Organoplatinum(IV) complexes with functional alkyl groups and their use in supramolecular chemistry[1]

Richard H.W. Au, Lisa J. Findlay-Shirras, Neil M. Woody, Michael C. Jennings, and Richard J. Puddephatt

Abstract: The oxidative addition of alkyl bromides RCH_2Br (R = C_5H_4N, C_6H_4CN, $CH_2C_6H_4CO_2H$, or $CH_2C_6H_4CH_2CO_2H$) to dimethylplatinum(II) complexes [$PtMe_2(LL)$] (LL = diimine ligand) gives the corresponding organoplatinum(IV) complexes [$PtBrMe_2(CH_2R)(LL)$] containing functionality in the alkyl group RCH_2. The pyridyl derivatives can be protonated, while abstraction of the bromide ligand from [$PtBrMe_2(CH_2R)(LL)$] can form cationic complexes, which can react with water or form oligomers by self-assembly.

Key words: platinum, organometallic, hydrogen bond, supramolecular.

Résumé : L'addition oxydante de bromures d'alkyle, RCH_2Br [R = C_5H_4N, C_6H_4CN, $CH_2C_6H_4COOH$ ou $CH_2C_6H_4CH_2COOH$] sur des complexes de diméthylplatine(II) [$PtMe_2(LL)$] [LL = ligand diimine], conduit à la formation de complexes organoplatine(IV) [$PtBrMe_2(CH_2R)(LL)$] comportant une fonctionnalité dans le groupe alkyle RCH_2. Les dérivés pyridyles peuvent être protonés alors que l'enlèvement du ligand bromure à partir de [$PtBrMe_2(CH_2R)(LL)$] peut conduire à la formation de complexes cationiques qui peuvent réagir avec de l'eau ou former des oligomères par autoassemblage.

Mots-clés : platine, organométallique, liaison hydrogène, supramoléculaire.

[Traduit par la Rédaction]

Introduction

The oxidative addition of small molecules to platinum(II) complexes to form organoplatinum(IV) complexes can be a key step in catalysis, and so this type of reaction has been studied in great detail.[2–6] The oxidative addition can also be a key step in the synthesis of binuclear or even polymeric organoplatinum(IV) complexes, which are of interest as molecular materials.[4–8] The building up of complex structures from simple building blocks is a feature of supramolecular chemistry,[9] and organoplatinum(IV) complexes have proved to be very versatile in the development of supramolecular organometallic chemistry of the transition metals.[10–14] The stability of organoplatinum(IV) complexes towards reactions of protic reagents, oxidants, and other functional groups is an important property in allowing this chemistry to be developed.[15] This paper describes chemistry of new organoplatinum(IV) complexes in which one of the alkyl groups carries a cyanide, a pyridine, or a carboxylic acid group.

Results

Formation of organoplatinum(IV) complexes through oxidative addition reactions

The oxidative addition of 3-cyanobenzyl bromide to complexes [$PtMe_2(LL)$], **1** or **2**, where LL = 4,4′-di-*t*-butyl-2,2′-bipyridine (bu_2bipy) or di-2-pyridyl ketone (DPK), respectively, gave the products of trans oxidative addition [$PtBrMe_2(CH_2C_6H_4$-3-CN)(LL)], **3** or **4** (Scheme 1).

The complexes were readily characterized by their ^{1}H NMR spectra. For example, complex **3** gave a single methylplatinum resonance at δ = 1.51 with coupling constant ^2J(PtH) = 69 Hz, and a single Pt-CH_2 resonance at δ = 2.79 with coupling constant ^2J(PtH) = 96 Hz, indicating formation of a single symmetrical isomer. Complex **3** was also characterized by X-ray structure determination (Fig. 1). The platinum(IV) centre has octahedral stereochemistry and the cyanophenyl group lies over one of the pyridyl groups of the bu_2bipy ligand.

The reactions of complex **1** with the three isomers of bromomethylpyridine are shown in Scheme 2. The organic reagents are available only as the hydrobromide salts, because the neutral compound self-react, but the simple reaction of the bromomethylpyridinium bromides were complex. They evidently act as a source of HBr, which reacts with **1** to give methane and [$PtBrMe(bu_2bipy)$], which can itself react with bromomethylpyridine. To obtain the products of Scheme 2, the pyridinium salts were neutralized with triethylamine to generate the neutral bromomethylpyridine in situ, and this solution was then used to react with complex **1**. Each of the complexes [$PtBrMe_2(CH_2py)(bu_2bipy)$], **5**–**7**

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Scheme 1.

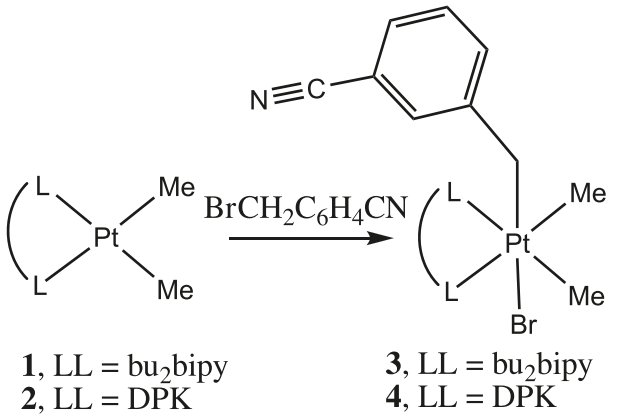
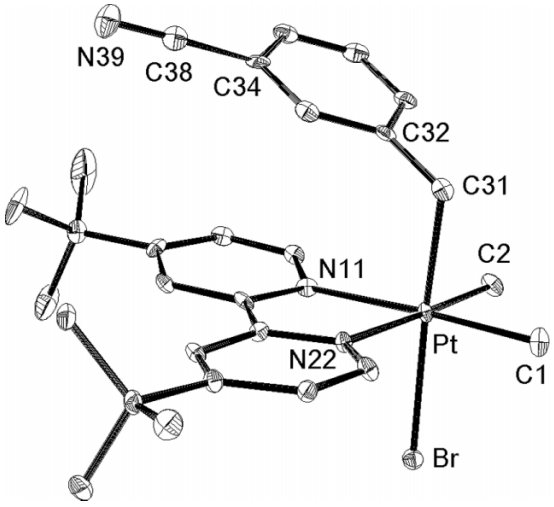


Fig. 1. Structure of [$PtBrMe_2(CH_2C_6H_4$-3-CN)(bu_2bipy)], **3**. Selected bond parameters: Pt–C(1) 2.06(1), Pt–C(2) 2.04(1), Pt–C(31) 2.10(1), Pt–N(11) 2.17(1), Pt–N(22) 2.13(1), Pt–Br 2.582(1), C(38)–N(39) 1.15(2) Å.



(py = 2-, 3-, or 4-C_5H_4N, respectively), gave a single methylplatinum resonance and a single $PtCH_2$ resonance in the ^{1}H NMR spectra, thus confirming that selective trans oxidative addition of the C–Br bond had occurred. The structure of complex **5** was confirmed by X-ray structure determination and is shown in Fig. 2. There are two independent molecules in the asymmetric unit, but they have similar structures and so only one is shown in Fig. 2. As in complex **3** (Fig. 1), the platinum(IV) centre has octahedral stereochemistry and the 2-pyridyl unit of the $PtCH_2$py group is π-stacked with one of the pyridyl groups of the bu_2bipy ligand.

The oxidative addition reactions of some bromomethyl derivatives of carboxylic acids are shown in Scheme 3. In all cases, *trans* oxidative addition was observed to give the products **8**–**11**. However, the DPK complexes also gave some cis isomer. Complexes **8** and **10** have been reported previously but the structures were not determined.[10]

The structure of complex **8** is shown in Fig. 3. The complex forms a hydrogen bonded dimer in the solid state with a distance of O(39)···O(40A) = O(40)···O(39A) = 2.61(1) Å. The structure of complex **10** is more complex and is illustrated in Figs. 4 and 5. The molecular structure is similar to that of complex **8** (Figs. 3 and 4), but there is disorder of the $CH_2C_6H_4CH_2CO_2H$ groups with roughly 50:50 occupation of the **A** [containing O(40) and O(41)] and **B** [containing O(60) and O(61)] forms. The supramolecular structure of **10** is more complex than for **8** (compare Figs. 3 and 5). The head-to-head dimerization of the type seen for **8** is not observed for complex **10**. Instead, the molecules of the form **A** and **B** alternate in forming hydrogen bonds O(61)=C(R)–O(60)H···O(41)=C(R)–O(40)H···Br. Molecule **A** acts as a hydrogen bond donor to the Br–Pt group of molecule **B**, and a hydrogen bond acceptor through its carbonyl oxygen atom. Molecule **B** acts as a hydrogen bond donor to the carbonyl group of molecule **A** and an acceptor through its Br–Pt group. The overall result is to form a hydrogen-bonded supramolecular polymer.

Scheme 2.

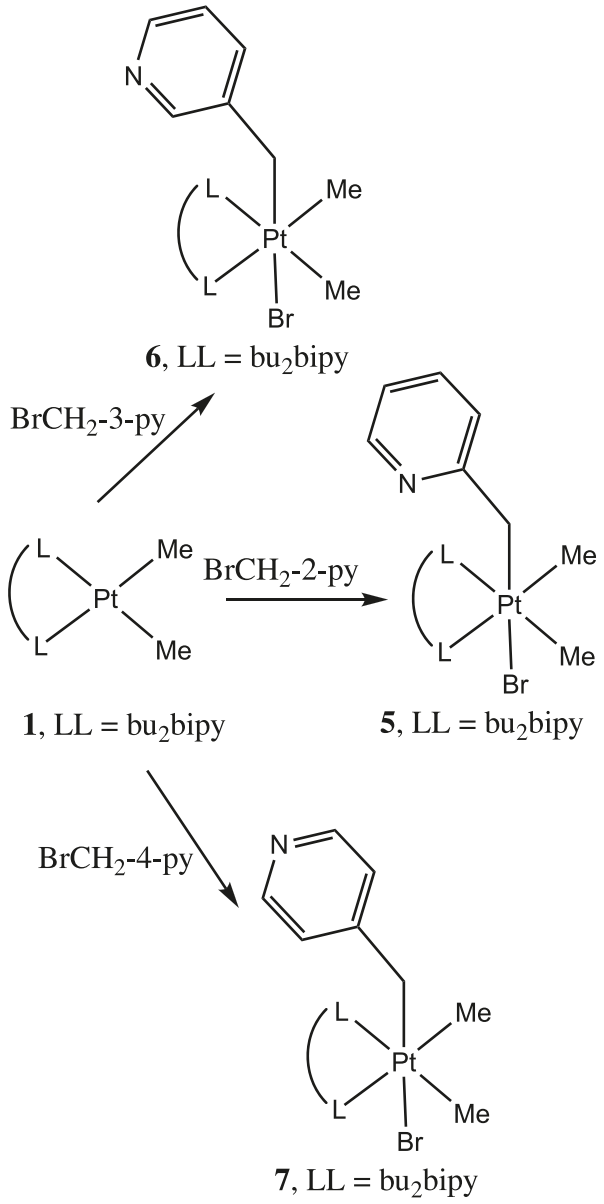
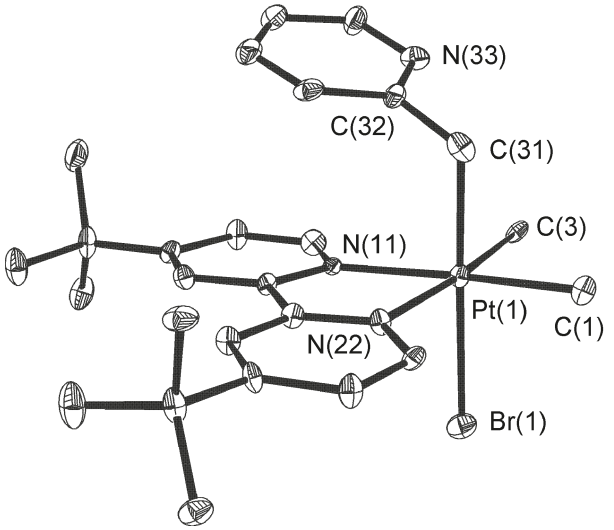
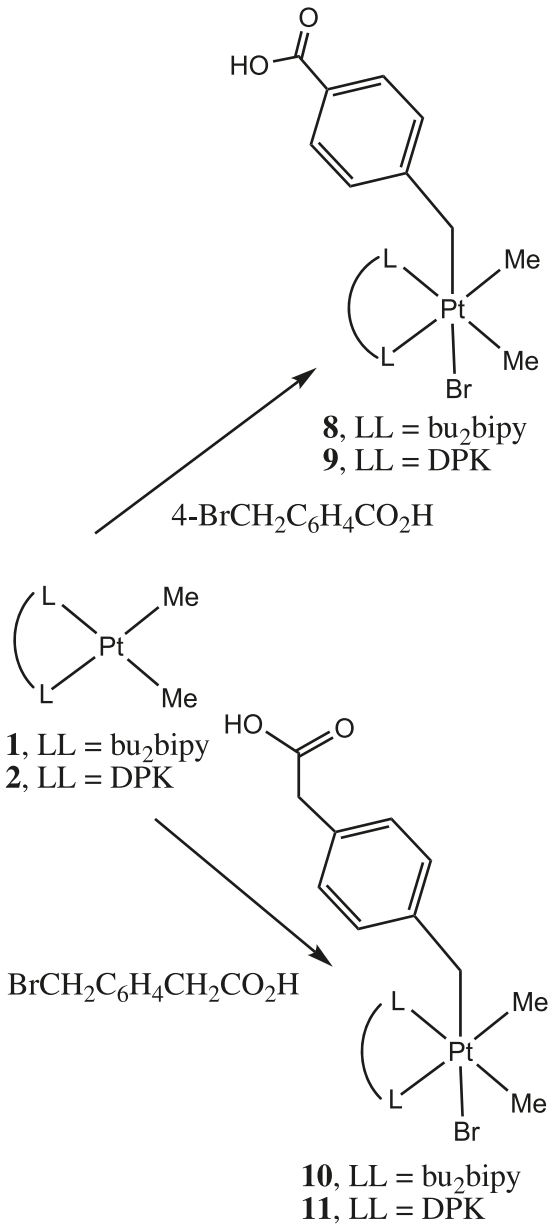


Fig. 2. The structure of [$PtBrMe_2(CH_2$-2-py)(bu_2bipy)], **5**. Selected bond distances: Pt(1)–C(1) 2.04(1), Pt(1)–C(3) 2.08(1), Pt(1)–C(31) 2.10(1), Pt(1)–N(11) 2.136(9), Pt(1)–N(22) 2.166(9), Pt(1)–Br(1) 2.5618(15) Å.



Scheme 3.

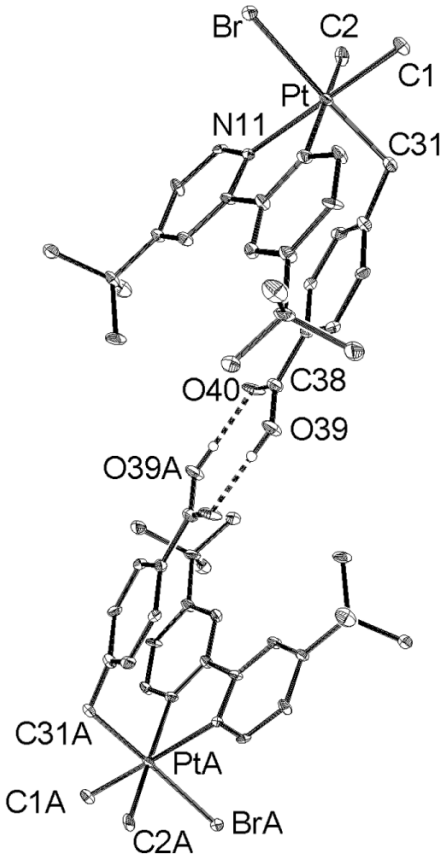


Further derivatization of the platinum(IV) complexes

The pyridyl complexes **5**–**7** could be protonated by addition of acid, as shown for the protonation of 4-pyridylmethylplatinum(IV) derivative (**7**) to give **12** in Scheme 4. The main effect on the ^{1}H NMR spectra was a shift of the $PtCH_2$ resonance on protonation. This shift defined as $\Delta(\delta) = \delta$(protonated complex) – δ(parent complex) = 1.78, 0.52, and 0.32 for the 2-, 3-, and 4-pyridylmethyl derivative, respectively. Two complications were observed in these reactions. Firstly, the reversible isomerization of **12** to the overall product of cis oxidative addition (**13**, in Scheme 4) was catalyzed by acid. It was not possible to isolate the cis isomers such as **13**, but these compounds could be identified by their NMR spectra. For example, the low symmetry of **13** leads to nonequivalent MePt resonances [δ(PtMe, axial) = 0.76, ^2J(PtH) = 72 Hz; δ(PtMe, equatorial) = 1.05, ^2J(PtH) = 68 Hz] and $PtCH^aH^b$py protons [$\delta(PtH^a) = 3.54$, ^2J(HH) = 7 Hz, ^2J(PtH) = 105 Hz; $\delta(PtH^b) = 4.41$, ^2J(HH) = 7 Hz, ^2J(PtH) = 110 Hz] in the ^{1}H NMR spectrum. The isomerization is expected to occur after bromide dissociation to give a five-coordinate intermediate [$PtMe_2(CH_2$-4-py)(bu_2bipy)]$^+$, and this reversible step is catalyzed by H^+.[16] At equilibrium, the ratio of **12**:**13** was ca. 3:1 when X = triflate. A similar isomerization occurred on protonation of the 3-pyridylmethylplatinum(IV) complex (**6**), but no cis isomer was detected on protonation of the 2-pyridylmethylplatinum(IV) complex (**5**). The second complication is that, if the group X in the acid HX can act as a ligand for platinum(IV), then partial exchange of the bromide ligand for X^- can occur. For example, crystallization of complex **7** in the presence of HCl gave complex **12** (X = Cl), but crystallographic characterization of the product showed partial displacement of the PtBr by the PtCl group to give **14** (Scheme 4, X = Cl). The structure of **12** (X = Cl) is shown in Fig. 6, showing only the Pt-Br component. The ratio of disorder components **12**:**14** (X = Cl) was refined as 0.36:0.64. The possibility of supramolecular association between the pyridyl base **7** and the acidic complexes **8** or **10** was investigated, but no such acid–base adducts could be crystallized.

The reactions of the pyridyl complexes **5**–**7** with silver salts of weakly coordinating anions were expected to occur by bromide abstraction followed by intramolecular or intermolecular coordination of the pyridine nitrogen atom to platinum(IV), as illustrated in Scheme 5.[17] The reaction of complex **5** with silver triflate occurred according to Scheme 5, and the product **15**(OTf) was isolated in analytically pure form, though single crystals could not be obtained. The ^{1}H NMR spectrum of **15** was broad at room temperature but, at –20 °C, it clearly showed two methylplatinum resonances and an [**AB**] multiplet for the $PtCH^aH^b$ protons. However, the ^{1}H NMR spectra of compounds obtained by treating the cyanobenzyl complex **3**, or the 3- or 4-pyridylmethyl complexes (**6** or **7**) with silver triflate were very complex, indicating that the self-assembly was nonse-

Fig. 3. The structure of complex **8**, showing the dimer formed by H-bonding. Selected parameters: Pt–C(31) 2.04(2), Pt–C(1) 2.08(1), Pt–C(2) 2.09(1), Pt–N(22) 2.16(1), Pt–N(11) 2.167(9), Pt–Br 2.563(2) Å. Hydrogen bond distance: O(39)···O(40A) = O(40)···O(39A) = 2.61(1) Å.



lective and gave a mixture of oligomers rather than a single product such as **16**. The unique behavior of the 2-pyridylmethyl complex (**5**) was also reflected in the ESI-MS of a solution in dichloromethane. The 2-pyridylmethyl complex (**15**), as the triflate salt, gave a molecular ion at m/z = 585, whereas the corresponding products with 3- or 4-pyridylmethyl groups gave the same envelope of peaks at m/z = 585 but also significant peaks at m/z = 1319 due to the dimer ion $[\{PtMe_2(CH_2py)(bu_2bipy)\}_2(OTf)]^+$ and, for the 4-pyridylmethyl complex only, trimer peaks.

Reaction of the toluic acid derivative (**8**) with silver tetrafluoroborate in moist solvent acetone occurred according to Scheme 6, to give the cationic aqua complex **17**, whose structure is shown in Fig. 7. The stereochemistry at the octahedral platinum(IV) centre is not changed in this reaction and so the effect is to substitute the bromide ligand by the aqua ligand. The carboxylic acid group hydrogen bonds to an acetone molecule, while one hydrogen atom of the aqua group hydrogen bonds to a second acetone molecule and the other hydrogen bonds to the tetrafluoroborate anion. It was anticipated that addition of base to complex **17** would give the carboxylate anion and that this would in turn displace the aqua ligand from a neighbouring molecule to give a dimer or, by repletion of these steps, an oligomer or polymer. However, the reaction gave only a mixture of complexes that could not be characterized.

Fig. 4. The 50:50 disordered structure of complex **10**. Selected parameters: Pt–C(1) 2.09(2), Pt–C(2) 2.07(2), Pt–C(31) 2.10(3), Pt–C(51) 2.11(3), Pt–N(11) 2.16(1), Pt–N(22) 2.18(1), Pt–Br 2.601(2) Å.

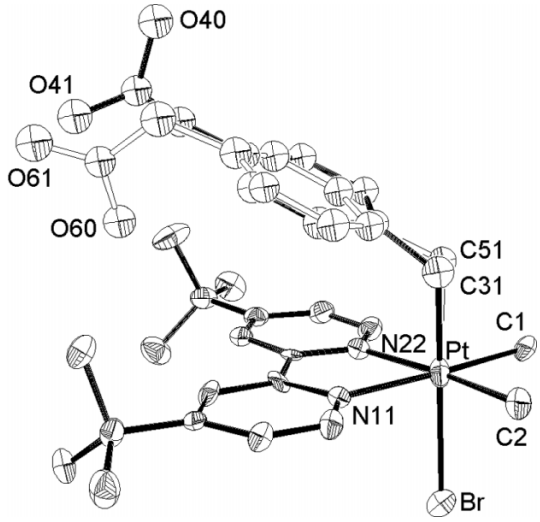
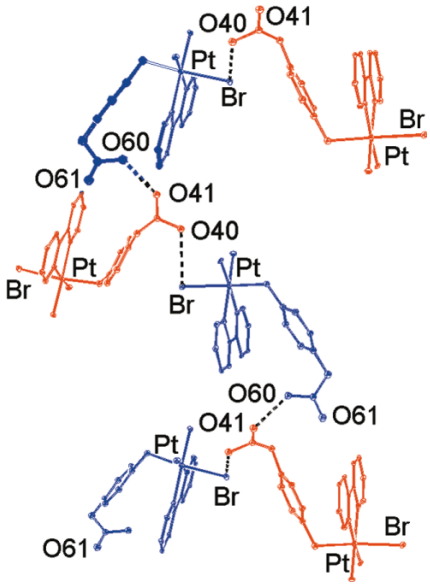
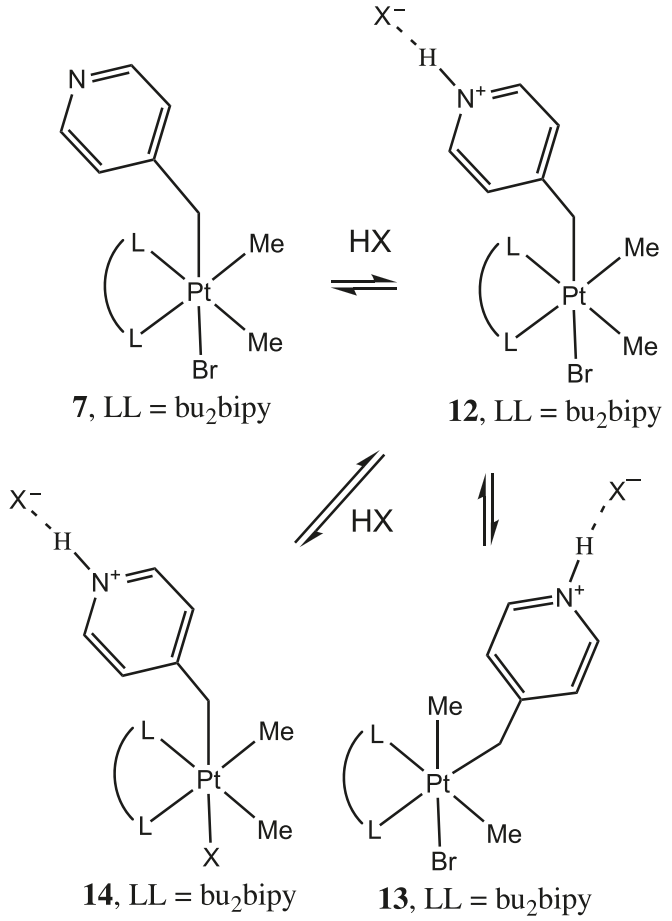


Fig. 5. The supramolecular structure of complex **10**, with alternating conformers **A** (red) and **B** (blue). Hydrogen-bonding parameters: O(40)···Br 3.26(4), O(41)···O(60) 2.67(5) Å. Other sequences, such as $(\mathbf{AABB})_n$ can be ruled out because they lead to unreasonably short contacts.



In some reactions of the platinum(IV) complexes with DPK ligands with silver salts, the carbonyl group of the DPK ligand was shown to be involved. The reaction of complex **4** with silver triflate gave the cationic complex **18**, as the triflate salt, according to Scheme 7. The two key features of complex **18** are the change in stereochemistry at platinum(IV) and the hydration of the DPK ligand to give the tridentate DPK-OH_2 ligand. None of the more symmetrical isomer, with the cyanobenzyl group trans to oxygen, was detected. In the ^{1}H NMR spectrum, complex **18** gave two methylplatinum resonances [δ = 1.18, ^2J(PtH) = 72 Hz and δ = 1.48, ^2J(PtH) = 81 Hz], and the $PtCH_2$ group gave an [AB] multiplet [δ = 3.03, ^2J(PtH) = 73 Hz; δ = 3.55,

Scheme 4.



Scheme 5.

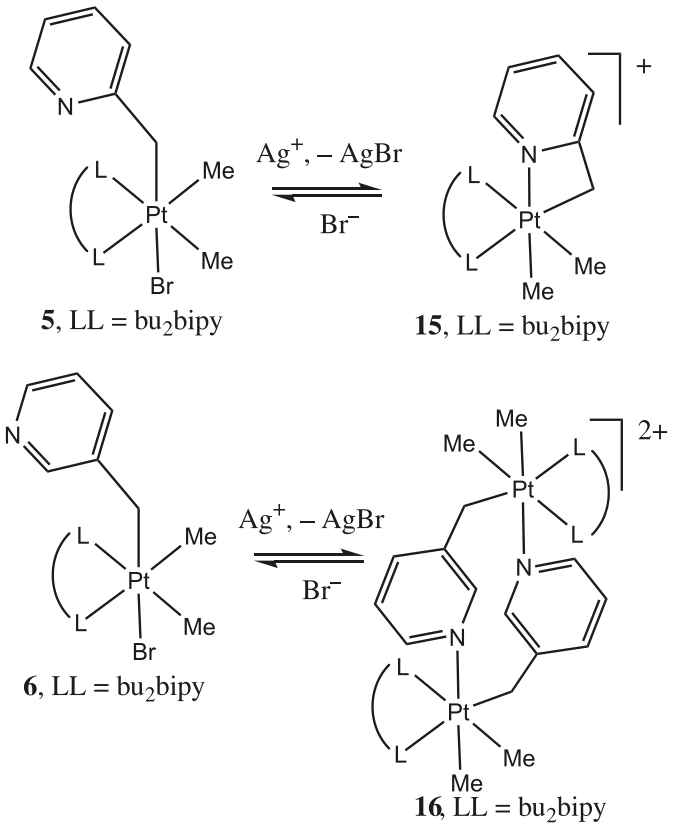
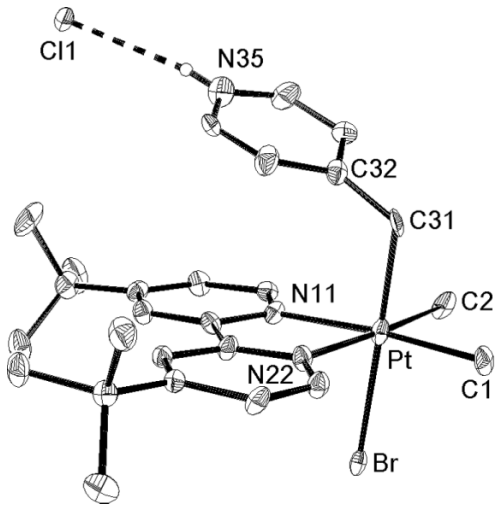
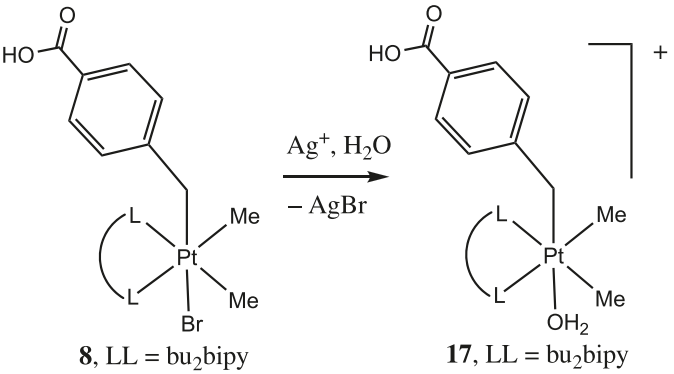


Fig. 6. The structure of disordered complex **12/14** (X = Cl), showing only component **12**. Selected bond parameters: Pt–C(1) 2.09(2), Pt–C(2) 1.99(3), Pt–C(31) 2.06(2), Pt–N(11) 2.15(2), Pt–N(22) 2.10(2), Pt–Br 2.55(2) Å. Hydrogen bond distance: N(35)···Cl(1) 3.61(3) Å.

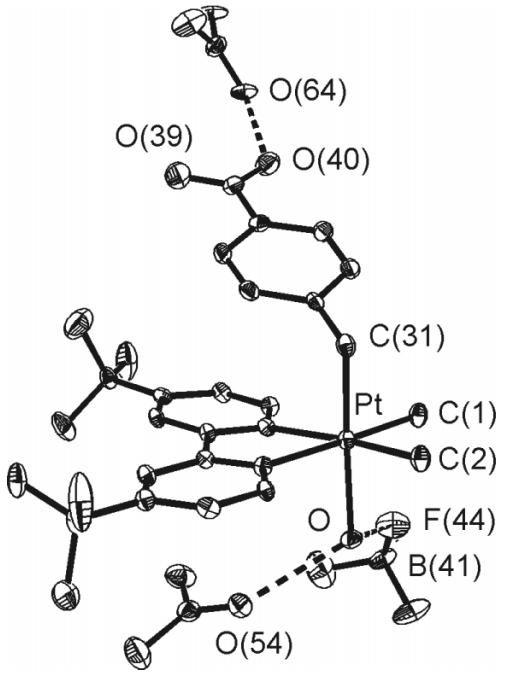


Scheme 6.



^2J(PtH) = 103 Hz; ^2J(HH) = 10 Hz], and there were two sets of pyridyl resonances. The ESI-MS gave a parent ion for **18** at *m*/*z* = 543 as well as a peak corresponding to a cation formed by loss of water at *m*/*z* = 525. In the IR spectrum, the carbonyl peak, found at 1677 cm^{-1} in **4** was absent in **18**. Hydrogen bonding between at least one of the OH groups in **18** to the cyano group was indicated by a shift in the value of ν(CN) from 2226 cm^{-1} in **4** to 2250 cm^{-1} in **18**. The peak assigned to ν(OH) was broad and centred at 3250 cm^{-1}, indicating that both OH groups are involved in hydrogen bonding. The data are most consistent with hydrogen bonding to the nitrogen atom only of the cyano group, because hydrogen bonding to the π-bond should lead to a decrease in ν(CN) whereas end-on hydrogen bonding leads to an increase,[18,19] but it is not clear if both OH groups hydrogen bond to the nitrogen atom or if one of them hydrogen bonds to the triflate anion. The stereochemical change at platinum(IV) in converting **4** to **18** (Scheme 7) is presumably in part to allow maximum hydrogen bonding. Intermolecular OH···NC hydrogen bonding could form a dimer,

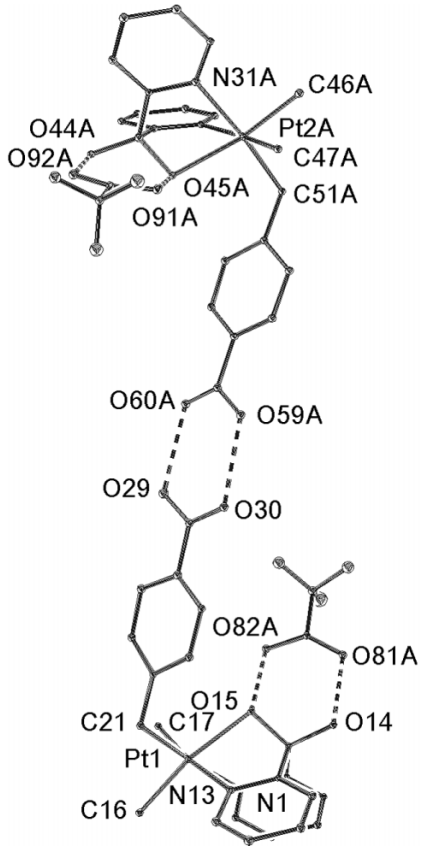
Fig. 7. Structure of the aqua complex **17**[BF_4]·2acetone·hexane. Selected bond parameters: Pt–C(1) 2.049(7), Pt–C(2) 2.048(8), Pt–C(31) 2.085(8), Pt–N(11) 2.154(6), Pt–N(22) 2.171(6), Pt–O 2.224(5) Å. Hydrogen bond distances: O···F(44) 2.703(9), O···O(54) 2.43(1), O(40)···O(64) 2.729(9) Å.



oligomer, or polymer. In the ESI-MS, an intense peak was at *m/z* = 543, corresponding to the cation **18**, and a less intense peak assigned to a dimer was observed at *m/z* = 1235 [(2 × **18**) + OTf]. No trimer or higher mass peaks were detected. There are several precedents for the hydration of the DPK ligand and for participation in hydrogen bonding of the DPK-OH_2 ligand.[20]

The reaction of complex **11** with siver trifluoroacetate occurred to give the cationic complex **19** according to Scheme 7. The reaction to give **19** occurred with a change in stereochemistry at platinum(IV) but this reaction was less selective and some trans isomer was also present. The ^{1}H NMR spectrum of the cis isomer **19** contained two methylplatinum resonances and two resonances for the $PtCH^aH^b$ protons, indicating the absence of a mirror plane of symmetry. The structure of complex **19** as the trifluoroacetate salt is shown in Fig. 8. There are two independent but similar molecules in the unit cell, and they are connected by hydrogen bonding between the carboxylic acid groups. In addition, the two OH groups of the ketone hydrate are hydrogen bonded to the trifluoroacetate anions. The hydrogen bond distances O··O are in the range of 2.59–2.65 Å. In the ESI-MS, the most intense envelope of peaks was at *m/z* = 576, corresponding to the cation **19**, with the second most intense peak at *m/z* = 558, corresponding to loss of H_2O. However, intense dimer peaks were also observed at *m/z* = 1151 [(2 × **19**) – H^+], 1133 [(2 × **19**) – H^+ – H_2O], and 1115 [(2 × **19**) – H^+ – 2H_2O]. The trifluoroacetate groups were not present in any observed fragments. These data indicate that the dimer units persist in solution, and that loss of water from the DPK-OH_2 groups occurs easily in the MS. Reactions of complex **11** with silver salts of weakly coordinating anions, such as Ag[BF_4] or Ag[PF_6], gave products that contained the cationic complex **19** but with unidentified side products. We suggest that the hydrogen bonding by the anion (Fig. 8) is significant in stabilizing **19** as the trifluoroacetate salt.

Fig. 8. Structure of the dimer of **19**·CF_3CO_2. Selected bond distances: Pt(1)–C(16) 2.05(1), Pt(1)–C(17) 2.06(1), Pt(1)–C(21) 2.08(1), Pt(1)–N(1) 2.16(1), Pt(1)–N(13) 2.17(1), Pt(1)–O(15) 2.188(9) Å. Hydrogen bond distances: O(14)···O(81) 2.62(1), O(15)···O(82) 2.59(1), O(29)···O(60) 2.61(1), O(44)···O(92) 2.65(2), O(45)···O(91) 2.56(1), O(59)···O(30) 2.61(1) Å.



Discussion

The oxidative addition reactions to give alkyl platinum(IV) complexes tolerate a range of functional groups.[4–8,10–16] In particular, it is possible to incorporate either basic or acidic groups into the organoplatinum(IV) products.[8,10] The reactions of [$PtMe_2$(LL)] with RCH_2Br usually occur by kinetic control to give the product of trans oxidative addition, [$PtBrMe_2(CH_2R)$(LL)], by way of an ionic intermediate, [$PtMe_2(CH_2R)(LL)]^+Br^-$.[4] However, if the ionic intermediate is long-lived, or if the bromide ligand can dissociate easily, the cis isomer may also be formed.[4,16] Several cases of isomerization were observed in this work, and some insight into the reasons for this were sought by computations using density functional theory (DFT).

For the complexes [$PtBrMe_2(CH_2R)$(bipy)] or [$PtBrMe_2(CH_2R)$(DPK)], the trans isomer is calculated to be more stable than the cis isomer in all cases. The example with R = 2-pyridyl is illustrated in Figs. 9*a* and 9*b*. The trans isomer has a preferred conformation with the 2-pyridyl

Scheme 7.

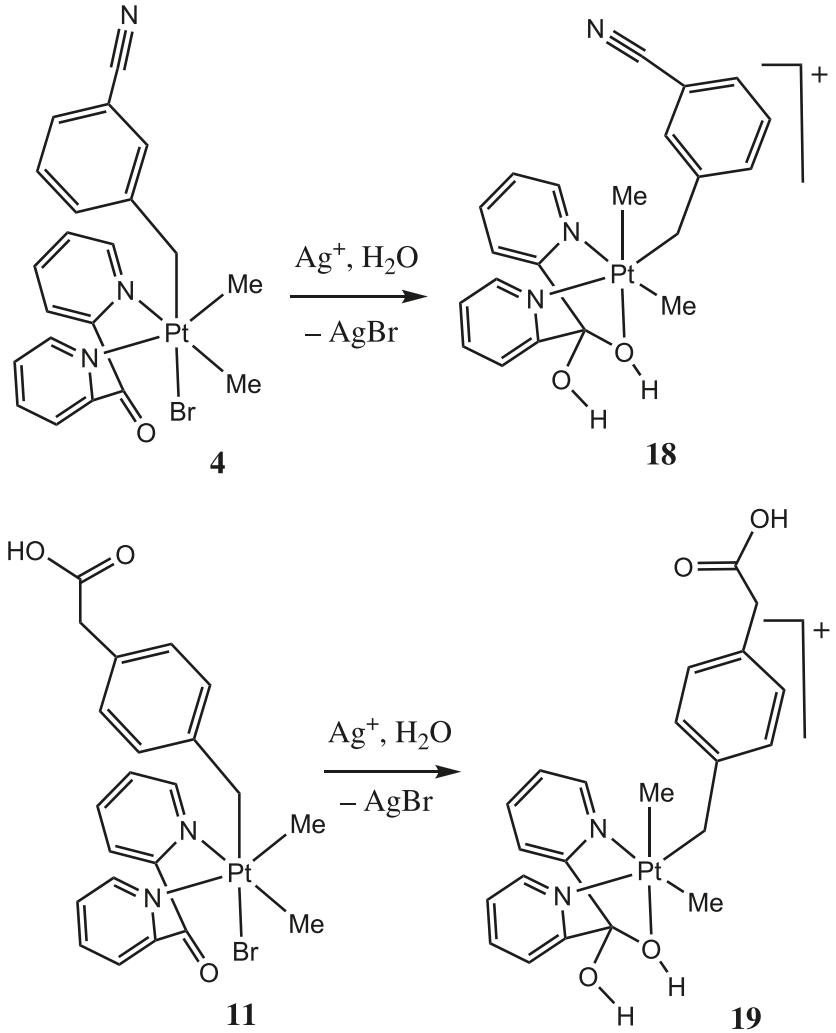
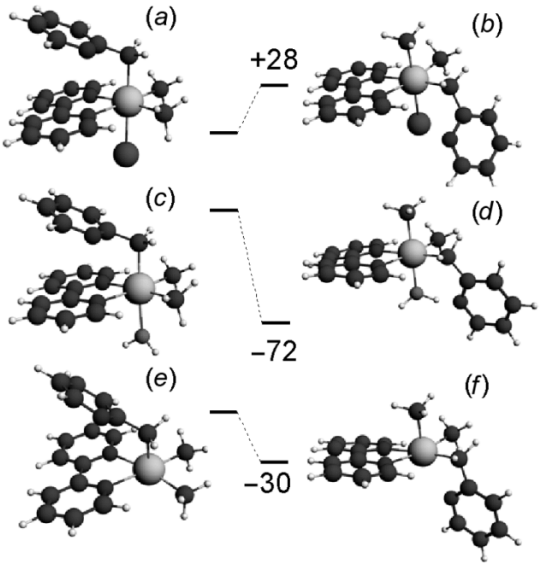


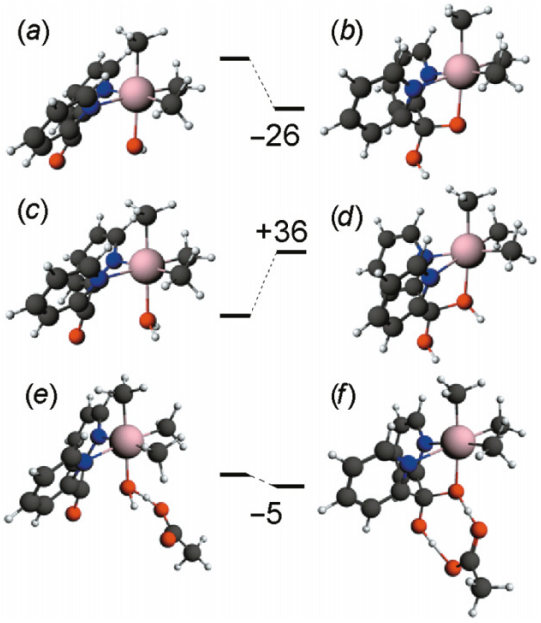
Fig. 9. Optimized structures and calculated relative energies (kJ mol^{-1}) of trans and cis isomers, respectively: (*a*), (*b*) [$PtBrMe_2(CH_2$-2-py)(bipy)]; (*c*), (*d*) [$PtMe_2(CH_2$-2-py)(OH_2)(bipy)]$^+$; (*e*), (*f*) [$PtMe_2(CH_2$-2-py)(bipy)]$^+$.



group π-stacked with the 2,2′-bipyridine ligand (Fig. 9*a*) but there is little barrier to rotation about the Pt–CH_2R bond for the cis isomer. The cis isomer can be more stable if there is a specific bonding effect in its favour. For example, the hypothetical aqua complex, [$PtMe_2(CH_2$-2-py)(OH_2)(bipy)]$^+$, is more stable as the cis isomer because an intramolecular hydrogen bond OH···N can exist between the aqua ligand and the 2-pyridyl group (Figs. 9*c*, 9*d*). Similarly, the intermediate five-coordinate complex [$PtMe_2(CH_2$-2-py)(bipy)]$^+$ is more stable as the cis isomer because the pyridylmethyl group can chelate to platinum (Figs. 9*e*, 9*f*). Ring strain in the $PtCH_2$-2-py chelate unit allows easy dissociation of the Pt–N bond. Thus, a conformation with d(Pt–N) increased from the optimized value of 2.23 Å (Fig. 9*f*) to 2.66 Å, with corresponding opening of the angle Pt–C–C(py) from 93° to 104°, was only 18 kJ mol^{-1} higher in energy. Easy reversible access to the coordinatively unsaturated square pyramidal intermediate accounts for the easy fluxionality in complex **15**.

A further complication in the chemistry of the DPK complexes arose from the ease of hydration of the ketone group. Some trimethylplatinum(IV) model complexes, used to avoid complications from cis and trans isomers in the actual complexes studied, are shown in Fig. 10. The ketone addi-

Fig. 10. Optimized structures and calculated relative energies (kJ mol^{-1}) of (*a*) [Pt(OH)Me$_3$(DPK)], (*b*) [PtMe$_3$(DPK-OH)]; (*c*) [PtMe$_3$(OH$_2$)(DPK)]$^+$, (*d*) [PtMe$_3$(DPK-OH$_2$)]$^+$; (*e*) [PtMe$_3$(OH$_2$)(DPK)][MeCO$_2$], (*f*) [PtMe$_3$(DPK-OH$_2$)][MeCO$_2$].

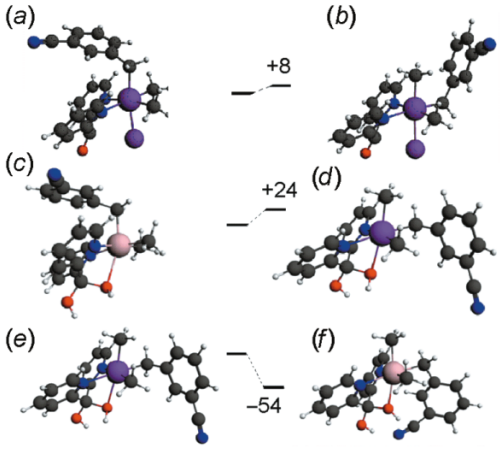


tion step is calculated to be favorable for conversion of neutral complex [Pt(OH)Me$_3$(DPK)] to [PtMe$_3$(DPK-OH)] (Figs. 10*a*, 10*b*). However, for the protonated cationic complexes [PtMe$_3$(OH$_2$)(DPK)]$^+$ and [PtMe$_3$(DPK-OH$_2$)]$^+$, the ketone addition step is unfavorable (Figs. 10*c*, 10*d*). Addition of an acetate anion, which can form a hydrogen bond with the aqua or DPK-OH$_2$ ligand, is enough to make the ketone addition step favorable, as illustrated in Figs. 10*e* and 10*f*. These calculations rationalize the observation that, in all known complexes of the DPK-OH$_2$ ligand, including complex **19**, the OH groups are involved in hydrogen bonding and that hydration is easily reversible.[20,21] The ligand DPK can form a hydrate in hydrochloric acid solution, under conditions where both pyridyl groups are protonated and there is hydrogen bonding between the C–OH groups and chloride anions, but the neutral ketone DPK is not hydrated.[22]

A feature of the complexes **18** and **19** with the DPK-OH$_2$ ligand is that the cis isomer is preferred. Calculations indicate that the trans isomer is expected to be more stable in the absence of hydrogen bonding, for both the ligand DPK and DPK-OH$_2$, as seen in Figs. 11*a*, 11*b* and Figs. 11*c*, 11*d*, respectively. For the cis isomer of the 3-cyanobenzyl derivative (**18**), intramolecular hydrogen bonding is possible and this greatly stabilizes this isomer, as illustrated in Figs. 11*e* and 11*f*. For complex **19**, intramolecular hydrogen bonding is not possible and the carboxylic acid group is involved in intermolecular hydrogen bonding (Fig. 9). In this case, the intermolecular hydrogen bonding is less favored for the trans isomer because of steric effects in the conformation with the aryl group lying over the DPK-OH$_2$ ligand and so the cis isomer is preferred.

Overall, this work has significantly expanded the range of known organoplatinum complexes containing functional alkyl groups. Some of the strengths and limitations in the use of these compounds in supramolecular chemistry are also

Fig. 11. Optimized structures and calculated relative energies (kJ mol^{-1}) of (*a*), (*b*) *trans*- and *cis*-[PtBrMe$_2$(CH$_2$-3-C$_6$H$_4$CN)(DPK)]; (*c*), (*d*) *trans*- and *cis*-[PtMe$_2$(CH$_2$-3-C$_6$H$_4$CN)(DPK-OH$_2$)]$^+$; (*e*), (*f*) *cis*-[PtMe$_2$(CH$_2$-3-C$_6$H$_4$CN)(DPK-OH$_2$)]$^+$ in conformations without and with OH···NC hydrogen bonding, respectively.



defined. The easy trans and cis isomerism and the easy hydration of the DPK ligand makes crystal engineering in these compounds challenging, and the relatively slow rate of ligand substitution at platinum(IV) limits the use of dynamic coordination chemistry for self-assembly. However, the use of hydrogen bonding for self-assembly has given interesting supramolecular dimers and a polymer, which have been structurally characterized.

Experimental

All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. The complexes [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$], [PtMe$_2$(bu$_2$bipy)], [PtMe$_2$(DPK)], [PtBrMe$_2$(bu$_2$bipy)(CH$_2$-4-C$_6$H$_4$CO$_2$H)], **8**, and [PtBrMe$_2$(bu$_2$bipy)(CH$_2$-4-C$_6$H$_4$CH$_2$CO$_2$H)], **10**, were prepared using the literature methods.[10,23,21] 1-D and 2-D ^{1}H NMR spectra were recorded using a Varian Mercury 400 NMR or a Varian Inova 400 NMR spectrometer at room temperature unless specified otherwise. ESI-MS were recorded using a Micromass LCT spectrometer. DFT calculations were carried out using the Becke–Perdew exchange-correlation functional in the Amsterdam Density Functional program,[24] including first-order scalar relativistic corrections and standard parameters used in previous studies of organoplatinum compounds.[2,25]

[PtBrMe$_2$(3-CH$_2$C$_6$H$_4$CN)(bu$_2$bipy)], 3

To a solution of [PtMe$_2$(bu$_2$bipy)] (0.1096 g, 0.22 mmol) in CH$_2$Cl$_2$ (5 mL) was added a solution of α-bromo-*m*-tolunitrile (0.0463 g, 0.24 mmol) in CH$_2$Cl$_2$ (5 mL). The solution was stirred for 30 min, the volume of solvent was reduced under vacuum, and the product was precipitated by addition of pentane (10 mL) and recrystallized from CH$_2$Cl$_2$/pentane. Yield: 0.085 g (0.12 mmol). ^{1}H NMR (CD$_2$Cl$_2$) δ: 1.43 [s, 18H, *t*-Bu], 1.51 [s, 6H, ^2J(PtH) = 69 Hz, *Me*Pt], 2.79 [s, 2H, ^2J(PtH) = 96 Hz, *CH*$_2$Pt], 6.19 [t, 1H, ^4J(HH) = 2 Hz, C$_6$H$_4$-H^2], 6.76 [d, 1H, ^3J(HH) = 7 Hz, C$_6$H$_4$-H^5], 6.79 [m, 1H, ^3J(HH) = 7 Hz, ^4J(HH) = 2 Hz, C$_6$H$_4$-H^6], 6.95 [m,

1H, ^3J(HH) = 7 Hz, ^4J(HH) = 2 Hz, C_6H_4-H^4], 7.93 [dd, 2H, ^3J(HH) = 6 Hz, ^4J(HH) = 2 Hz, bipy-H^5], 7.95 [d, 2H, ^4J(HH) = 2 Hz, bipy-H^3], 8.58 [d, 2H, ^3J(HH) = 6 Hz, bipy-H^6]. ESI-MS *m*/*z*: 609 (100) [$PtMe_2$(bu$_2$bipy)(3-$CH_2C_6H_4CN$)]$^+$. Anal. calcd. for $C_{28}H_{36}BrN_3Pt$ (%): C 48.77, H 5.26, N 6.09; found: C 48.43, H 5.19, N 5.96.

[$PtBrMe_2$(3-$CH_2C_6H_4CN$)(DPK)], 4

This was prepared similarly from [$PtMe_2$(DPK)] (0.149 g, 0.36 mmol) and α-bromo-*m*-tolunitrile (0.080 g, 0.41 mmol). Yield: 0.162 g (74%). IR (cm^{-1}): ν(CN) 2226 , ν(CO) 1677. ^{1}H NMR (CD_2Cl_2) δ: 1.35 [s, 6H, ^2J(PtH) = 70 Hz, *Me*Pt], 3.14 [s, 2H, ^2J(PtH) = 96 Hz, CH_2Pt], 6.93 [d, 1H, ^3J(HH) = 7 Hz, C_6H_4-H^6], 6.97 [s, 1H, C_6H_4-H^2], 7.01 [dd, 1H, ^3J(HH) = 7 Hz, ^3J(HH) = 6 Hz, C_6H_4-H^5], 7.28 [d, 1H, ^3J(HH) = 6 Hz, C_6H_4-H^4], 7.58 [dd, 2H, ^3J(HH) = 7 Hz, ^3J(HH) = 8 Hz, ^4J(HH) = 2 Hz, bipy-H^5], 8.12 [dd, 2H, ^3J(HH) = 8 Hz, ^4J(HH) = 2 Hz, bipy-H^4], 8.22 [d, 2H, ^3J(HH) = 8 Hz, ^4J(HH) = 2 Hz, bipy-H^3], 8.52 [d, 2H, ^3J(HH) = 7 Hz, ^4J(HH) = 2 Hz, bipy-H^6]. Anal. calcd. for $C_{21}H_{20}BrN_3PtO$ (%): C 41.66, H 3.33, N 6.94; found: C 41.34, H 3.02, N 6.60.

[$PtBrMe_2$(2-$CH_2C_5H_4N$)(bu$_2$bipy)], 5

To a solution of [$PtMe_2$(bu$_2$bipy)] (0.205 g, 0.4 mmol) in CH_2Cl_2 (4 mL) was added a solution of 2-(bromomethyl)-pyridine hydrobromide (0.123 g, 0.48 mmol) and excess NEt_3 (2.5 mL) in CH_2Cl_2 (5 mL). After 10 min, water (5 mL) was added, the mixture was extracted with CH_2Cl_2 (3 × 5 mL), the extracts were dried over anhydrous $MgSO_4$, filtered, and the solvent was removed under vacuum to give the product as a white solid, which was recrystallized from CH_2Cl_2/pentane. Yield: 197 mg. ^{1}H NMR (CD_2Cl_2) δ: 1.41 [s, 18H, *t*-Bu], 1.53 [s, 6H, ^2J(PtH) = 69 Hz, *Me*Pt], 2.97 [s, 2H, ^2J(PtH) = 99 Hz, CH_2Pt], 6.56 [m, 1H, ^3J(HH) = 7 Hz, py-H^5], 6.69 [d, 1H, ^3J(HH) = 7 Hz, py-H^3], 7.06 [m, 1H, ^3J(HH) = 7 Hz, py-H^4], 7.40 [d, 2H, ^3J(HH) = 6 Hz, bipy-H^5], 7.58 [m, 1H, ^4J(HH) = 2 Hz, py-H^6], 7.94 [s, 2H, bipy-H^3], 8.51 [d, 2H, ^3J(HH) = 6 Hz, bipy-H^6]. ESI-MS *m*/*z*: 585 (100) [$PtMe_2$(bu2bipy)(2-CH_2py)]$^+$. Anal. calcd. for $C_{26}H_{36}BrN_3Pt$ (%): C 46.92, H 5.45, N 6.31; found: C 46.48, H 5.07, N 6.04.

[$PtBrMe_2$(3-$CH_2C_5H_4N$)(bu$_2$bipy)], 6

This was prepared similarly from [$PtMe_2$(bu$_2$bipy)] (0.205 g, 0.4 mmol) and 3-(bromomethyl)pyridine hydrobromide (0.123 g, 0.48 mmol). Yield: 110 mg. ^{1}H NMR (CD_2Cl_2) δ: 1.42 [s, 18H, *t*-Bu], 1.50 [s, 6H, ^2J(PtH) = 68 Hz, *Me*Pt], 2.74 [s, 2H, ^2J(PtH) = 95 Hz, CH_2Pt], 6.54 [dd, 1H, ^3J(HH) = 7.5 Hz, ^3J(HH) = 5 Hz, py-H^5], 6.77 [d, 1H, ^3J(HH) = 7.5 Hz, py-H^4], 7.41 [s, 1H, py-H^2], 7.45 [d, 2H, ^3J(HH) = 6 Hz, bipy-H^5], 7.90 [m, 1H, ^3J(HH) = 5 Hz, py-H^6], 7.93 [s, 2H, bipy-H^3], 8.56 [d, 2H, ^3J(HH) = 6 Hz, bipy-H^6]. ESI-MS *m*/*z*: 585.2 (27) [$PtMe_2$(bu$_2$bipy)(3-CH_2py)]$^+$; 1250.4 (100) [[$PtMe_2$(bu$_2$bipy)(3-CH_2py)]$^+{}_2$Br$^-$]$^+$. Anal. calcd. for $C_{26}H_{36}BrN_3Pt$ (%): C 46.92, H 5.45, N 6.31; found: C 46.71, H 5.22, N 6.08.

[$PtBrMe_2$(4-$CH_2C_5H_4N$)(bu$_2$bipy)], 7

This was prepared similarly from [$PtMe_2$(bu$_2$bipy)] (0.106 g, 0.22 mmol) and 4-(bromomethyl)pyridine hydrobromide (0.065 g, 0.26 mmol). Yield: 92 mg. ^{1}H NMR (CD_2Cl_2) δ: 1.40 [s, 18H, *t*-Bu], 1.52 [s, 6H, ^2J(PtH) = 69 Hz, *Me*Pt], 2.74 [s, 2H, ^2J(PtH) = 99 Hz, CH_2Pt], 6.17 [d, 2H, ^3J(HH) = 5 Hz, py-H^{3,5}], 7.47 [d, 2H, ^3J(HH) = 5 Hz, py-H^{2,6}], 7.74 [d, 2H, ^3J(HH) = 6 Hz, bipy-H^5], 7.94 [s, 2H, bipy-H^3], 8.54 [d, 2H, ^3J(HH) = 6 Hz, bipy-H^6]. ESI-MS *m*/*z*: 585 (7) [$PtMe_2$(bu2bipy)(4-CH_2py)]$^+$, 666 (47) [$PtBrMe_2$(bu$_2$bipy)(4-CH_2pyH)]$^+$, 1250 (100) [[$PtMe_2$(-bu$_2$bipy)(4-CH_2py)]$^+{}_2$Br$^-$]$^+$. Anal. calcd. for $C_{26}H_{36}BrN_3Pt$ (%): C 46.92, H 5.45, N 6.31; found: C 46.87, H 5.19, N 6.10.

[$PtBrMe_2$(CH_2-4-$C_6H_4CO_2H$)(DPK)], 9

To a solution of [$PtMe_2$(DPK)] (0.25 g, 0.61 mmol) in Et_2O (10 mL) was added a solution of 4-(bromomethyl)benzoic acid (0.17 g, 0.79 mmol) in Et_2O (50 mL). After 1 h, the solvent was evaporated and the product was recrystallized from CH_2Cl_2/pentane. Yield: 0.38 g (91%). ^{1}H NMR (acetone-d_6) δ: 1.36 [s, 6H, ^3J(PtH) = 71 Hz, *Me*Pt], 3.29 [s, 2H, ^3J(PtH) = 95 Hz, CH_2Pt], 6.84 [d, 2H, ^3J(HH) = 8 Hz, C_6H_4-H^2], 7.50 [d, 2H, ^3J(HH) = 8 Hz, C_6H_4-H^3], 7.73 [m, 2H, DPK-H^5], 8.25 [m, 4H, DPK-H^{3,4}], 8.61 [m, 2H, DPK-H^6]. ESI-MS *m*/*z*: 544 (100) [$PtMe_2$(CH_2-4-$C_6H_4CO_2H$)(DPK)]$^+$. Anal. calcd. for $C_{21}H_{21}BrN_2O_3Pt$ (%): C 40.40, H 3.39, N 4.49; found: C 40.10, H 3.08, N 4.12.

[$PtBrMe_2$(CH_2-4-$C_6H_4CH_2CO_2H$)(DPK)], 11

To a solution of [$PtMe_2$(DPK)] (0.061 g, 0.149 mmol) in Et_2O (4 mL) was added a solution of 4-(bromomethyl)phenylacetic acid (0.043 g, 0.188 mmol) in Et_2O (10 mL). The solvent was evaporated and the product was recrystallized from CH_2Cl_2/pentane. Yield: 0.061 g (91.1%). ^{1}H NMR (acetone-d_6) δ: 1.36 [s, 6H, ^3J(PtH) = 70 Hz, *Me*Pt], 3.19 [s, 2H, ^3J(PtH) = 92 Hz, CH_2Pt], 3.60 [s, 2H, CCH_2], 7.24 [d, 2H, ^3J(HH) = 8 Hz, C_6H_4-H^2], 7.36 [d, 2H, ^3J(HH) = 8 Hz, C_6H_4-H^3], 7.55 [m, 2H, DPK-H^5], 7.95 [m, 4H, DPK-H^{3,4}], 8.76 [m, 2H, DPK-H^6]. ESI-MS *m*/*z*: 558 (100) [$PtMe_2$(CH_2-4-$C_6H_4CH_2CO_2H$)(DPK)]$^+$. The cis isomer was identified by its ^{1}H NMR spectrum δ: 0.99 [s, 3H, ^2J(PtH) = 71 Hz, Me^a], 1.62 [s, 3H, ^2J(PtH) = 72 Hz, Me^b], 2.81 [d, lH, ^2J(H^{a}H^b) = 9 Hz, ^2J(PtH^a) = 78 Hz, PtCH^a], 3.35, 3.48 [m, 2H, ^2J(HH) = 14 Hz, CCH_2], 3.65 [d, lH, ^2J(H^{a}H^b) = 9 Hz, ^2J(PtH^b) = 98 Hz, PtCH^b]. Anal. calcd. for $C_{22}H_{23}BrN_2O_3Pt$ (%): C 41.39, H 3.63, N 4.39; found: C 41.18, H 3.53, N 4.34.

[$PtBrMe_2$(4-$CH_2C_5H_4NH$)(bu$_2$bipy)]OTf, 12/13

This was prepared in situ by addition of triflic acid (5 equiv.) to a solution of complex **7** in CD_2Cl_2. **12**: ^{1}H NMR (CD_2Cl_2) δ: 1.56 [s, 6H, ^2J(PtH) = 68 Hz, *Me*Pt], 3.07 [s, 2H, ^2J(PtH) = 106 Hz, CH_2Pt]. **13**: ^{1}H NMR (CD_2Cl_2) δ: 0.78 [s, 3H, ^2J(PtH) = 72 Hz, *Me*Pt], 1.03 [s, 3H, ^2J(PtH) = 67 Hz, *Me*Pt], 3.54 [ms, 1H, ^2J(HH) = 7 Hz, ^2J(PtH) = 78 Hz, Pt*CH*^{a}H^b], 4.40 [m, 2H, ^2J(PtH) = 110 Hz, PtCH^a*H*^{b}]. ESI-MS *m*/*z*: 666 (100) [$PtBrMe_2$(4-CH_2py-H$^+$) (bu$_2$bipy)].

Similarly prepared were the following

[$PtBrMe_2$(2-$CH_2C_5H_4NH$)(bu$_2$bipy)]OTf

^{1}H NMR (CD_2Cl_2, trans isomer) δ: 1.68 [s, 6H, ^2J(PtH) = 72 Hz, *Me*Pt], 3.75 [s, 2H, ^2J(PtH) = 115 Hz, CH_2Pt]. ESI-

MS *m*/*z*: 585 (100) [$PtMe_2$(2-CH_2py) (bu_2bipy)]$^+$, 666 (11) [$PtBrMe_2$(2-CH_2py-H^+) (bu_2bipy)].

[PtBrMe$_2$(3-CH$_2$C$_5$H$_4$NH)(bu$_2$bipy)]OTf

^{1}H NMR (CD_2Cl_2, trans isomer) δ: 1.71 [s, 6H, ^2J(PtH) = 75 Hz, *Me*Pt], 3.26 [s, 2H, ^2J(PtH) = 102 Hz, *CH*$_2$Pt]. ESI-MS *m*/*z*: 585 (100) [$PtMe_2$(3-CH_2py) (bu_2bipy)]$^+$, 666 (10) [$PtBrMe_2$(3-CH_2py-H^+) (bu_2bipy)].

[PtMe$_2$(bu$_2$bipy)(2-CH$_2$py)]OTf, 15·OTf

To a solution of [$PtBrMe_2$(2-CH_2py)(bu_2bipy)] (0.0524 g, 0.08 mmol) in CH_2Cl_2 (6 mL) was added a solution of AgOTf (0.0442 g, 0.17 mmol) in acetone (2 mL). The mixture was stirred for 20 min, decolorizing charcoal was added, the solution was filtered, and the solvent was evaporated to give the product as a pale yellow solid. Yield: 0.046 g. ^{1}H NMR (CD_2Cl_2 at –10 °C) δ: 0.56 [s, 3H, ^2J(PtH) = 69 Hz, *Me*Pt], 1.43, 1.44 [s, 18H, *t*-Bu], 1.85 [s, 3H, ^2J(PtH) = 69 Hz, *Me*Pt], 2.53, 2.62 [m, 2H, ^2J(PtH) = 99 Hz, *CH*^{a}*H*^{b}Pt], 6.95–8.95 [m, 10H, py, bipy]. ESI-MS *m*/*z*: 585 (100) [$PtMe_2$(bu_2bipy)(2-CH_2py)]$^+$. Anal. ca1cd. for $C_{27}H_{36}F_3N_3O_3PtS$ (%): C 44.14, H 4.94, N 5.72; found: C 43.76, H 5.13, N 5.41.

[{PtMe$_2$(bu$_2$bipy)(3-CH$_2$py)}$_n$]OTf$_n$, 16·OTf

This was prepared similarly from [$PtBrMe_2$(3-CH_2py)(bu_2bipy)] (0.051 g, 0.08 mmol) and AgOTf (0.047 g, 0.18 mmol). Yield: 0.041 g. ESI-MS *m*/*z*: 585 (100) [$PtMe_2$(3-CH_2py)(bu_2bipy)]$^+$, 1319 (23) [{$PtMe_2$(bu_2bipy)(3-CH_2py)}$_2$OTf]$^+$. Anal. ca1cd. for $C_{27}H_{36}F_3N_3O_3PtS$ (%): C 44.14, H 4.94, N 5.72; found: C 43.68, H 5.02, N 5.36.

[{PtMe$_2$(bu$_2$bipy)(4-CH$_2$py)}$_n$]OTf$_n$

This was prepared similarly from [$PtBrMe_2$(4-CH_2py)(bu_2bipy)] (0.0498 g, 0.075 mmol) and AgOTf (0.040 g, 0.16 mmol). Yield: 0.030 g. ESI-MS *m*/*z*: 585 (100) [$PtMe_2$(bu_2bipy)(4-CH_2py)]$^+$, 1319 (4) [$PtMe_2$(bu_2bipy)(4-CH_2py)]$^+{}_2OTf^-]^+$, 1027 (5) [$PtMe_2$(bu_2bipy)(4-CH_2py)]$^+{}_3OTf^-]^{2+}$. Anal. ca1cd. for $C_{27}H_{36}F_3N_3O_3PtS$ (%): C 44.14, H 4.94, N 5.72; found: C 43.90, H 5.13, N 5.30.

[PtMe$_2$(CH$_2$-4-C$_6$H$_4$COOH)(bu$_2$bipy)(OH$_2$)][BF$_4$], 17·BF$_4$

A solution of $AgBF_4$ (10.5 mg, 0.054 mmol) in acetone (5 mL) was added dropwise to complex **11** (38.5 mg, 0.054 mmol) in acetone (10 mL) and allowed to stir for 1 h. AgBr began to precipitate and the mixture was filtered through Celite. After 2 h of stirring at room temperature, the solvent was evaporated. The product was washed with pentane to give a white solid. Yield: 35.0 mg (88%). ^{1}H NMR (acetone-d_6) δ: 1.33 [s, br, 6H, ^2J(PtH) = 64 Hz, *Me*Pt], 1.41 [s, 18H, *t*-Bu], 2.38 [s, 2H, ^2J(PtH) = 94 Hz, *CH*$_2$Pt], 3.19 [s, br, 2H, $PtOH_2$], 6.52 [br, 2H, C_6H_4(H^2, H^6)], 7.26 [br, 2H, C_6H_4(H^3, H^5)], 7.79 [br, 2H, bipy(H^5, H$^{5'}$)], 8.55 [br, 2H, bipy(H^3, H$^{3'}$)], 8.74 [br, 2H, bipy(H^6, H$^{6'}$)]. Anal calcd. for $C_{28}H_{39}BF_4N_2O_3Pt{\cdot}Me_2CO$ (%): C 47.04, H 5.73, N 3.54; found: C 47.11, H 5.76, N 3.42.

[PtMe$_2$(3-CH$_2$C$_6$H$_4$CN)(DPK-OH$_2$)]OTf, 18·OTf

To a solution of [$PtBrMe_2$(DPK)(3-$CH_2C_6H_4CN$)] (0.056 g, 0.09 mmol) in CH_2Cl_2 (6 mL) was added a solution of AgOTf (0.026 g, 0.1 mmol) in acetone (2 mL). The mixture was stirred for 20 min, decolorizing charcoal was added, the solution was filtered, and the solvent was removed under vacuum to give a pale yellow solid, which was recrystallized from CH_2Cl_2/pentane. Yield: 0.033 g. IR (cm^{-1}): ν(OH) 3250, ν(CN) 2250, ν(C=O) absent. ^{1}H NMR (CD_2Cl_2) δ: 1.18 [s, 3H, ^2J(PtH) = 72 Hz, *Me*Pt], 1.48 [s, 3H, ^2J(PtH) = 81 Hz, *Me*Pt], 3.03 [d, 1H, ^2J(PtH) = 73 Hz, ^2J(HH) = 10 Hz, *CH*$_2$Pt], 3.55 [d, 1H, ^2J(PtH) = 103 Hz, ^2J(HH) = 10 Hz, *CH*$_2$Pt], 7.08 [t, 1H, ^3J(HH) = 8 Hz, C_6H_4-H^5], 7.24 [d, 1H, ^3J(HH) = 6 Hz, C_6H_4-H^4], 7.25 [s, 1H, C_6H_4-H^2], 7.30 [m, 1H, ^3J(HH) = 6 Hz, bipy-H$^{5'}$], 7.34 [d, 1H, ^3J(HH) = 8 Hz, C_6H_4-H^6], 7.57 [t, 1H, ^3J(HH) = 7 Hz, bipy-H^5], 7.78 [d, 1H, ^3J(HH) = 5 Hz, bipy-H$^{3'}$], 8.02 [m, 1H, ^3J(HH) = 7 Hz, bipy-H^3], 8.03 [m, 1H, ^3J(HH) = 5 Hz, bipy-H$^{4'}$], 8.05 [m, 1H, bipy-H^4], 8.08 [d, 1H, ^3J(HH) = 8 Hz bipy-H$^{6'}$], 8.44 [d, 1H, ^3J(HH) = 6 Hz bipy-H^6]. ESI-MS *m*/*z*: 495 (100) [Pt(DPK)(3-$CH_2C_6H_4CN$)]$^+$, 525 (66) [$PtMe_2$(DPK)(3-$CH_2C_6H_4CN$)]$^+$, 543 (16) [$PtMe_2$(DPK)(3-$CH_2C_6H_4CN$) + H_2O]$^+$. Anal. calcd. for $C_{22}H_{22}F_3N_3O_5PtS$ (%): C 38.15, H 3.20, N 6.07; found: C 37.90, H 3.29, N 5.77.

[PtMe$_2$(4-CH$_2$C$_6$H$_4$CH$_2$CO$_2$H)(DPK-OH$_2$)][CF$_3$CO$_2$], 19·O$_2$CCF$_3$

To a solution of [$PtBrMe_2$(4-$CH_2C_6H_4CH_2CO_2H$)(DPK)] (0.050 g, 0.0783 mmol) in Et_2O (15 mL) was added a solution of AgO_2CCF_3 (0.018 g, 0.0815 mmol) in THF (2 mL). The mixture was stirred for 30 min, decolorizing charcoal was added, the mixture was filtered, and the solvent was evaporated to give a yellow solid, which was recrystallized from ether/pentane. ^{1}H NMR (CD_2Cl_2) δ: 1.05 [s, 3H, ^2J(PtH) = 71 Hz, *Me*^{a}Pt], 1.34 [s, 3H, ^2J(PtH) = 71 Hz, *Me*^{b}Pt], 2.80 [d, lH, ^2J(H^{a}H^b) = 10 Hz, ^2J(PtH^a) = 88 Hz, *CH*^{a}Pt], 3.44, 3.47 [m, 2H, CCH_2], 3.65 [d, lH, ^2J(H^{a}H^b) = 10 Hz, ^2J(PtH^b) = 95 Hz, *CH*^{b}Pt], 6.74 [d, 2H, ^3J(HH) = 8 Hz, C_6H_4-H^3], 6.92 [d, 2H, C_6H_4-H^2], 7.20–8.33 [m, 8H, DPK]. ESI-MS (M = [$PtMe_2$(4-$CH_2C_6H_4CH_2CO_2H$)(DPK-OH_2)][CF_3CO_2]) *m*/*z*: 1151 (5) [2M-2CF_3CO_2-H_3O]$^+$, 1133 (7) [2M-2CF_3CO_2-H_3O]$^+$, 1115 (5) [2M-2CF_3CO_2-2H_2O-H)]$^+$, 576 (100) [M-CF_3CO_2]$^+$, 558 (94) [M-CF_3CO_2-H_2O]$^+$. The trans isomer was identified by its ^{1}H NMR spectrum δ: 1.13 [s, 6H, ^2J(PtH) = 71 Hz, *Me*Pt], 3.39 [s, 2H, ^2J(PtH) = 91 Hz, *CH*$_2$Pt], 3.51 [s, 2H, CCH_2]. Anal. calcd. for $C_{24}H_{25}F_3N_2O_6Pt$ (%): C 41.80, H 3.65, N 4.06; found: C 41.56, H 3.87, N 3.81.

X-ray structure determinations

A crystal was mounted on a glass fibre and data were collected using a Nonius Kappa CCD diffractometer. Details of the data collection, absorption correction, and structure refinement are given in Table 1 and in the Supplementary data. Nonhydrogen atoms were refined with anisotropic thermal parameters, except in cases of disorder. The hydrogen atom positions were calculated geometrically and were included as riding on their respective heavy atoms. Brief comments on unusual features of individual structures are given below. The accuracy of bond distances was low in some cases as a result of disorder, but the structures are all well-defined.

Table 1. Crystal data and structure refinement.

Complex	**3**	**5**	**8**	**10**	**12/14**· $CHCl_3$	**17**· $1.5Me_2CO{\cdot}0.5C_6H_{14}$	**19**·O_2CCF_3
Formula	$C_{28}H_{36}BrN_3Pt$	$C_{26}H_{36}BrN_3Pt$	$C_{28}H_{37}BrN_2O_2Pt$	$C_{29}H_{39}BrN_2O_2Pt$	$C_{27}H_{38}Br_{0.36}Cl_{4.64}N_3Pt$	$C_{35.}H_{48}BF_4N_2O_{4.5}Pt$	$C_{23}H_{23}F_3N_2O_6Pt$
Fw	689.60	665.58	708.60	722.62	792.95	856.66	675.52
T (K)	150(2)	150(2)	150(2)	298(2)	295(2)	150(2)	100(2)
λ	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Cryst. syst.	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Tetragonal	Triclinic
Sp. Gp.	*Pbca*	$P2_1/c$	$P2_1/n$	*Pbca*	$P2_1/c$	$P\text{-}42_1c$	*P*-1
Cell dimensions							
a (Å)	22.9401(8)	12.7645(3)	7.1812(4)	22.6325(3)	12.1138(5)	26.7467(3)	7.8246(5)
b (Å)	20.2766(6)	11.5506(3)	12.7284(7)	21.5949(3)	21.932(1)	26.7467(3)	17.515(1)
c (Å)	11.4773(4)	35.2208(9)	30.2139(17)	12.0756(2)	12.1444(6)	10.9285(2)	17.683(1)
α	90	90	90	90	90	90	87.580(4)
β	90	93.674(1)	93.785(2)	90	91.870(4)	90	85.829(4)
γ	90	90	90	90	90	90	86.391(4)
V (Å^3)	5338.6(3)	5182.2(2)	2755.7(3)	5901.9(1)	3224.8(3)	7818.1(2)	2410.5(3)
Z	8	8	4	8	4	8	4
$D_{calcd.}$ (Mg m^{-3})	1.716	1.706	1.708	1.627	1.633	1.456	1.861
μ (mm^{-1})	6.774	6.975	6.568	6.135	5.202	3.647	5.885
Reflns.	46409	50713	12865	61611	26097	76143	16428
Data/restr./param.	4719/279/306	9150/0/559	4155/288/309	5208/244/291	5675/283/337	6867/29/461	9418/596/632
Gof	1.127	1.043	1.079	1.412	1.255	1.024	1.095
R_1 ($I>2\sigma(I)$)	0.058	0.062	0.065	0.092	0.137	0.037	0.066
wR_2 (all data)	0.095	0.167	0.160	0.223	0.313	0.099	0.175

[$PtBrMe_2$(3-$CH_2C_6H_4CN$)(bu_2bipy)], 3

There was minor unresolved disorder of the *t*-butyl groups.

[$PtBrMe_2$(2-$CH_2C_5H_4N$)(bu_2bipy)], 5

There were two independent molecules in the asymmetric unit.

[$PtBrMe_2$(CH_2-4-$C_6H_4CO_2H$)(bu_2bipy)], 8

The crystal was twinned and the twinning was successfully modelled.

[$PtBrMe_2$(CH_2-4-$C_6H_4CH_2CO_2H$)(bu_2bipy)], 10

The CH_2-4-$C_6H_4CH_2CO_2H$ groups were disordered. The disordered atoms were modeled isotropically at a 0.50/0.50 ratio.

[$PtBr_{0.36}(Cl_{0.64})Me_2$(4-$CH_2C_5H_4NH$)($bu_2bipy$)]$Cl{\cdot}CHCl_3$, 12/14

The crystal was twinned, with evidence for a multiple twin. The twinning was not modeled successfully, and so the agreement factors are large, but the structure is clearly defined.

[$PtMe_2$(CH_2-4-$C_6H_4CO_2H$)(OH_2)(bu_2bipy)][BF_4]$\cdot 1.5Me_2CO{\cdot}0.5C_6H_{14}$, 17

There was 50:50 disorder of the carboxylic acid group. In one component form, there was a hydrogen bond to an acetone molecule while, in the other component, that void contained a disordered hexane molecule, which was refined isotropically. The hexane molecule was not well-defined.

[$PtMe_2$(4-$CH_2C_6H_4CH_2CO_2H$)(DPK-OH_2)][CF_3CO_2], 19$\cdot O_2CCF_3$

There were two independent molecules in the asymmetric unit, and they were connected through hydrogen bonds. The crystal was twinned and the twinning was successfully modeled.

Supplementary data

Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 3933. For more information on obtaining material, refer to cisti-icist.nrc-cnrc.gc.ca/cms/unpub_e.shtml. CCDC 711234–711240 contain the X-ray data in CIF format for seven complexes for this manuscript. These data can be obtained, free of charge, via 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 336033; or deposit@ccdc.cam.ac.uk).

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