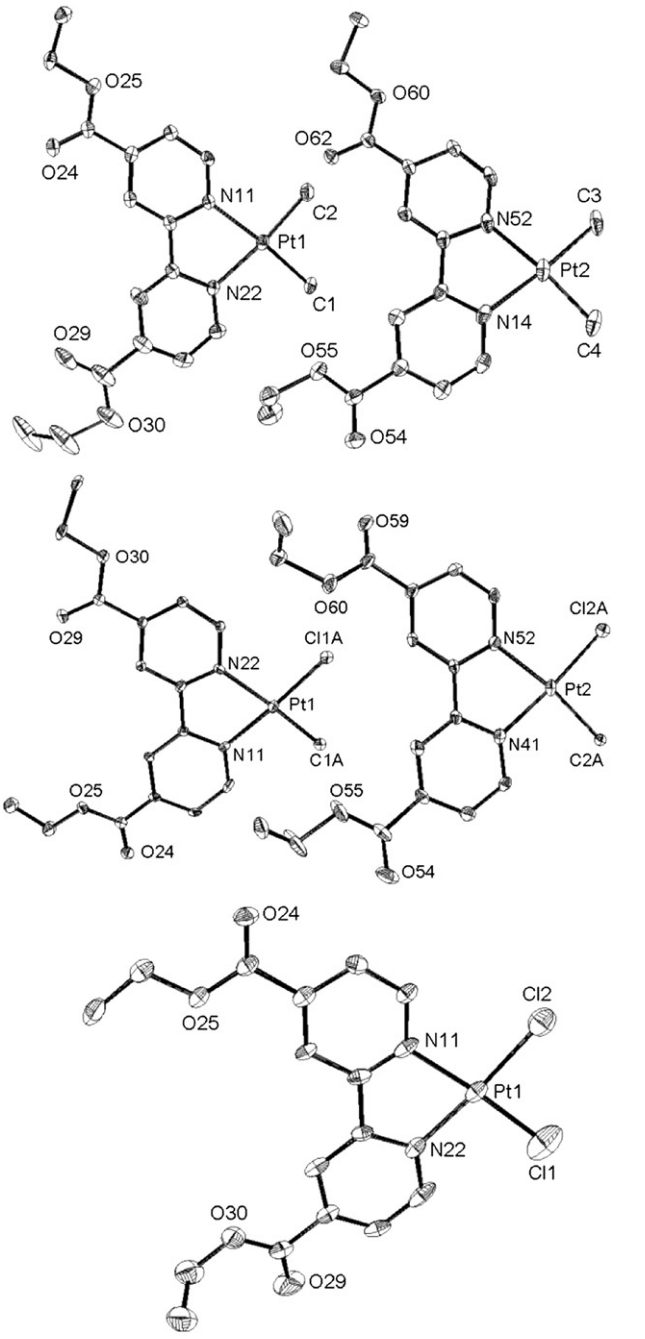


Fig. 1. The molecular structures of: top, two inequivalent molecules of **1**; center, two inequivalent molecules of **2**, showing only the major component due to Me/Cl disorder in each case; bottom, one of the two inequivalent molecules of **3** (the second is very similar).

the *endo,exo* and *exo,exo* conformation, with the major component of the Pt(1) molecule having the *endo* conformation *trans* to the methyl group and the *exo* conformation *trans* to the chloride ligand. We have carried out DFT calculations for all of the possible conformers for each molecule, and find that the calculated gas phase energies are equal within 2 kJ mol^{-1} in each case. It is likely, therefore, that the observed conformations arise through crystal packing or weak intermolecular secondary bonding forces.

The molecules of complexes **1**–**3** pack in columns, as shown in Figs. 2–4, a form of packing which is common for planar molecules [31,32,33,34]. Complex **1** packs with alternating Pt(1) and Pt(2) molecules as $[Pt(1)Pt(2)]_n$ (Fig. 2), while complexes **2** and **3** pack

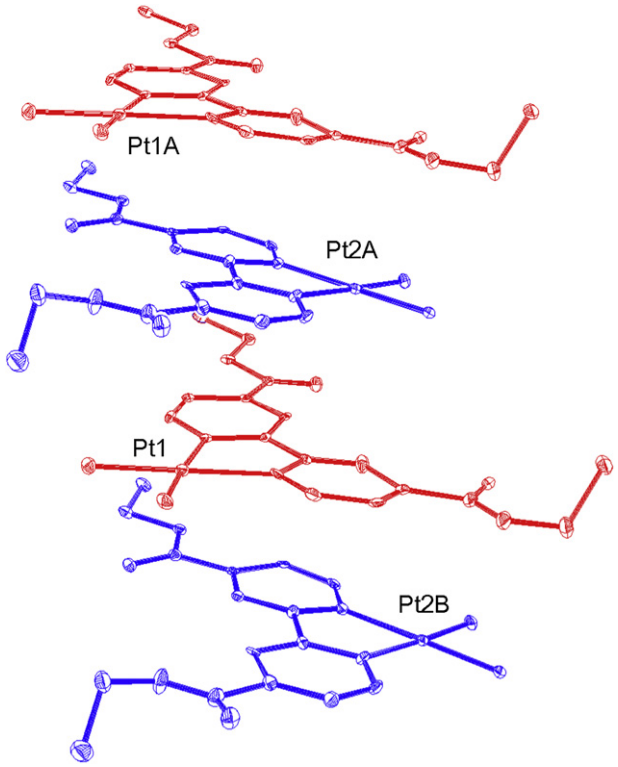


Fig. 2. Stacking of molecules of complex **1**.

in pairs of equivalent molecules, as [Pt(1)Pt(1)Pt(2)Pt(2)]$_n$ (Figs. 3 and 4).

2.2. Oxidative addition reactions of complex *1* with halogens and hydrogen peroxide

The reaction of bromine, iodine or hydrogen peroxide to complex **1** occurred by *trans* oxidative addition, as shown in Scheme 2. The ^{1}H NMR spectra of complexes **4**–**6** each contained a single methylplatinum resonance [**4**, $\delta = 2.07$, $^2J_{PtH} = 71$ Hz; **5**, $\delta = 2.42$, $^2J_{PtH} = 73$ Hz; **6**, $\delta = 1.66$, $^2J_{PtH} = 70$ Hz], and a single set of pyridyl and ethyl resonances, as expected for a complex with C_{2v} symmetry. The low value of the coupling constant $^3J_{PtH}$ for the *ortho* pyridyl protons in **4**–**6** [$^3J_{PtH} = 18$ Hz in each case] shows that the pyridyl groups are *trans* to methyl groups.

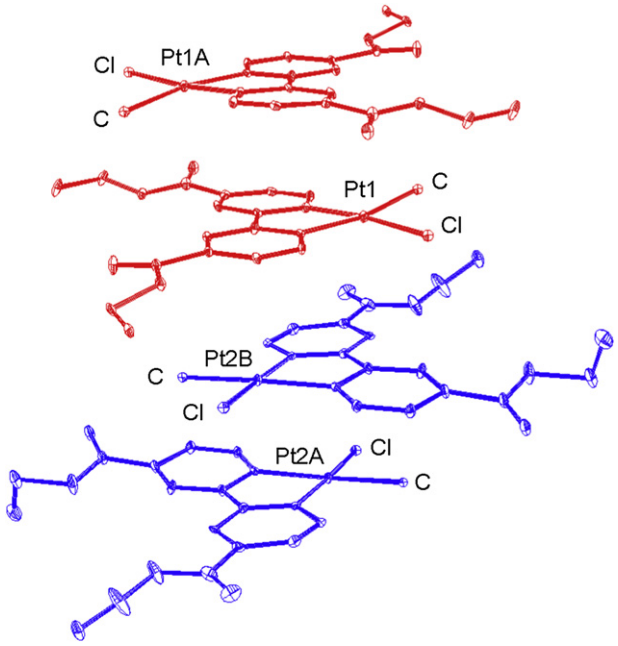


Fig. 3. Stacking of molecules of complex **2**.

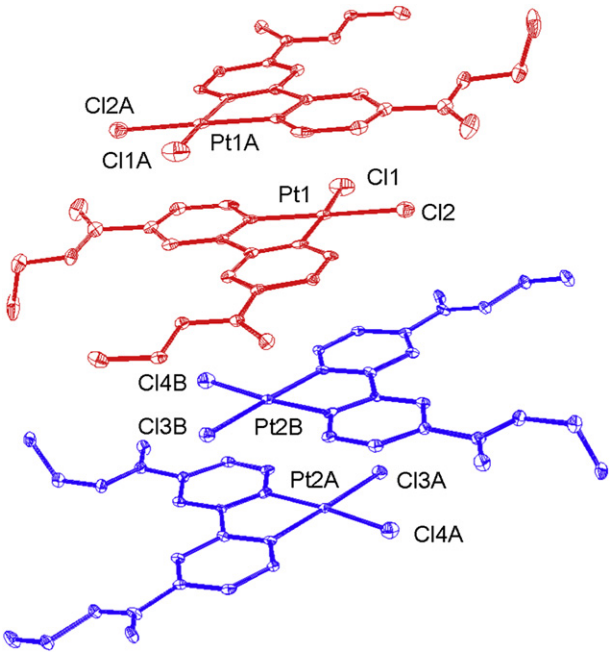
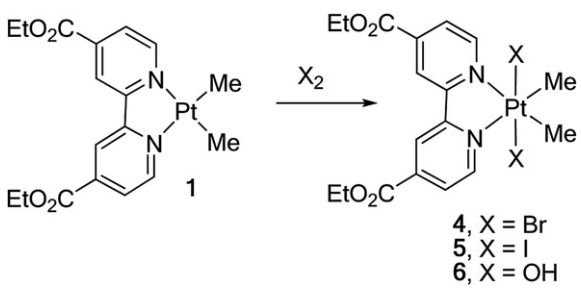


Fig. 4. Stacking of molecules of complex **3**.

The structure of complex **4** is shown in Fig. 5, and confirms that it is formed by *trans* oxidative addition of bromine. In complex **4**, the ester groups adopt the *endo,exo* conformation. The reaction of complex **4** with bromine occurred very rapidly and was monitored by ^{1}H NMR spectroscopy in CD_2Cl_2 solution. At −80 °C, complex **4** was already present, but an intermediate was also observed in which the methylplatinum resonance occurred at $\delta = 1.97$, with $^2J_{PtH} = 70$ Hz. This resonance decayed on warming the solution, and **4** was formed as the sole product. The intermediate is tentatively identified as the bromine complex, ***D*** with X = Br, as shown in the mechanism of Scheme 3. The mechanism is consistent with that proposed for oxidative addition of halogens and hydrogen peroxide to [$PtMe_2$(bipy)] [35,36,37,38,39,40,41], and the NMR spectrum of the intermediate is similar to that of the analogous iodine complex [$PtMe_2(I_2)$(bipy)] [35].

Complex **5** was difficult to crystallize but good crystals were finally obtained from a reaction of complex **1** with excess iodine. The structure is shown in Fig. 6, which shows the *trans*-PtI_2



Scheme 2. Oxidative addition of bromine, iodine and hydrogen peroxide.

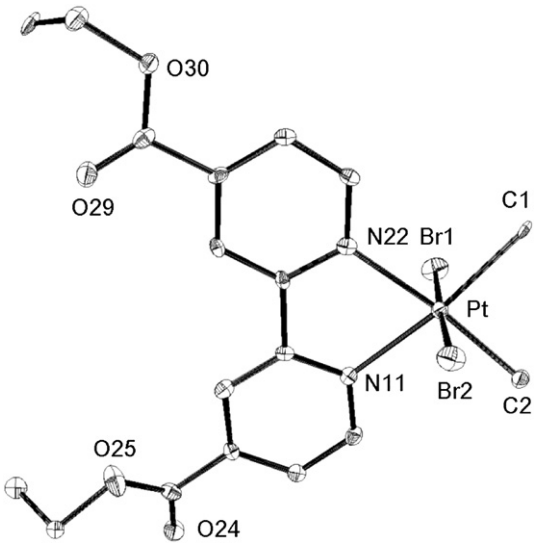
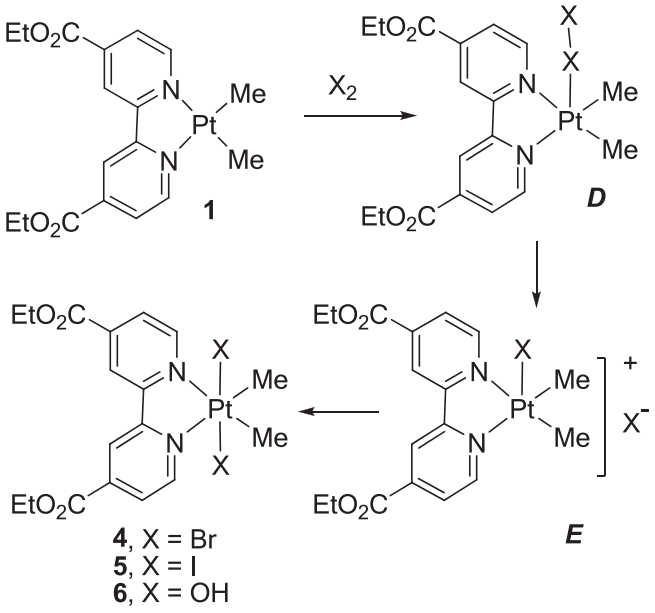


Fig. 5. The structure of complex **4**. Selected bond parameters: Pt–N(11) 2.17(1); Pt–N(22) 2.17(1); Pt–C(1) 2.17(1); Pt–C(2) 2.10(1); Pt–Br(1) 2.405(2); Pt–Br(2) 2.437(2) Å.

stereochemistry, the presence of extra iodine molecules and the *endo,endo* conformation of the ester groups. The association of platinum(IV) iodide complexes with molecular iodine has been observed previously [35,40,41], but the arrangement in complex **5**·1.5I_2 appears to be unprecedented. The atom I(2) is associated with one iodine molecule, with distances I(2)···I(3) = 3.245(1) and I(3)–I(4) = 2.7327(7) Å, while a second iodine molecule bridges between the I(1) atoms of neighboring molecules of complex **5**, with I(1)···I(5) = 3.407(1) and I(5)–I(5A) = 2.748(1) Å. The complex could be considered to contain an I_3^- ligand and a bridging I_4^{2-} ligand, but the distances suggest only secondary bonding between the iodine molecules and iodide ligands [35,40,41,42,43,44].

The oxidative addition of hydrogen peroxide to complex **1** to give the dihydroxo complex **6** (Scheme 2) is similar to reactions with similar complexes [$PtMe_2$(NN)] [37,38,39,45], but with one unusual feature. Complex **6** was formed in high yield but it decomposed in solution to give the free ligand bebipy, with



Scheme 3. Proposed mechanism of formation of complexes **4**–**6**.

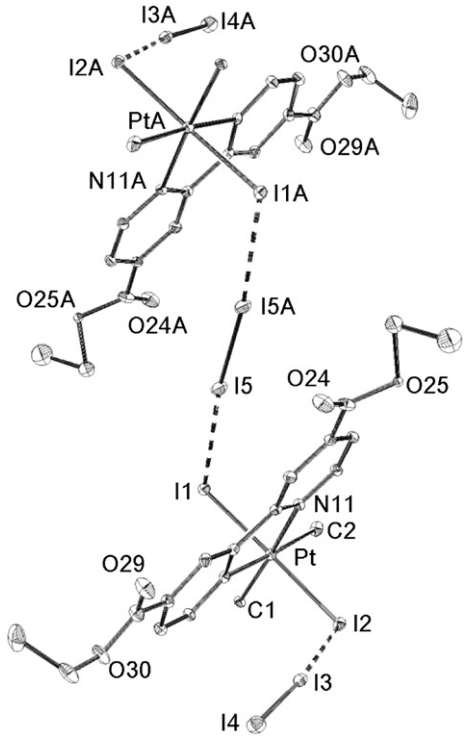


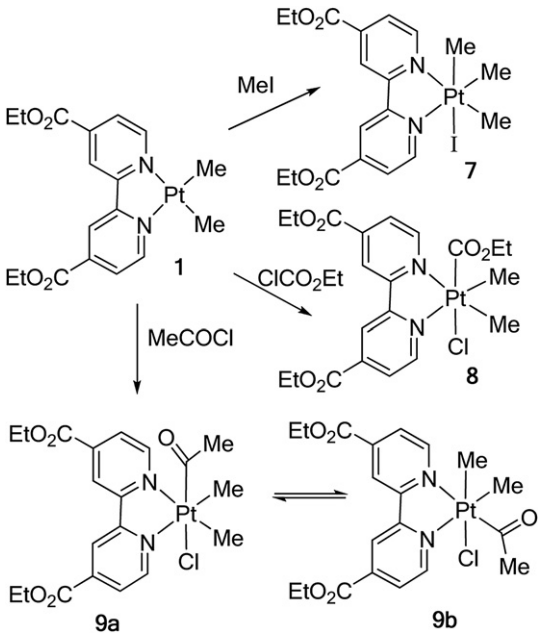
Fig. 6. The structure of complex **5**·1.5I_2: Selected bond distances: Pt–N(11) 2.179(5); Pt–N(22) 2.171(5); Pt–C(1) 2.119(6); Pt–C(2) 2.104(7); Pt–I(1) 2.6376(5); Pt–I(2) 2.6421(5); I(3)–I(4) 2.7327(7); I(5)–I(5A) 2.748(1) Å.

precipitation of [{$PtMe_2(OH)_2$}$_n$] as a white solid. The reaction was complete in two days at room temperature, and the polymeric complex [{$PtMe_2(OH)_2$}$_n$] was isolated and identified by dissolving in dilute D_2SO_4/D_2O to give the characteristic NMR spectrum of the cation *cis*-[$PtMe_2(OD_2)_4$]$^{2+}$ with δ(MePt) = 2.26, $^2J_{PtH}$ = 66 Hz [46,47,48]. The easy dissociation of the bebipy ligand from complex **6** is probably a result of the electron withdrawing properties of the carboxylic ester substituents, which make bebipy a weaker donor than the parent 2,2′-bipyridine.

2.3. Oxidative addition reactions of complex *1* with carbon–halogen bonds

The oxidative addition reactions of some compounds with carbon–halogen bonds to complex **1** are illustrated in Scheme 4. Methyl iodide reacted rapidly with **1** to give [$PtIMe_3$(bebipy)], **7**. This complex was readily characterized by its ^{1}H NMR spectrum, which contained two methylplatinum resonances in a 1:2 ratio at δ = 0.60, $^2J_{PtH}$ = 72 Hz, and δ = 1.52, $^2J_{PtH}$ = 71 Hz, corresponding to the methyl groups *trans* to iodide and nitrogen respectively. The reaction with CD_3I occurred by *trans* oxidative addition. Similarly, ethyl chloroformate reacted with **1** by *trans* oxidative addition to give complex **8** (Scheme 4). The ^{1}H NMR spectrum of **8** contained only a single methylplatinum resonance at δ = 1.65, $^2J_{PtH}$ = 74 Hz, as expected for a complex with C_s symmetry. Complex **8** decomposed slowly in solution to give [PtClMe(bebipy)], **2**, by reductive elimination of ethyl acetate.

The reaction of acetyl chloride with complex **1** gave [$PtClMe_2$(COMe)(bebipy)], as a mixture of the products of *trans* and *cis* oxidative addition **9a** and **9b** in a 25:75 ratio. The *cis* isomer **9b** was characterized in the ^{1}H NMR spectrum by the presence of two equal intensity methylplatinum resonances at δ = 0.75, $^2J_{PtH}$ = 74 Hz, and 1.57, $^2J_{PtH}$ = 72 Hz. The resonance for the methyl group of the acetyl



Scheme 4. Oxidative addition of carbon–halogen bonds.

ligand occurred at $\delta = 2.58$. $^3J_{PtH} = 10$ Hz. On the other hand, the *trans* isomer **9a** was identified by the presence of only one methylplatinum resonance in the ^{1}H NMR spectrum at $\delta = 1.59$, $^2J_{PtH} = 72$ Hz, and the acetyl group resonance was at $\delta = 2.00$, $^3J_{PtH} = 14$ Hz. Once isolated, the complex was stable in solution at room temperature, and the ratio of the isomers **9a**:**9b** did not change with time. The structure of the major isomer **9b** was determined and is shown in Fig. 7. In the unsymmetrical complex formed by overall *cis* oxidative addition, the complex is chiral at platinum, but the lattice contains a racemic mixture of the ***C*** and ***A*** enantiomers. The Pt–C distance to the acetyl group is slightly shorter than those to the two methyl groups (Fig. 7). The ester groups adopt the *endo,endo* conformation.

The reaction of complex **1** with acetyl chloride in CD_2Cl_2 solution was monitored by ^{1}H NMR spectroscopy. The reaction occurred rapidly at room temperature and gave an initial ratio of **9a**:**9b** of 50:50 which changed to 25:75 after one day, and then remained constant indicating that equilibrium was reached. No further intermediates were detected when the reaction was monitored at low temperature, the initial ratio of **9a**:**9b** being roughly 50:50. Thus, the initial reaction gives a mixture of isomers and then a slower isomerization occurs, favoring the product of *cis* oxidative addition at equilibrium. Previous examples of oxidative addition of acetyl chloride with organoplatinum(II) complexes have been shown to occur more selectively by *trans* oxidative addition [49,50,51,52,53]. Oxidative addition to rhodium(I) complexes can also occur with *trans* stereochemistry, though in many cases the stereochemistry of oxidative addition cannot be determined [54,55]. The reductive elimination of acetyl iodide or acetic anhydride is a key step in the Monsanto and Cativa processes for manufacture of acetic acid, and has been proposed to occur with *cis* stereochemistry [56,57]. The oxidative addition occurs by nucleophilic attack by the electron-rich platinum(II) complex **1** and so there is an analogy to the mechanism of nucleophilic substitution at a trigonal carbon center, which occurs by the addition–elimination mechanism involving a tetrahedral intermediate, $MeClNuCO^-$, where Nu^- is the nucleophile, followed by elimination of the chloride ion to give the product [58]. In the reaction with complex **1**, the initial tetrahedral intermediate would be ***F*** (Scheme 5), but this cannot rearrange directly to either **9a** or **9b**. To give the product of *trans* oxidative addition, chloride elimination must occur to give ***G*** and then chloride coordination can occur to give **9a**. By analogy with the nucleophilic substitution mechanism [58], this could be termed an addition–elimination–coordination mechanism. Complex **8** is probably formed in an analogous way from **1** and ethyl chloroformate (Scheme 4). The formation of **9b** requires a Berry pseudorotation step within a 5-coordinate platinum(IV) intermediate [59,60]. The isomerization of **9a** to **9b** probably involves dissociation of the chloride ligand to regenerate intermediate ***G***, which can rearrange to ***H*** followed by chloride coordination to give **9b**. However, **9b** can also be formed by rearrangement of the initially formed intermediate ***F*** to give ***I***, which can undergo intramolecular chloride ion migration to give **9b**. This more direct formation of **9b** could be termed an addition–pseudorotation–

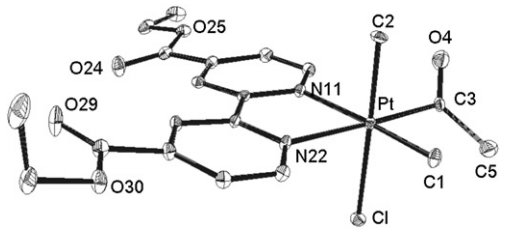
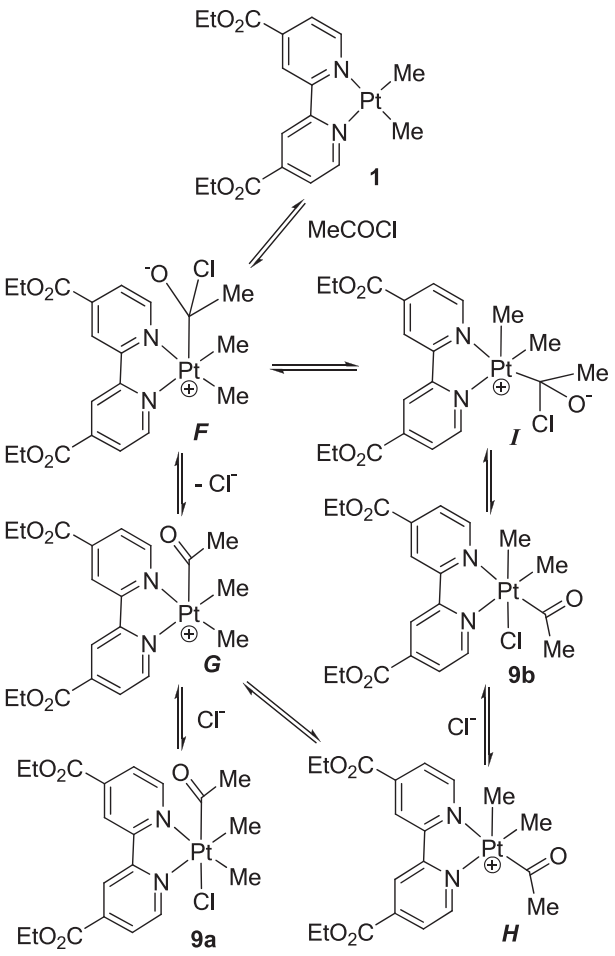


Fig. 7. The structure of the *A* enantiomer of complex **9b**. Selected bond parameters: Pt–N(11) 2.177(5); Pt–N(22) 2.184(5); Pt–C(1) 2.068(6); Pt–C(2) 2.072(6); Pt–C(3) 2.026(6); Pt–Cl 2.437(1) Å.



Scheme 5. Possible mechanisms of formation and isomerization of **9a** and **9b**.

migration mechanism (Scheme 5), and is likely to be responsible for the *cis* product that is formed by kinetic control.

The structures of the complexes of Scheme 5, as calculated by DFT in the gas phase, are shown in Fig. 8 and the corresponding energies are in Fig. 9. The reaction is initiated by nucleophilic attack by the mostly $5d_z2$ orbital of complex **1** on the LUMO of acetyl chloride (Fig. 8), and this leads easily to formation of the tetrahedral intermediate ***F***. There is a barrier to the pseudorotation to give the intermediate ***I***, which arises through steric effects when the tertiary alkyl group is in the equatorial plane, but ***I*** can easily rearrange to give the stable complex **9b** (Figs. 8 and 9). It should be noted that ***I*** is chiral at both carbon and platinum, and the diastereomer which is calculated to be more stable is shown in Fig. 8. The gas phase calculation predicts a very high barrier to formation of the ionic 5-coordinate intermediates ***G*** and ***H***, but this is misleading because the ions will be stabilized in solution by solvation and probably by reversible solvent coordination [35]. Intermediate ***G*** appears to be a necessary intermediate in forming **9a**, and ***G*** and ***H*** are calculated to have similar energies, so there is a second viable route to **9b** through the intermediates ***G*** and ***H***. Complex **9b** is calculated to be 9 kJ mol^{-1} more stable than **9a**, which is consistent with the observed 3:1 ratio of these isomers at equilibrium. Overall, the calculations support the formation of an initial tetrahedral intermediate ***F***, and show that it is possible for it to rearrange to **9b**, but a more detailed study will be needed to determine if this is preferred to the more familiar ionic mechanism.

2.4. Derivatives with hydrogen bonding groups

The bromomethyl derivatives of carboxylic acids shown in Scheme 6 reacted with complex **1** to give the corresponding

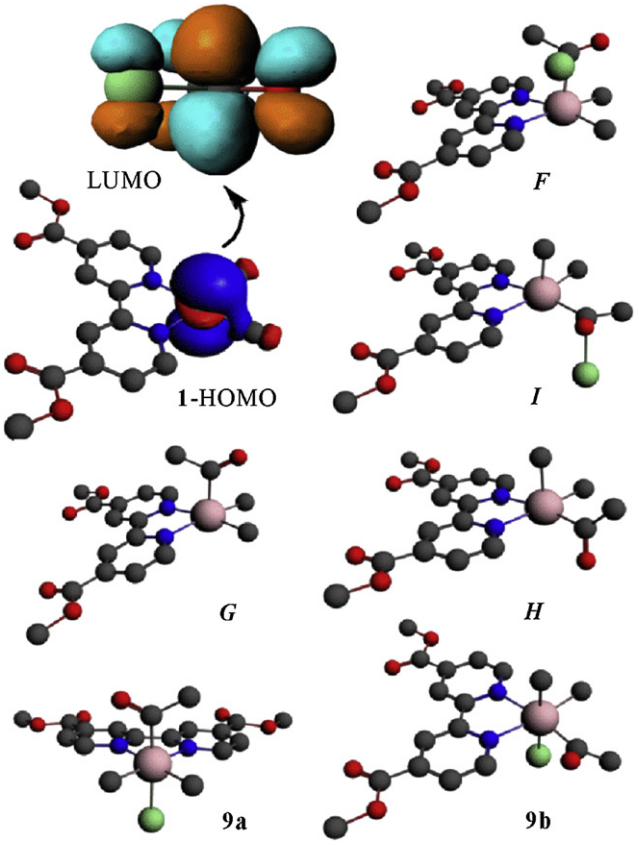


Fig. 8. Calculated structures of reagents, intermediates and products, and frontier orbitals for **1** and MeCOCl.

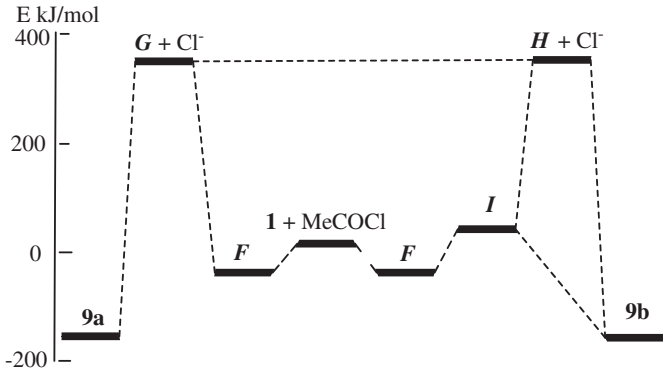
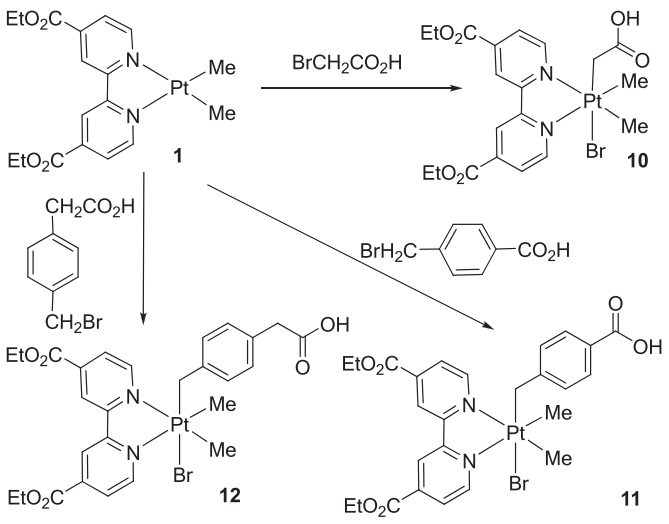


Fig. 9. DFT calculated energies, with respect to complex **1** + acetyl chloride, in the gas phase for the intermediates and products of the reactions of Scheme 5.

organoplatinum(IV) derivatives **10**–**12**. The products were formed selectively by *trans* oxidative addition, as could easily be shown by the ^{1}H NMR spectra. For example, complex **10** gave only one methylplatinum resonance at $\delta = 1.53$, $^2J_{PtH} = 70$ Hz, and also a single resonance for the CH_2Pt protons at $\delta = 2.01$, $^2J_{PtH} = 95$ Hz.

The structures of complexes **10** and **11** were determined and are shown in Figs. 10 and 11. In complexes of this type, there can be competition between potential hydrogen bond acceptor groups [8,24,25,61,62,63]. In this case, the potential hydrogen bond acceptors are the carbonyl group of the carboxylic acid, the bromide ligand, or one of the oxygen atoms of the ethoxycarbonyl groups. In both **10** and **11** the hydrogen bonding occurs between the carboxylic acid groups of neighboring molecules, to give the classic carboxylic acid dimer structures [**10**, O(5)···O(6A) 2.65(1); **11**, O(5)···O(6A) 2.64(1) Å]. The ester groups adopt the *endo,exo* or *exo,exo* conformation in **10** or **11**, respectively, and may be involved in π-stacking interactions, but they are not involved in hydrogen bonding.

Platinum(IV) complexes containing amide or alcohol functional groups were prepared according to Scheme 7. They were formed selectively as the products of *trans* oxidative addition, as shown by the ^{1}H NMR spectra. For example, complex **14** gave only one methylplatinum resonance at $\delta = 1.56$, $^2J_{PtH} = 69$ Hz, and one CH_2Pt resonance at $\delta = 2.10$, $^2J_{PtH} = 92$ Hz and complex **15** gave one methylplatinum resonance at $\delta = 1.57$, $^2J_{PtH} = 71$ Hz, and one $PtCH_2$ resonance at $\delta = 2.88$, $^2J_{PtH} = 91$ Hz.



Scheme 6. Platinum(IV) complexes with carboxylic acid groups.

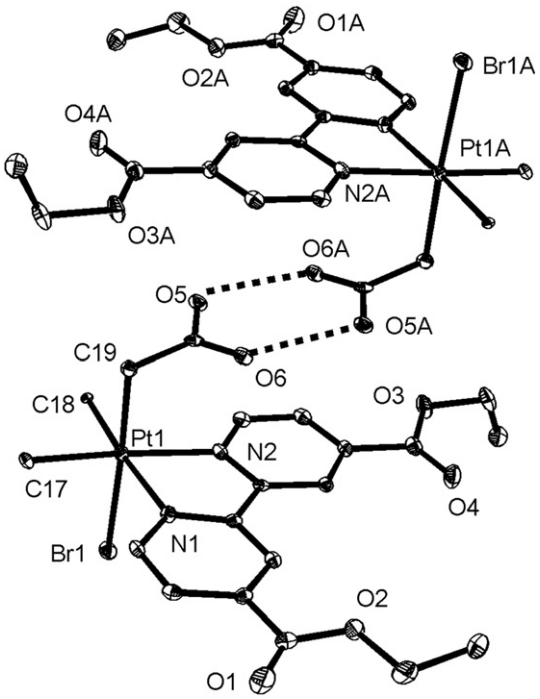


Fig. 10. The structure of complex **10**, showing the dimer formed by hydrogen bonding. Selected bond parameters: Pt(1)–N(1) 2.155(6); Pt(1)–N(2) 2.166(6); Pt(1)–C(17) 2.085(7); Pt(1)–C(18) 2.124(6); Pt(1)–C(19) 2.099(7); Pt(1)–Br(1) 2.533(8); O(5)···O(6A) 2.65(1) Å.

The structure of complex **13** was determined and is shown in Fig. 12, and confirms that it is the product of *trans* oxidative addition to complex **1**. The complex forms a supramolecular polymer by forming intermolecular NH···BrPt hydrogen bonds. The hydrogen bond distance N(3)···Br(1) = 3.51 Å is in the accepted range of 3.12–3.69 Å for such hydrogen bonds [64], and the PtBr group is evidently preferred over the amide or ester carbonyl groups as hydrogen bond acceptor [65,66,67,68,69,70]. The ester groups adopt the *endo,endo* conformation and they are not involved in the hydrogen bonding.

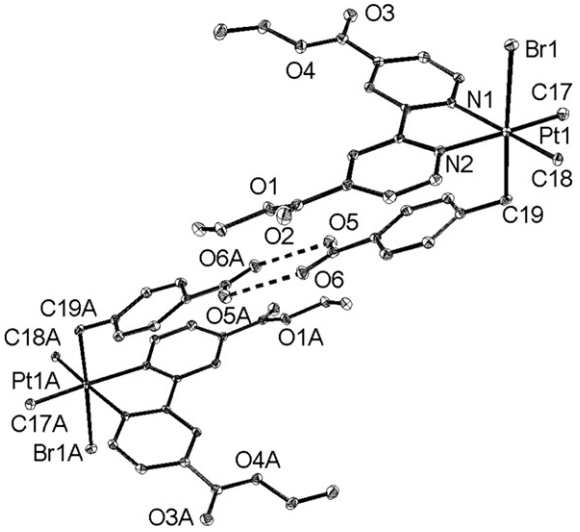
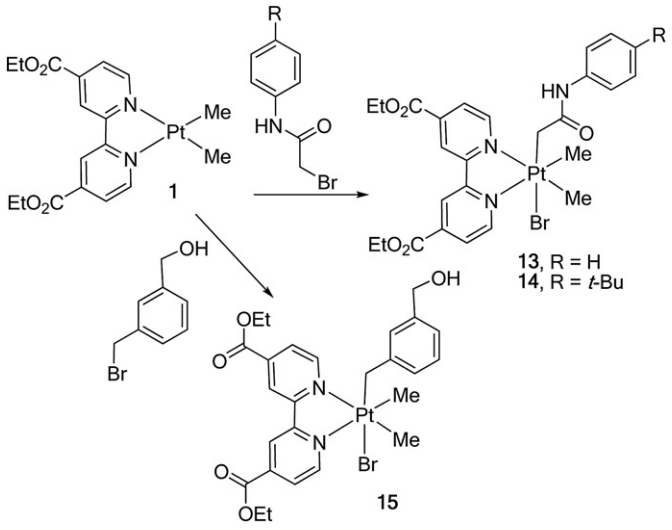


Fig. 11. The structure of complex **11**, showing the dimer formed by hydrogen bonding. Selected bond parameters: Pt(1)–N(1) 2.160(4); Pt(1)–N(2) 2.162(4); Pt(1)–C(17) 2.048(6); Pt(1)–C(18) 2.063(5); Pt(1)–C(19) 2.103(5); Pt(1)–Br(1) 2.5955(6); O(5)···O(6A) 2.64(1) Å.



Scheme 7. Platinum(IV) complexes with amide or alcohol functional groups.

3. Conclusions

For the complexes [$PtMe_2$(NN)], where NN = bebipy or bipy, both the HOMO and LUMO are calculated to be lower in energy for bepipy [HOMO, mostly platinum $5d_z2$, −4.486 and −4.978 eV; LUMO, mostly ligand $2p_\pi^*$, −3.407 and −4.027 eV, for NN = bipy and bebipy respectively], and the HOMO–LUMO gap is also smaller

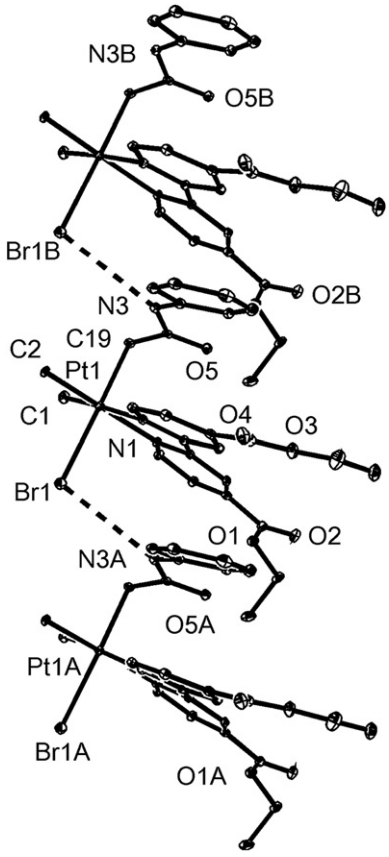


Fig. 12. The structure of complex **13**, showing the supramolecular polymer formed by hydrogen bonding. Selected bond parameters: Pt(1)–N(1) 2.154(5); Pt(1)–N(2) 2.163(5); Pt(1)–C(1) 2.067(7); Pt(1)–C(2) 2.074(6); Pt(1)–C(19) 2.103(7); Pt(1)–Br(1) 2.545(1); Br(1)···N(3A) 3.51(1) Å.

for bebipy [1.079 and 0.951 eV for bipy and bepipy respectively]. These differences reflect the electronic properties of the ethoxycarbonyl substituents in bebipy, and lead to it being a weaker donor ligand than bipy. The weaker ligating ability of bebipy is most clearly seen in the instability of the hydrogen peroxide adduct [$Pt(OH)_2Me_2$(bebipy)] towards dissociation of the bebipy ligand, whereas the corresponding bipy complex is thermally stable [37,39]. The π-conjugation of the ester substituents of bebipy leads the $-CO_2C$ groups to be roughly coplanar with the pyridyl groups, but there seems little preference for any of the possible *endo,endo*, *endo,exo* or *exo,exo* conformations of the ester groups, and all have been observed in the solid state structures of the platinum complexes, with the preferred conformation probably determined by π-stacking or other intermolecular packing forces.

The complex [$PtMe_2$(bebipy)] takes part in a wide range of oxidative addition reactions to give functional organoplatinum(IV) complexes, some of which contain hydrogen bonding functionality (carboxylic acids, amides or alcohol). These complexes can form supramolecular dimers or, in one case, a polymer through intermolecular hydrogen bonding.

4. Experimental

All reactions were carried out under nitrogen using standard Schlenk techniques, unless otherwise specified. NMR spectra were recorded by using a Varian Mercury 400, or Varian Inova 400 or 600 spectrometer. The ligand bebipy and complex [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] were prepared according to the literature [26,71]. DFT calculations were carried out by using the Amsterdam Density Functional program based on the BLYP functional, with double-zeta basis set and first-order scalar relativistic corrections [72,73]. The reported results are from gas phase calculations .The energy minima were confirmed by vibrational frequency analysis in each case.

4.1. X-ray structure determinations

A crystal was mounted on a glass fiber and data were collected at 150(2) K by using a Nonius Kappa-CCD or Bruker Smart Apex II CCD diffractometer. The unit cell parameters were calculated and refined from the full data set, and the structures were solved and refined by using the SHELX software [74,75]. Details of the crystal data and refinement parameters, and bond distances and angles, for all complexes are given in the CIF files. In complex **2**, there was disorder of the methyl/chloro ligands in both independent molecules, so bond parameters for these groups are not precise, and there was a molecule of CH_2Cl_2 of crystallization. In complexes **4** and **5**, one of the ethoxy groups was disordered over two positions and was modeled with isotropic carbon atoms in each case. Complex **11** crystallized with a molecule of acetone of crystallization.

4.1.1. [$PtMe_2$(bebipy)], **1**

To a solution of 4,4′-diethoxycarbonyl-2-2′-bipyridine (0.52 g, 1.73 mmol) in ether (20 mL) was added [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] (0.50 g, 0.87 mmol). The color of the solution quickly turned to purple, and the product precipitated as a purple solid. After 40 min, the product was separated, washed with pentane (3 × 3 mL) and then dried under high vacuum. Yield: 91%. NMR in acetone-d_6: $\delta(^1H) = 1.14$ (s, 6H, $^2J_{PtH} = 86$ Hz, $PtCH_3$), 1.45 (t, 6H, $^3J_{HH} = 7$ Hz, CH_3C), 4.49 (q, 4H, $^3J_{HH} = 7$ Hz, CH_2C), 8.14 (d, 2H, $^3J_{HH} = 6$ Hz, H^5), 8.79 (s, 2H, H^3), 9.42 (d, 2H, $^3J_{HH} = 6$ Hz, $^3J_{PtH} = 28$ Hz, H^6). Anal. Calcd. for $C_{18}H_{22}N_2O_4Pt$: C, 41.14; H, 4.22; N, 5.33. Found: C, 40.85; H, 4.04; N, 5.45%.

4.1.2. [$PtCl_2$(bebipy)], **3**

Excess hydrochloric acid (0.0035 mL, 3 M) was added to a solution of complex **1** (0.0034 g, 0.006 mmol) in CH_2Cl_2 (1 g) in an NMR tube. The color of the solution changed from purple to yellow, and the product was isolated by evaporation of the solvent and recrystallization from CH_2Cl_2/pentane. NMR in CD_2Cl_2: $\delta(^1H) = 1.48$ (t, 6H, $^3J_{HH} = 7$ Hz, CH_3C), 4.53 (q, 4H, $^3J_{HH} = 7$ Hz, CH_2C), 8.17 (d, 2H, $^3J_{HH} = 5$ Hz, H^5), 8.66 (s, 2H, H^3), 9.97 (d, 2H, $^3J_{HH} = 5$ Hz, $^3J_{PtH} = 48$ Hz, H^6). Anal. Calcd. for $C_{16}H_{16}Cl_2N_2O_4Pt$: C, 33.94; H, 2.85; N, 4.95. Found: C, 33.54; H, 2.63; N, 4.68%.

4.1.3. [$PtBr_2Me_2$(bebipy)], **4**

Excess bromine (0.01 mL) was added slowly to a solution of complex **1** (0.030 g, 0.057 mmol) in dry CH_2Cl_2 (5 mL). The color of the solution rapidly changed from purple to orange. After 30 min, the volume of solvent was reduced and pentane (2 mL) was added to precipitate the product as an orange powder, which was separated, washed with pentane (3 × 2 mL) and ether (3 × 2 mL) and then dried under high vacuum. Yield 80%. NMR in CD_2Cl_2: $\delta(^1H) = 1.48$ (t, 6H, $^3J_{HH} = 7$ Hz, CH_3C), 2.07 (s, 6H, $^2J_{PtH} = 71$ Hz, $PtCH_3$), 4.54 (q, 4H, $^3J_{HH} = 7$ Hz, CH_2C), 8.29 (d, 2H, $^3J_{HH} = 5$ Hz, H^5), 8.97 (s, 2H, H^3), 9.07 (d, 2H, $^3J_{HH} = 5$ Hz, $^3J_{PtH} = 18$ Hz, H^6). Anal. Calcd. for $C_{18}H_{22}Br_2N_2O_4Pt$: C, 31.55; H, 3.24; N, 4.09. Found: C, 31.37; H, 3.13; N, 3.88%.

4.1.4. [PtI_2Me_2(bebipy)], **5**

To a solution of complex **1** (0.035 g, 0.066 mmol) in dry CH_2Cl_2 (15 mL) was added excess iodine (0.033 g, 0.129 mmol). The color changed from purple to dark red. After 5 min, the solvent was evaporated to give the product as a red powder, which was recrystallized from CH_2Cl_2/pentane. Yield: 83%. NMR in CD_2Cl_2: $\delta(^1H) = 1.49$ (t, 6H, $^3J_{HH} = 7$ Hz, CH_3C), 2.42 (s, 6H, $^2J_{PtH} = 73$ Hz, $PtCH_3$), 4.55 (q, 4H, $^3J_{HH} = 7$ Hz, CH_2C), 8.30 (d, 2H, $^3J_{HH} = 5$ Hz, H^5), 9.02 (s, 2H, H^3), 9.07 (d, 2H, $^3J_{HH} = 5$ Hz, $^3J_{PtH} = 21$ Hz, H^6). Anal. Calcd. for $C_{18}H_{22}I_2N_2O_4Pt$: C, 27.74; H: 2.85; N, 3.59. Found: C, 28.08; H, 2.86; N, 3.59%. Crystals of **5**·1.5I_2 were grown directly by slow diffusion of pentane into a similar reaction mixture.

4.1.5. [$Pt(OH)_2Me_2$(bebipy)], **6**

To a solution of complex **1** (0.030 g, 0.057 mmol) in acetone was added excess H_2O_2 (0.01 mL). The color changed from purple to colorless. After 30 min, the solvent was evaporated to give the product as a white solid, which was washed with pentane (2 × 3 mL) and ether (2 × 3 mL) and dried under high vacuum. Yield: 80%. NMR in CD_2Cl_2: $\delta(^1H) = 1.47$ (t, 6H, $^3J_{HH} = 7$ Hz, CH_3C), 1.66 (s, 6H, $^2J_{PtH} = 70$ Hz, $PtCH_3$), 4.52 (q, 4H, $^3J_{HH} = 7$ Hz, CH_2C), 8.21 (d, 2H, $^3J_{HH} = 5$ Hz, H^5), 8.91 (s, 2H, H^3), 9.01 (d, 2H, $^3J_{HH} = 5$ Hz, $^3J_{PtH} = 18$ Hz, H^6). Anal. Calcd. for $C_{18}H_{24}N_2O_6Pt.2H_2O$: C, 36.30; H, 4.74; N, 4.70. Found: C, 36.37; H, 4.30; N, 4.82%.

4.1.6. [$PtIMe_3$(bebipy)], **7**

Excess iodomethane (0.025 mL) was added to a solution of complex **1** (0.050 g, 0.095 mmol) in acetone (10 mL). The color of the solution changed from purple to yellow. The solution was cooled to 0 °C overnight, to precipitate the product as a pale yellow solid, which was separated, washed with pentane (3 × 2 mL) and dried under high vacuum. Yield: 84%. NMR in acetone-d_6: $\delta(^1H) = 0.60$ (s, 3H, $^2J_{PtH} = 72$ Hz, PtMe *trans* to I), 1.45 (t, 6H, $^3J_{HH} = 7$ Hz, CH_3C), 1.52 (s, 6H, $^2J_{PtH} = 71$ Hz, PtMe *trans* to N), 4.53 (q, 4H, $^3J_{HH} = 7$ Hz, CH_2C), 8.33 (d, 2H, $^3J_{HH} = 6$ Hz, H^5), 9.20 (s, 2H, H^3), 9.25 (d, 2H, $^3J_{HH} = 6$ Hz, $^3J_{PtH} = 20$ Hz, H^6). Anal. Calcd. for $C_{19}H_{25}IN_2O_4Pt$: C, 34.19; H, 3.78; N, 4.20. Found: C, 34.30; H, 3.89; N, 4.16%.

4.1.7. [$PtClMe_2(CO_2Et)$(bebipy)], **8**

This was synthesized in a similar way from complex **1** (0.035 g, 0.066 mmol) in dry CH_2Cl_2 (15 mL) and ethyl chloroformate (0.007 mL). Yield: 79%. NMR in CD_2Cl_2: $\delta(^1H) = 0.85$ (t, 3H, $^3J_{HH} = 7$ Hz, CH_3C), 1.48 (t, 6H, $^3J_{HH} = 7$ Hz, CH_3C), 1.65 (s, 6H,

$^2J_{PtH}$ = 71 Hz, $PtCH_3$), 3.77 (q, 2H, $^3J_{HH}$ = 7 Hz, $^4J_{PtH}$ = 5 Hz, CH_2C), 4.54 (q, 4H, $^3J_{HH}$ = 7 Hz, CH_2C), 8.27 (d, 2H, $^3J_{HH}$ = 5 Hz, H^5), 8.93 (s, 2H, H^3), 9.13 (d, 2H, $^3J_{HH}$ = 5 Hz, $^3J_{PtH}$ = 17 Hz, H^6). Anal. Calcd. for $C_{21}H_{27}ClN_2O_6Pt$: C, 39.78; H, 4.29; N, 4.42. Found: C, 39.79; H, 4.52; N, 4.37%.

4.1.8. *[PtClMe$_2$(COMe)(bebipy)],* ***9***

To a stirred solution of complex **1** (0.038 g, 0.063 mmol) in dry CH_2Cl_2 (15 mL) was added acetyl chloride (0.004 g, 0.063 mmol). The color of the solution turned to yellow within 5 min. After 1 h, the solvent was removed and the product was washed pentane (3 × 3 mL) and ether (3 × 3 mL) and then dried under high vacuum. Yield: 84%. NMR in CD_2Cl_2: **9b**, $\delta(^1H)$ = 0.75 (s, 3H, $^2J_{PtH}$ = 74 Hz, PtMe *trans* to Cl), 1.47 (t, 6H, $^3J_{HH}$ = 7 Hz, CH_3C), 1.57 (s, 3H, $^2J_{PtH}$ = 72 Hz, PtMe *trans* to N), 2.58 (s, 3H, $^3J_{PtH}$ = 10 Hz, CH_3C), 4.53 (q, 4H, $^3J_{HH}$ = 7 Hz, CH_2C), 8.22 (d, 1H, $^3J_{HH}$ = 5 Hz, H^3), 8.23 (d, 1H, $^3J_{HH}$ = 5 Hz, H^5), 8.90 (s, 2H, H^3), 8.97 (d, 1H, $^3J_{HH}$ = 5 Hz, $^3J_{PtH}$ = 20 Hz, H^6), 9.33 (d, 1H, $^3J_{HH}$ = 5 Hz, $^3J_{PtH}$ = 19 Hz, H^6); **9a**, $\delta(^1H)$ = 1.48 (t, 3H, $^3J_{HH}$ = 7 Hz, CH_3C), 1.59 (s, 6H, $^2J_{PtH}$ = 72 Hz, $PtCH_3$), 2.00 (s, 3H, $^3J_{PtH}$ = 14 Hz, CH_3C), 4.54 (q, 4H, $^3J_{HH}$ = 7 Hz, CH_2C), 8.27 (d, 2H, $^3J_{HH}$ = 5 Hz, H^5), 8.97 (s, 2H, H^3), 9.13 (d, 2H, $^3J_{HH}$ = 5 Hz, $^3J_{PtH}$ = 20 Hz, H^6). Anal. Calcd. for $C_{20}H_{25}ClN_2O_5Pt$: C, 39.77; H, 4.17; N, 4.64. Found: C, 39.51; H, 4.40; N, 4.55%.

4.1.9. *[PtBrMe$_2$(CH$_2$CO$_2$H)(bebipy)],* ***10***

To a solution of complex **1** (0.050 g, 0.095 mmol) in acetone (15 mL) was added $BrCH_2CO_2H$ (0.013 g, 0.095 mmol). After 3 h, the solvent was evaporated under vacuum, and the yellow solid product was washed with water (3 × 3 mL) and pentane (3 × 3 mL), and dried under high vacuum. Yield: 88%. NMR in acetone-d_6: $\delta(^1H)$ = 1.46 (t, 6H, $^3J_{HH}$ = 7 Hz, CH_3C), 1.53 (s, 6H, $^2J_{PtH}$ = 70 Hz, $PtCH_3$), 2.01 (s, 2H, $^2J_{PtH}$ = 95 Hz, $PtCH_2$), 4.53 (q, 4H, $^3J_{HH}$ = 7 Hz, CH_2C), 8.31 (d, 2H, $^3J_{HH}$ = 6 Hz, H^5), 9.09 (d, 2H, $^3J_{HH}$ = 6 Hz, $^3J_{PtH}$ = 19 Hz, H^6), 9.13 (s, 2H, H^3). Anal. Calcd. for $C_{20}H_{25}BrN_2O_6Pt$: C, 36.16; H, 3.79; N, 4.22. Found: C, 35.71; H, 3.66; N, 4.08%.

4.1.10. *[PtBrMe$_2$(CH$_2$-4-C$_6$H$_4$-CO$_2$H)(bebipy)],* ***11***

This was prepared similarly from complex **1** (0.050 g, 0.095 mmol) and $BrCH_2$-4-C_6H_4-CO_2H (0.021 g, 0.095 mmol). Yield: 86%. NMR in acetone-d_6: $\delta(^1H)$ = 1.44 (t, 6H, $^3J_{HH}$ = 7 Hz, CH_3C), 1.54 (s, 6H, $^2J_{PtH}$ = 72 Hz, $PtCH_3$), 2.87 (s, 2H, $^2J_{PtH}$ = 95 Hz, $PtCH_2$), 4.49 (q, 4H, $^3J_{HH}$ = 7 Hz, CH_2C), 6.46 (d, 2H, $^3J_{HH}$ = 8 Hz, $^3J_{PtH}$ = 18 Hz, H*o*), 7.27 (d, 2H, $^3J_{HH}$ = 8 Hz, H^m), 8.17 (d, 2H, $^3J_{HH}$ = 7 Hz, H^5), 8.93 (s, 2H, H^3), 8.97 (d, 2H, $^3J_{HH}$ = 7 Hz, $^3J_{PtH}$ = 19 Hz, H^6). Anal. Calcd. for $C_{26}H_{29}BrN_2O_6Pt$: C, 42.17; H, 3.95; N, 3.78. Found: C, 41.73; H, 4.06; N, 3.44%. Single crystals of the acetone solvate were grown from acetone/pentane.

4.1.11. *[PtBrMe$_2$(CH$_2$-4-C$_6$H$_4$-CH$_2$CO$_2$H)(bebipy)],* ***12***

This was prepared in a similar way from complex **1** (0.050 g, 0.095 mmol) and $BrCH_2$-4-C_6H_4-CH_2CO_2H (0.022 g, 0.095 mmol). Yield: 88%. NMR in acetone-d_6: $\delta(^1H)$ = 1.44 (t, 6H, $^3J_{HH}$ = 7 Hz, CH_3C), 1.50 (s, 6H, $^2J_{PtH}$ = 70 Hz, $PtCH_3$), 2.77 (s, 2H, $^2J_{PtH}$ = 90 Hz, $PtCH_2$), 3.21 (s, 2H, CH_2CO), 4.50 (q, 4H, $^3J_{HH}$ = 7 Hz, CH_2C), 6.27 (d, 2H, $^3J_{HH}$ = 8 Hz, $^3J_{PtH}$ = 18 Hz, H*o*), 6.51 (d, 2H, $^3J_{HH}$ = 8 Hz, H^m), 8.15 (d, 2H, $^3J_{HH}$ = 6 Hz, H^5), 8.86 (s, 2H, H^3), 8.95 (d, 2H, $^3J_{HH}$ = 6 Hz, $^3J_{PtH}$ = 19 Hz, H^6). Anal. Calcd. for $C_{27}H_{31}BrN_2O_6Pt$: C, 42.98; H, 4.14; N, 3.71. Found: C, 42.75; H, 3.99; N, 3.65%.

4.1.12. *[PtBrMe$_2$(CH$_2$CONHC$_6$H$_5$)(bebipy)],* ***13***

This was prepared similarly from complex **1** (0.050 g, 0.095 mmol) and $BrCH_2CONHPh$ (0.021 g, 0.095 mmol). Yield 85%. NMR in CD_2Cl_2: $\delta(^1H)$ = 1.45 (t, 6H, $^3J_{HH}$ = 7 Hz, CH_3C), 1.56 (s, 6H, $^2J_{PtH}$ = 69 Hz, $PtCH_3$), 2.12 (s, 2H, $^2J_{PtH}$ = 92 Hz, $PtCH_2$), 4.47 (q, 4H,

Table 1
Crystal and refinement data for the complexes.

Complex	**1**	**2**.0.5CH_2Cl_2	**3**	**4**	**5**.1.5I_2
Formula	$C_{18}H_{22}N_2O_4Pt$	$C_{17.5}H_{20}Cl_2N_2O_4Pt$	$C_{16}H_{16}Cl_2N_2O_4Pt$	$C_{18}H_{22}Br_2N_2O_4Pt$	$C_{18}H_{22}I_5N_2O_4Pt$
fw	525.47	588.34	566.30	685.29	1159.97
Cryst. syst.	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Sp.gp.	P 2$_1$/c	P-1	P-1	P 2$_1$/n	P-1
a/Å	8.1368(3)	9.7977(5)	9.1862(10)	12.0683(13)	6.9682(3)
b/Å	31.7979(10)	13.4431(10)	14.743(2)	6.4596(7)	11.7601(7)
c/Å	13.7885(5)	14.7147(10)	15.111(2)	26.273(3)	17.1027(8)
α/°	90	95.261(3)	61.463(4)	90	97.245(3)
β/°	92.392(2)	93.083(4)	84.528(6)	95.308(5)	93.582(3)
γ/°	90	90.059(4)	85.249(7)	90	96.167(3)
V/Å^3	3564.4(2)	1927.1(2)	1788.1(4)	2039.4(4)	1378.16(12)
Z	8	4	4	4	2
d_c/Mg m^{-3}	1.958	2.028	2.104	2.232	2.795
μ/mm^{-1}	7.898	7.584	8.170	10.825	10.716
R1 (I > 2σI)	0.096	0.061	0.063	0.068	0.035
wR2 (all data)	0.243	0.171	0.199	0.198	0.091

Complex	**9b**	**10**	**11**	**12**
Formula	$C_{20}H_{25}ClN_2O_5Pt$	$C_{20}H_{25}BrN_2O_6Pt$	$C_{29}H_{35}BrN_2O_7Pt$	$C_{26}H_{30}BrN_3O_5Pt$
fw	603.96	664.42	798.59	739.51
Cryst. syst.	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Sp.gp.	P 2$_1$/c	C2/c	P 2$_1$/n	P 2$_1$/c
a/Å	9.8457(3)	23.1244(14)	7.4337(3)	7.2694(15)
b/Å	12.2735(4)	6.8372(4)	33.1080(14)	16.904(3)
c/Å	18.0778(5)	30.2233(19)	12.0101(5)	22.105(4)
α/°	90	90	90	90
β/°	100.873(2)	92.465(2)	94.137(2)	96.66(3)
γ/°	90	90	90	90
V/Å^3	2145.33(11)	4774.1(5)	2948.2(2)	2697.9(9)
Z	4	8	4	4
d_c/Mg m^{-3}	1.870	1.849	1.799	1.821
μ/mm^{-1}	6.698	7.588	6.163	6.722
R1 (I > 2σI)	0.045	0.056	0.037	0.052
wR2 (all data)	0.122	0.107	0.071	0.164

$^3J_{HH}$ = 7 Hz, CH_2C), 6.65 (s, 1H, NH), 6.82 (d, 2H, $^3J_{HH}$ = 8 Hz, H*o*), 6.88 (t, 1H, $^3J_{HH}$ = 8 Hz, H^p), 7.02 (t, 2H, $^3J_{HH}$ = 8 Hz, H^m), 7.98 (d, 2H, $^3J_{HH}$ = 6 Hz, H^5), 8.75 (s, 2H, H^3), 8.91 (d, 2H, $^3J_{HH}$ = 6 Hz, $^3J_{PtH}$ = 19 Hz, H^6). Anal. Calcd. for $C_{26}H_{30}BrN_3O_5Pt$: C, 42.23; H, 4.09; N, 5.68. Found: C, 42.27; H, 3.99; N, 5.33%.

4.1.13. [$PtBrMe_2(CH_2CONH\text{-}4\text{-}C_6H_4\text{-}t\text{-}Bu)(bebipy)$], **14**

This was prepared similarly from complex **1** (0.050 g, 0.095 mmol) and $BrCH_2CONH\text{-}4\text{-}C_6H_4\text{-}t\text{-}Bu$ (0.022 g, 0.095 mmol). Yield: 87%. NMR in CD_2Cl_2: $\delta(^1H)$ = 1.24 (s, 9H, *t*-Bu), 1.45 (t, 6H, $^3J_{HH}$ = 7 Hz, CH_3C), 1.56 (s, 6H, $^2J_{PtH}$ = 69 Hz, $PtCH_3$), 2.10 (s, 2H, $^2J_{PtH}$ = 92 Hz, $PtCH_2$), 4.49 (q, 4H, $^3J_{HH}$ = 7 Hz, CH_2C), 6.62 (s, 1H, NH), 6.74 (d, 2H, $^3J_{HH}$ = 9 Hz, H*o*), 7.06 (d, 2H, $^3J_{HH}$ = 9 Hz, H^m), 7.99 (d, 2H, $^3J_{HH}$ = 6 Hz, H^5), 8.80 (s, 2H, H^3), 8.92 (d, 2H, $^3J_{HH}$ = 6 Hz, $^3J_{PtH}$ = 19 Hz, H^6). Anal. Calcd. for $C_{30}H_{38}BrN_3O_5Pt$: C, 45.29; H, 4.81; N, 5.28. Found: C, 44.93; H, 4.89; N, 5.19%.

4.1.14. [$PtBrMe_2(CH_2\text{-}3\text{-}C_6H_4\text{-}CH_2OH)(bebipy)$], **15**

This was prepared similarly from complex **1** (0.050 g, 0.095 mmol) and $BrCH_2\text{-}3\text{-}C_6H_4\text{-}CH_2OH$ (0.019 g, 0.095 mmol). Yield: 84%. NMR acetone-d_6: $\delta(^1H)$ = 1.45 (t, 6H, $^3J_{HH}$ = 7 Hz, CH_3C), 1.57 (s, 6H, $^2J_{PtH}$ = 71 Hz, $PtCH_3$), 2.88 (s, 2H, $^2J_{PtH}$ = 91 Hz, $PtCH_2$), 4.03 (s, 2H, CH_2O), 4.51 (q, 4H, $^3J_{HH}$ = 7 Hz, CH_2C), 6.12 (d, 1H, $^3J_{HH}$ = 8 Hz, $^3J_{PtH}$ = 18 Hz, H*o*), 6.47 (t, 1H, $^3J_{HH}$ = 8 Hz, H^m), 6.68 (t, 1H, $^3J_{HH}$ = 8 Hz, H^p), 6.78 (d, 1H, $^3J_{HH}$ = 8 Hz, $H^{m'}$), 8.19 (d, 2H, $^3J_{HH}$ = 6 Hz, H^5), 8.81 (s, 2H, H^3), 9.10 (d, 2H, $^3J_{HH}$ = 6 Hz, $^3J_{PtH}$ = 19 Hz, H^6). Anal. Calcd. for $C_{26}H_{31}BrN_2O_5Pt$: C, 42.98; H, 4.30; N, 3.86. Found: C, 42.81; H, 4.26; N, 3.79% (Table 1).

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Appendix A. Supplementary material

CCDC 902716-902724; contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] N. Chaudhury, R.J. Puddephatt, J. Organomet. Chem. 84 (1975) 105.
[2] P.K. Monaghan, R.J. Puddephatt, Organometallics 3 (1984) 444.
[3] L.M. Rendina, R.J. Puddephatt, Chem. Rev. 97 (1997) 1735.
[4] J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, California, 1987.
[5] R.H. Crabtree, The Organometallic Chemistry of the Transition Metals, fourth ed., Wiley, New Jersey, 2005.
[6] J. Kuyper, Inorg. Chem. 17 (1978) 1458.
[7] R.P. Hughes, R.B. Laritchev, L.N. Zakharov, A.L. Rheingold, Organometallics 24 (2005) 4845.
[8] M.A. Safa, A. Abo-Amer, A. Borecki, B.F.T. Cooper, R.J. Puddephatt, Organometallics 31 (2012) 2675.
[9] M. Crespo, Organometallics 31 (2012) 1216.
[10] B.Z. Momeni, M. Rashidi, M.M. Jafari, B.O. Patrick, A.S. Abd-el-Aziz, J. Organomet. Chem. 700 (2012) 83.
[11] R.J. Puddephatt, Coord. Chem. Rev. 219 (2001) 157.
[12] A. Bayler, A.J. Canty, J.H. Ryan, B.W. Skelton, A.H. White, Inorg. Chem. Commun. 3 (2000) 575.
[13] S.A. O'Reilly, P.S. White, J.L. Templeton, J. Am. Chem. Soc. 118 (1996) 5684.
[14] A.J. Canty, A. Dedieu, H. Jin, A. Milet, M.K. Richmond, Organometallics 15 (1996) 2845.
[15] S. Achar, R.J. Puddephatt, J. Chem. Soc. Chem. Commun. (1994) 1895.
[16] C.M. Anderson, M. Crespo, M.C. Jennings, A.J. Lough, G. Ferguson, R.J. Puddephatt, Organometallics 10 (1991) 2672.
[17] S. Achar, J.J. Vittal, R.J. Puddephatt, Organometallics 15 (1996) 43.
[18] T. Calvet, M. Crespo, M. Font-Bardia, S. Jansat, M. Martinez, Organometallics 31 (2012) 4367.
[19] B.A. McKeown, H.E. Gonzalez, M.R. Friedfeld, T.B. Gunnoe, T.R. Cundari, M. Sabat, J. Am. Chem. Soc. 133 (2011) 19131.
[20] G. Mazzone, N. Russo, E. Sicilia, Inorg. Chem. 50 (2011) 10091.
[21] P.K. Monaghan, R.J. Puddephatt, J. Chem. Soc. Dalton Trans. (1988) 595.
[22] G.S. Hill, G.P.A. Yap, R.J. Puddephatt, Organometallics 18 (1999) 1408.
[23] S.M. Nabavizadeh, S. Habibzadeh, M. Rashidi, R.J. Puddephatt, Organometallics 29 (2010) 6359.
[24] S. Achar, J.D. Scott, J.J. Vittal, R.J. Puddephatt, Organometallics 12 (1993) 4592.
[25] R.H.W. Au, M.C. Jennings, R.J. Puddephatt, Organometallics 28 (2009) 5052.
[26] G. Sprintschnik, H.W. Sprintschnik, P.P. Kirsch, D.G. Whitten, J. Am. Chem. Soc. 99 (1977) 4947.
[27] V. Shklover, M.-K. Nazeeruddin, S.M. Zakeeruddin, C. Barbe, A. Kay, T. Haibach, W. Steurer, R. Hermann, H.-U. Nissen, M. Gratzel, Chem. Mater. 9 (1997) 430.
[28] D. Hanss, J.C. Freys, G. Bernardinelli, O.S. Wenger, Eur. J. Inorg. Chem. (2009) 4850.
[29] C.L. Linfoot, P. Richardson, T.E. Hewat, O. Moudam, M.M. Forde, A. Collins, F. White, N. Robertson, Dalton Trans. 39 (2010) 8945.
[30] A. Gunyar, D. Betz, M. Drees, E. Herdtweck, F.E. Kuhn, J. Mol. Catal. A 331 (2010) 117.
[31] S. Achar, V.J. Catalano, Polyhedron 16 (1997) 1555.
[32] Y. Nishiuchi, A. Takatama, T. Suzuki, K. Shinozaki, Eur. J. Inorg. Chem. (2011) 1815.
[33] G. Janjic, J. Andric, A. Kapor, Z.D. Bugarcic, S.D. Zaric, Cryst. Eng. Commun. 12 (2010) 3773.
[34] A.J. Canty, M.G. Gardiner, R.C. Jones, M. Sharma, Aust. J. Chem. 64 (2011) 1355.
[35] S.M. Nabavizadeh, H. Amini, M. Rashidi, K.R. Pellarin, M.S. McCready, B.F.T. Cooper, R.J. Puddephatt, J. Organomet. Chem. 713 (2012) 60.
[36] N. Margiotta, R. Ranaldo, F.P. Intini, G. Natile, Dalton Trans. 40 (2011) 12877.
[37] K. Thorshaug, I. Fjeldahl, C. Romming, M. Tilset, J. Chem. Soc. Dalton Trans. (2003) 4051.
[38] M. Safa, M.C. Jennings, R.J. Puddephatt, Organometallics 31 (2012) 3539.
[39] V.V. Rostovtsev, L.M. Henling, J.A. Labinger, J.E. Bercaw, Inorg. Chem. 41 (2002) 3608.
[40] R.A. Gossage, A.D. Ryabov, A.L. Spek, D.J. Stufkens, J.A.M. van Beek, R. van Eldik, G. van Koten, J. Am. Chem. Soc. 121 (1999) 2488.
[41] J.A.M. van Beek, G. van Koten, W.J.J. Smeets, A.L. Spek, J. Am. Chem. Soc. 108 (1986) 5010.
[42] A. Yahav, I. Goldberg, A. Vigalok, Organometallics 24 (2005) 5654.
[43] M. Werner, C. Wagner, D. Steinborn, J. Organomet. Chem. 694 (2009) 190.
[44] J.R. Webb, C. Munro-Leighton, A.W. Pierpoint, J.T. Gurkin, T.B. Gunnoe, T.R. Cundari, M. Sabat, J.L. Petersen, P.D. Boyle, Inorg. Chem. 50 (2011) 4195.
[45] K.-T. Aye, J.J. Vittal, R.J. Puddephatt, J. Chem. Soc. Dalton Trans. (1993) 1805.
[46] J.R. Hall, G.A. Swile, J. Organomet. Chem. 122 (1976) C22.
[47] H.N. Agnew, T.G. Appleton, J.R. Hall, Aust. J. Chem. 35 (1982) 894.
[48] M. Safa, M.C. Jennings, R.J. Puddephatt, Organometallics 30 (2011) 5625.
[49] J.D. Ruddick, B.L. Shaw, J. Chem. Soc. A (1969) 2801.
[50] J.D. Ruddick, B.L. Shaw, J. Chem. Soc. A (1969) 2964.
[51] M.P. Brown, R.J. Puddephatt, C.E.E. Upton, S.W. Lavington, J. Chem. Soc. Dalton (1974) 1613.
[52] A.J. Blake, A.G. Osborne, R.E. Hollands, Acta Cryst. E 57 (2001) m313.
[53] F. Zhang, M.E. Broczkowski, M.C. Jennings, R.J. Puddephatt, Can. J. Chem. 83 (2005) 595.
[54] M.A. Bennett, J.C. Jeffery, G.B. Robertson, Inorg. Chem. 20 (1981) 323.
[55] H.F. Haarman, J.-W.F. Kaagman, W.J.J. Smeets, A.L. Spek, K. Vrieze, Inorg. Chim. Acta 270 (1998) 34.
[56] T. Kinnunen, K. Laasonen, J. Organomet. Chem. 628 (2001) 222.
[57] N. Lassauque, T. Davin, D.H. Nguyen, R.J. Adcock, Y. Coppel, C. Le Berre, P. Serp, L. Maron, P. Kalck, Inorg. Chem. 51 (2012) 4.
[58] M.B. Smith, J. March, March's Advanced Organic Chemistry, sixth ed., Wiley, New Jersey, 2007, pp. 1254–1260.
[59] K.A. Grice, M.L. Scheuermann, K.I. Goldberg, Top. Organomet. Chem. 35 (2011) 1.
[60] R.J. Puddephatt, Angew. Chem. Int. Ed. 41 (2002) 261.
[61] C.S.A. Fraser, H.A. Jenkins, M.C. Jennings, R.J. Puddephatt, Organometallics 19 (2000) 1635.
[62] M.P. Brown, J.R. Fisher, R.H. Hill, R.J. Puddephatt, K.R. Seddon, Inorg. Chem. 20 (1981) 3516.
[63] R.H.W. Au, L.J. Findlay-Shirras, N.M. Woody, M.C. Jennings, R.J. Puddephatt, Can. J. Chem. 87 (2009) 904.
[64] L. Dobrzanska, Acta Cryst. E 61 (2005) m1625.
[65] H.J. Bohm, G. Klebe, S. Brode, U. Hesse, Chem. Eur. J. 2 (1996) 1509.
[66] K.R. Gleitsman, H.A. Lester, D.A. Dougherty, Chem. Bio. Chem. 10 (2009) 1385.
[67] Z. Qin, M.C. Jennings, R.J. Puddephatt, J. Chem. Soc. Chem. Commun. (2001) 2676.
[68] T.J. Burchell, D.J. Eisler, M.C. Jennings, R.J. Puddephatt, J. Chem. Soc. Chem. Commun. (2003) 2228.
[69] T.J. Burchell, D.J. Eisler, R.J. Puddephatt, Inorg. Chem. 43 (2004) 5550.
[70] T.J. Burchell, R.J. Puddephatt, Inorg. Chem. 44 (2005) 3718.
[71] J.D. Scott, R.J. Puddephatt, Organometallics 2 (1983) 1643.
[72] G. te Velde, F.M. Bickelhaupt, E.J. Baerends, S. van Gisbergen, C.F. Guerra, J.G. Snijders, T. Ziegler, J. Comput. Chem. 22 (2001) 931.
[73] A. Becke, Phys. Rev. A 38 (1988) 3098.
[74] APEX 2, Crystallography Software Package, Bruker AXS, Madison, WI, 2005.
[75] G.M. Sheldrick, Acta Cryst. A64 (2008) 112.