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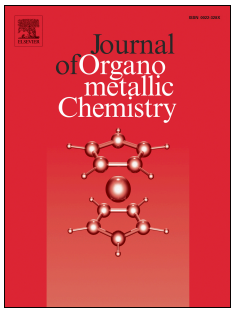

Chelating Imidazole Ligands Promote Oxidative Addition in Dimethylplatinum(II) Complexes

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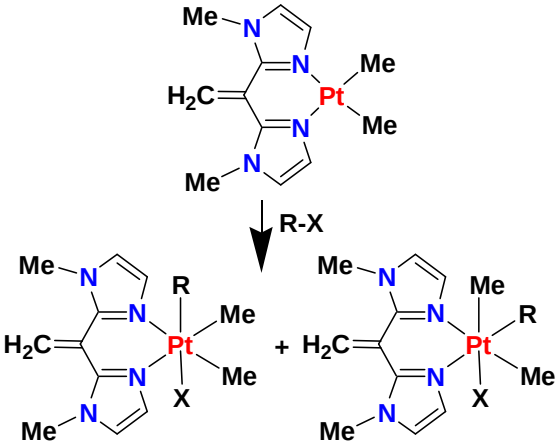

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Highlights

- Dimethylplatinum(II) complexes of two bis(imidazolyl) ligands are prepared.
- These complexes are highly reactive to oxidative addition.
- The stereochemistry of the oxidative addition reaction is established.

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Chelating Imidazole Ligands Promote Oxidative Addition in Dimethylplatinum(II) Complexes

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ABSTRACT

The oxidative addition chemistry of the complexes $[PtMe_2\{(mim)_2C{=}CH_2\}]$, **1**, and $[PtMe_2\{(mim)_2CHMe\}]$, **2**, where mim = N-methylimidazol-2-yl, is described. Complex **1** undergoes oxidative addition with alkyl halides RX to give $[PtXRMe_2\{(mim)_2C{=}CH_2\}]$, X= I, R = Me; X = Br, R = CH_2Ph, $CH_2C_6H_4$-4-CF_3, $CH_2C_6H_4$-2-CF_3, $CH_2C_6H_3$-3,5-*t*-Bu_2; X = Cl, R = CH_2Cl, and with hydrogen peroxide to give $[Pt(OH)_2Me_2\{(mim)_2C{=}CH_2\}]$. Complex **2** undergoes oxidative addition with alkyl halides RX to give $[PtXRMe_2\{(mim)_2CHMe\}]$, X= I, R = Me; X = Br, R = $CH_2C_6H_4$-4-CF_3, $CH_2C_6H_4$-2-CF_3, and with iodine and hydrogen peroxide to give $[PtX_2Me_2\{(mim)_2CHMe\}]$, X = I or OH. The stereochemistry of the reaction has been determined in each case, and several complexes have been structurally characterized. The high reactivity of complexes **1** and **2** towards oxidative addition is rationalized in terms of the strong donating property of the imidazolyl ligands, as supported by theoretical (DFT) studies.

1. Introduction

Dimethylplatinum(II) complexes of formula $[PtMe_2(NN)]$, where NN is a chelating nitrogen donor ligand such as 2,2'-bipyridine, are among the most reactive substrates for oxidative addition and their derivatives [PtMeX(NN)], in which X is a weakly bound ligand, are important reagents in studies of carbon-hydrogen bond activation [1,2]. In both reactions, there are significant differences in reactivity between *bis*(pyridine) complexes in which there is a 5-membered chelate ring (***A***, Chart 1) or a 6-membered chelate ring (***B***, ***C***, ***D***, Chart 1) [3-10]. The complexes $[PtMe_2(NN)]$, such as ***A*** – ***C***, react with alkyl halides, RX, to give platinum(IV) complexes $[PtXMe_2R(NN)]$ by oxidative addition and these reactions have been used to prepare a wide range of

functional organoplatinum(IV) complexes [1,9-17], as well as in fundamental studies of reactivity and mechanism in oxidative addition reactions [1,18-23].

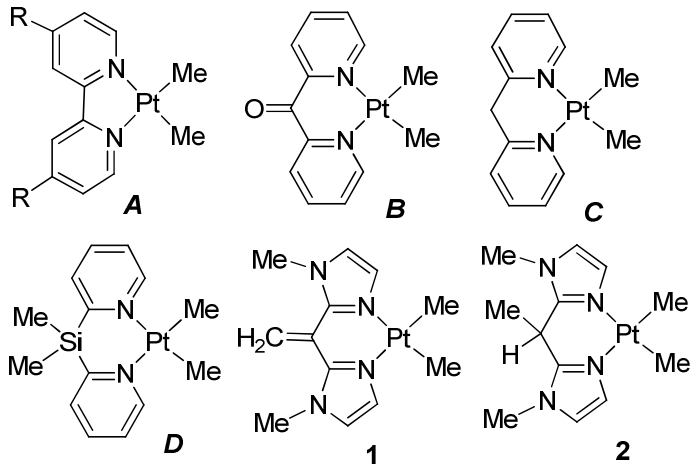
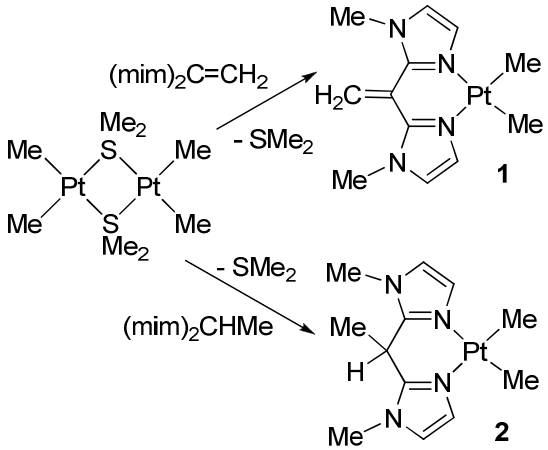


Chart 1. Dimethylplatinum(II) complexes.

Most of the above studies have used pyridine donors as components of the bidentate ligands NN (Chart 1) and, in the present work, a comparison is made with the bidentate ligands $(mim)_2C{=}CH_2$ and $(mim)_2CHMe$, which contain N-methylimidazole donors, in the dimethylplatinum(II) complexes **1** and **2** (Chart 1) [24]. These ligands were originally reported to give the palladium(II) complexes [PdMeX(NN)], and $[PdMe_2(NN)]$, and they, and similar ligands, have since been used in forming complexes with several other transition metals [24-31]. Platinum complexes of these ligands have not been reported, but several platinum(II) complexes with monodentate imidazole derivatives are known and they have been shown to exhibit cytostatic activity [32-33].

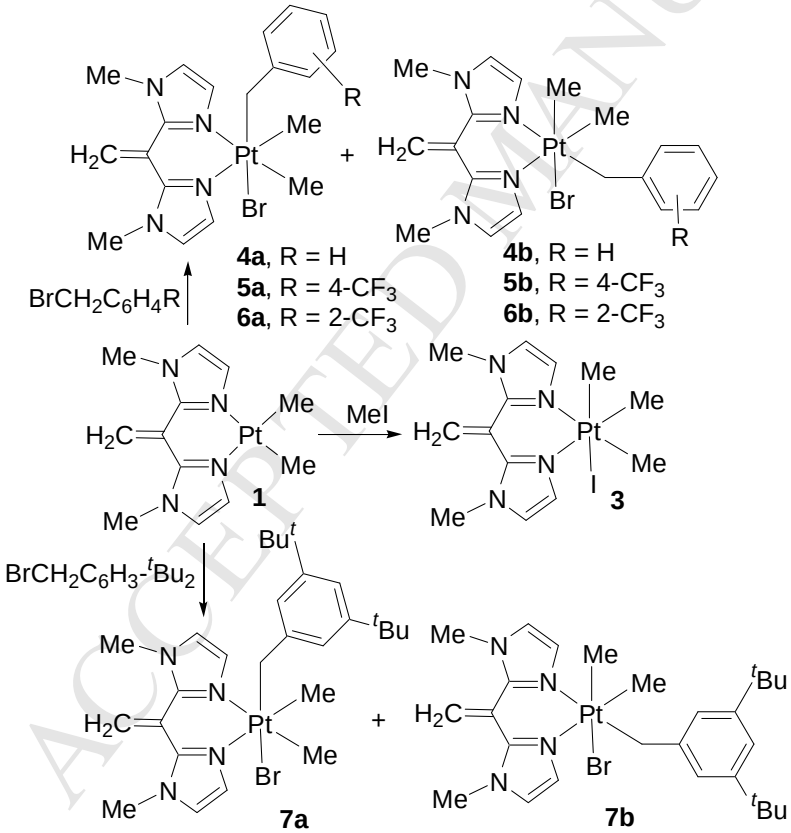
2. Results and Discussion

The ligands were prepared according to the literature procedure [24], and the dimethylplatinum(II) complexes were then prepared according to Scheme 1by reaction with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ [34]. The complexes were characterized by their spectroscopic properties. For example, the yellow complex **1** gave, in the ^{1}H NMR spectrum, a single methylplatinum resonance at δ = 0.53, with coupling constant $^2J_{PtH}$ = 86 Hz, while the imidazole protons appeared as two doublets at δ = 7.19, $^3J_{HH}$ = 1 Hz, $^3J_{PtH}$ = 13 Hz, and at δ = 7.23, $^3J_{HH}$ = 1 Hz. Singlet resonances were observed for the NMe groups at δ = 3.91 and for the $=CH_2$ protons at δ = 6.18. The chemical shifts are similar to those observed for $[PdMe_2\{(mim)_2C{=}CH_2\}]$ [24]. The mass spectrum for complex **1** showed a peak at m/z = 412 corresponding to $[PtMe_2\{(mim)_2C{=}CH_2\} - H]^+$.



Scheme 1. Synthesis of platinum(II) complexes **1** and **2**.

Some oxidative addition reactions of complex **1** with alkyl halides, which are expected to occur by the polar, bimolecular S_N2 mechanism [1,20,35,36], are shown in Scheme 2.



Scheme 2. Oxidative addition of alkyl halides to complex **1**.

The simplest reaction with methyl iodide gave the complex $[PtIMe_3\{(mim)_2C{=}CH_2\}]$, **3**. The ^1H NMR spectrum of complex **3** contained two methylplatinum resonances in 1:2 ratio for the methyl groups *trans* to iodine and nitrogen

atoms [35,36]. The structure of complex **3** was determined and is shown in Figure 1. The complex has octahedral coordination geometry and has crystallographic C_s symmetry, with the mirror plane containing the atoms Pt(1)C(8)I(1)C(5)C(6). The 6-membered chelate ring adopts the boat conformation, with the vinylidene group oriented towards the iodide side of the molecule.

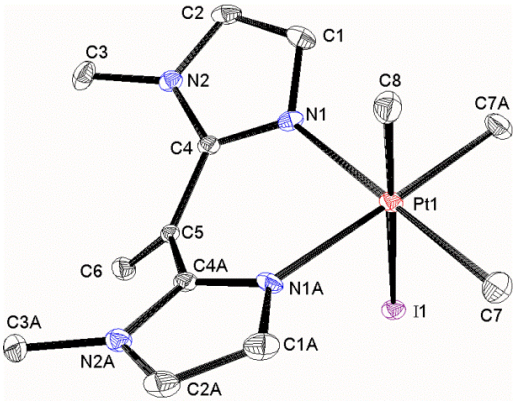


Figure 1. The structure of complex **3**. Selected bond parameters: Pt(1)-I(1) 2.804(1); Pt(1)-N(1) 2.155(7); Pt(1)-C(7) 2.062(9); Pt(1)-C(8) 2.046(13) Å; N(1)-Pt(1)-N(1A) 85.7(4)^o.

The reaction of benzyl bromide with complex **1** was more complex since it gave the product [PtBr($CH_2C_6H_5$)Me_2{$(mim)_2C=CH_2$}] as a mixture of isomers **4a** and **4b**, formed by *trans* and *cis* oxidative addition, respectively. The isomers were formed with ratio **4a**:**4b** *ca.* 2:1, as determined by integration of the ^{1}H NMR spectra. Complex **4a** has effective C_s symmetry and, as expected [20], it gave a single methylplatinum resonance, a single $PtCH_2$ resonance, and only one set of imidazole resonances in the ^{1}H NMR spectrum. On the other hand, complex **4b** has no symmetry (C_1) and so it gave two methylplatinum resonances and two resonances due to the $C=CH^AH^B$ protons. Similarly, two peaks were expected for the diastereotopic protons of the $PtCH_2$ group, but only a single broad peak was observed at room temperature (Figure 2a). However, as the temperature was lowered, the peak broadened and it then split into two broad resonances at -60^{o}C (Figure 2b). Rotation about the Pt-CH^AH^BPh bond cannot make the diastereotopic protons equivalent, so this observation is unusual. We do not have a definitive explanation but we suggest that, as a result of rotation of the benzyl group at higher temperatures, the chemical shifts of the $PtCH^AH^B$ protons are accidentally degenerate but that, as rotation is slowed at low temperature, the individual resonances are partly resolved. The substituted derivatives of benzyl bromide reacted in a similar way to give complexes **5** – **7**, in each case as a mixture of products of *trans* and *cis* oxidative addition (Scheme 2) as determined by the ^{1}H NMR spectra. In these complexes, the $PtCH^AH^B$ protons of the substituted benzylplatinum groups of **5b** – **7b** were resolved, even at room temperature, in contrast to **4b**. The ratio of isomers was *ca.* 2:1 for **5a**:**5b** but *ca.* 3:1 for **6a**:**6b** and **7a**:**7b**, suggesting that greater steric bulk of the substituted benzyl group favors the product of *trans* oxidative addition.

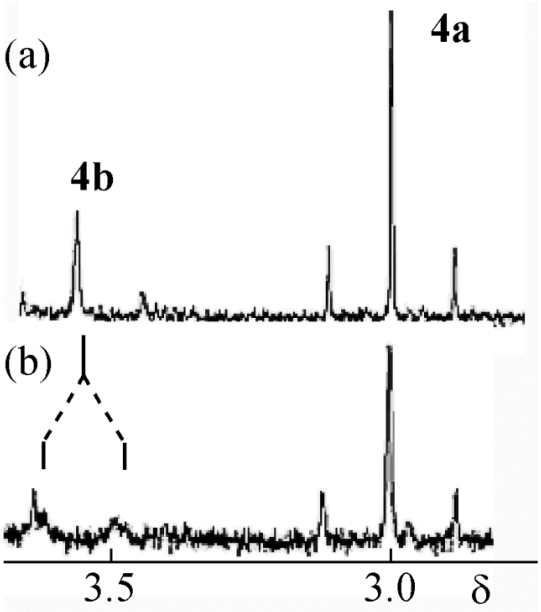


Figure 2. ^{1}H NMR spectra (600 MHz, CD_2Cl_2) of complex **4** in the region of the $PtCH_2$ resonances: (a) at 20^{o}C; (b) at -60^{o}C.

The structure of complex **4a** was determined and is shown in Figure 3. Again, the platinum(IV) center has octahedral coordination geometry, with the benzyl and bromo groups mutually *trans*. The thermal ellipsoids for the phenyl group carbon atoms are large, suggesting that there is unresolved librational disorder of this group.

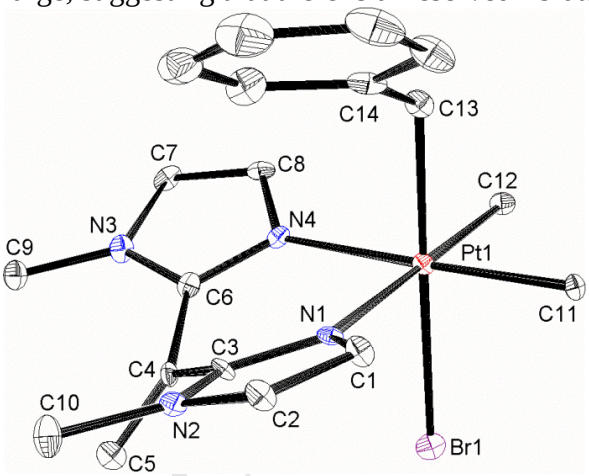


Figure 3. The structure of complex **4a**. Selected bond parameters: Pt(1)-Br(1) 2.617(1) ; Pt(1)-N(1) 2.153(7); Pt(1)-N(4) 2.150(7); Pt(1)-C(11) 2.071(8); Pt(1)-C(12) 2.071(9); Pt(1)-C(13) 2.095(1) Å; N(1)-Pt(1)-N(4) 87.0(3)°.

The structures of complexes **6a** and **7a** are similar and are shown in Figures 4 and 5. In each case, the chelate ring adopts the boat conformation with the $C{=}CH_2$ group *syn* to the bromo ligand and *anti* to the benzyl group. The benzyl group is oriented above one

of the imidazole rings in **4a**, **6a** and **7a** (Figures 3-5). Unfortunately, we have not been able to obtain single crystals for X-ray structure determination of the *cis* isomers **4b** – **7b**.

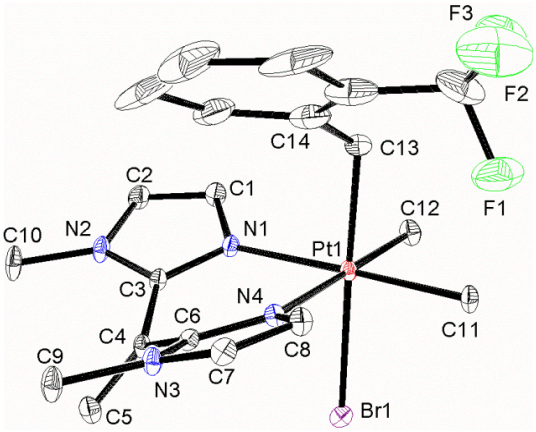


Figure 4. The structure of complex **6a**. Selected bond parameters: Pt(1)-Br(1) 2.5997(6) ; Pt(1)-N(1) 2.149(4); Pt(1)-N(4) 2.156(4); Pt(1)-C(11) 2.050(5); Pt(1)-C(12) 2.050(5); Pt(1)-C(13) 2.078(6) Å; N(1)-Pt(1)-N(4) 86.1(2)°.

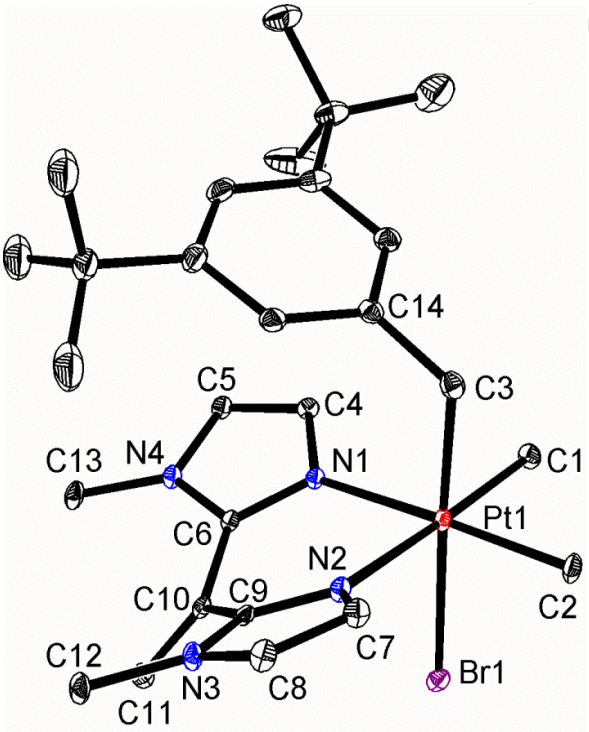
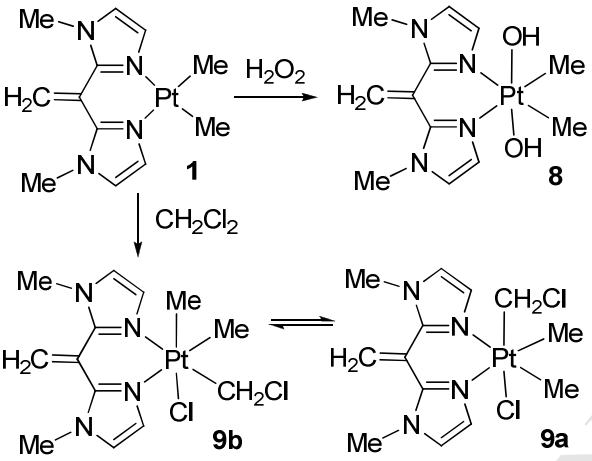


Figure 5. The structure of complex **7a**. Selected bond parameters: Pt(1)-Br(1) 2.6364(6); Pt(1)-N(1) 2.152(4); Pt(1)-N(2) 2.160(4); Pt(1)-C(1) 2.049(5); Pt(1)-C(2) 2.049(5); Pt(1)-C(3) 2.084(6) Å; N(1)-Pt(1)-N(2) 85.7(2)°.

Complex **1** reacted rapidly with hydrogen peroxide in acetone solution to give the dihydroxoplatinum(IV) complex $[Pt(OH)_2Me_2\{(mim)_2C{=}CH_2\}]$, **8**, according to Scheme

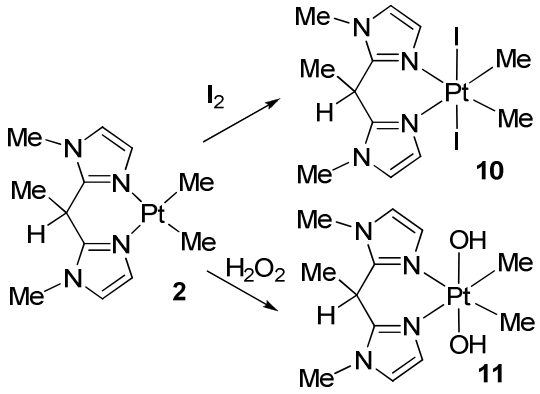
3. The ^{1}H NMR spectrum showed that **8** was formed by *trans* oxidative addition of the HO-OH bond to complex **1**. Thus, there was only one methylplatinum resonance and one set of imidazole peaks. The complex could not be crystallized but it was characterized by the mass spectrum, which contained a peak at m/z = 430 corresponding to $[Pt(OH)Me_2\{(mim)_2C{=}CH_2\}]^+$, and by comparison to several similar complexes [37-40].



Scheme 3. Oxidative addition of H_2O_2 and CH_2Cl_2.

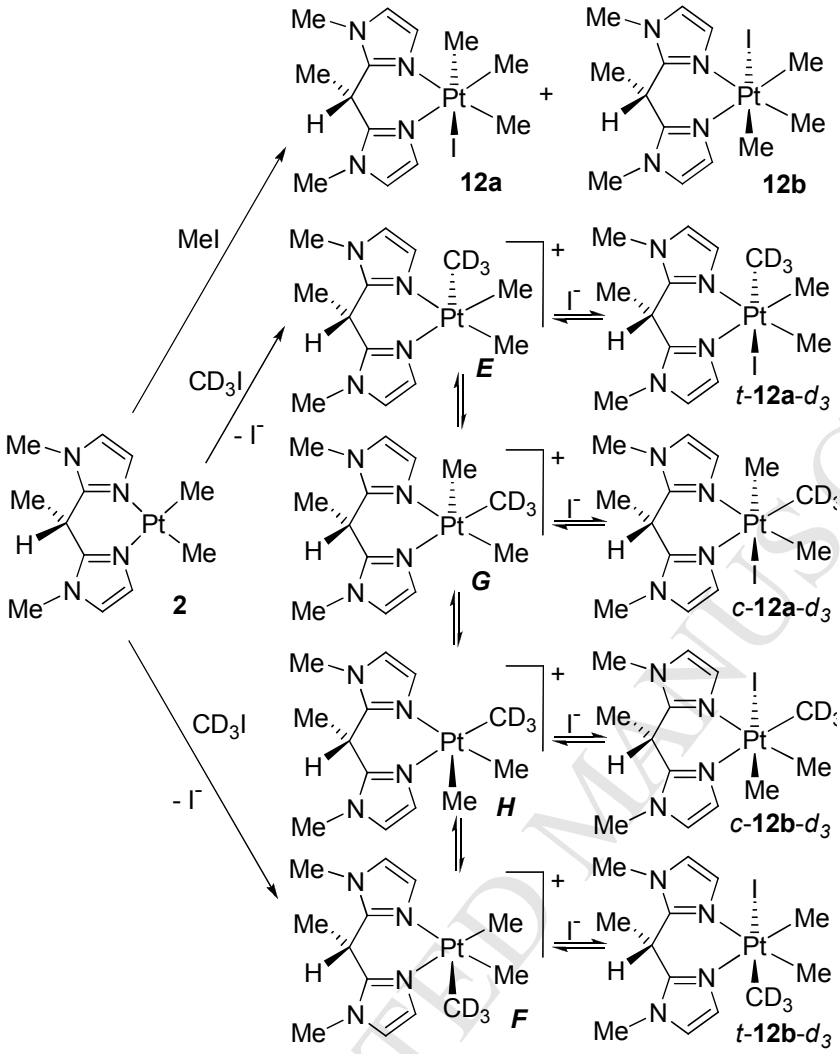
Complex **1** was unstable in chlorinated solvents dichloromethane and chloroform, and the reaction with dichloromethane was shown to occur by oxidative addition to give $[PtCl(CH_2Cl)Me_2\{(mim)_2C{=}CH_2\}]$, **9** (Scheme 3). Complex **9** was isolated as a mixture of the products of *trans* and *cis* oxidative addition, **9a** and **9b** respectively. In the ^{1}H NMR spectrum, the *trans* isomer **9a** gave a single methylplatinum resonance and a single $PtCH_2Cl$ resonance. On the other hand, the *cis* isomer **9b** gave two equal intensity methylplatinum resonances and two resonances for the diastereotopic $PtCH^aH^bCl$ protons. The course of the reaction was monitored by recording the ^{1}H NMR spectrum of a solution of complex **1** in CD_2Cl_2 over time. The resonances for complex **1** decayed over a period of one hour at room temperature and were replaced by resonances for **9b**-d_2. Over a period of several days, the resonances for **9b**-d_2 decayed and resonances for **9a**-d_2 grew in intensity, to finally give an equilibrium mixture with ratio **9a**-d_2:**9b**-d_2 = 5:2. The reaction occurs more rapidly than with most related dimethylplatinum(II) complexes [41], and the kinetically controlled product is **9b**-d_2 but **9a**-d_2 is slightly more stable thermodynamically. The ^{2}H NMR spectrum of **9a**-d_2 gave a single $PtCD_2Cl$ resonance while **9b**-d_2 gave two resonances. Oxidative addition of dichloromethane usually occurs by a free radical mechanism [41,42].

Oxidative addition reactions to complex **2** tended to occur with *trans* stereochemistry. The simplest examples are with symmetrical reagents iodine and hydrogen peroxide which gave complexes **10** and **11**, respectively, by selective *trans* oxidative addition (Scheme 4). In the ^{1}H NMR spectrum, each product gave a single methylplatinum resonance and a single set of imidazole resonances, as expected for a complex with effective C_s symmetry. While *trans* oxidative addition is typical with hydrogen peroxide, iodine often gives a mixture of products of *trans* and *cis* addition [43].



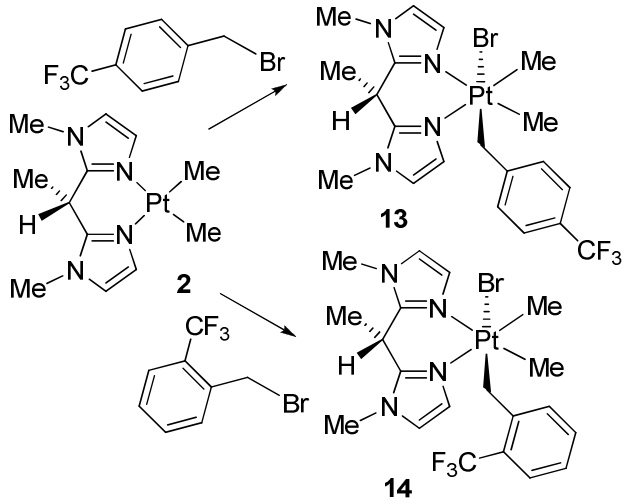
Scheme 4. Oxidative addition of iodine and hydrogen peroxide to complex **2**.

The oxidative addition of methyl iodide to complex **2** gave [$PtIMe_3${$(mim)_2CHMe$}], **12**, as a mixture of two isomers **12a** and **12b**. The isomers arise because the two faces of complex **2** are not equivalent and methyl iodide can approach from either side. The isomers were identified by a correlation in the ^1H NOESY NMR spectrum between the MeC and axial MePt groups for isomer **12a** only. The ratio of isomers **12a**:**12b** was *ca.* 4:3 for an isolated sample. Further insight into the reaction was obtained by carrying out the reaction of complex **2** with CD_3I in acetone-d_6 solution, with monitoring by ^1H NMR spectroscopy as the solution warmed. For this reaction, there are four possible isomers identified as *t*-**12a**-d_3 and *t*-**12b**-d_3, formed by *trans* oxidative addition, and *c*-**12a**-d_3 and *c*-**12b**-d_3 formed by *cis* oxidative addition (Scheme 5). The relative abundance of each isomer can be determined by integration of the spectra. At the lowest temperature at which reaction was complete, the ratio **12b**-d_3:**12a**-d_3 was *ca*. 3:2 and the ratios *t*-**12b**-d_3:*c*-**12b**-d_3 = 1:1 and *t*-**12a**-d_3:*c*-**12a**-d_3 = 1:2. As the solution warmed, the ratios changed to give the equilibrium values **12b**-d_3:**12a**-d_3 = 3:4 and *t*-**12b**-d_3:*c*-**12b**-d_3 = *t*-**12a**-d_3:*c*-**12a**-d_3 = 1:2, which is the statistical ratio. The data are interpreted in terms of the mechanism shown in Scheme 5 [44,45]. The S_N2 mechanism can give either 5-coordinate cationic intermediate ***E*** or ***F***, on approach from either side of the square plane of platinum(II), and iodide coordination can then give *t*-**12a**-d_3 and *t*-**12b**-d_3, respectively. The 5-coordinate intermediates can undergo pseudorotation to give ***G*** and ***H***, and iodide coordination can then give *c*-**12a**-d_3 and *c*-**12b**-d_3. Iodide dissociation from any of the octahedral isomers can reform the 5-coordinate precursor complexes and then further isomerization can occur. The data suggest that CD_3I approach to the less hindered side of complex **2** to give intermediate ***F*** is preferred over formation of ***G*** by approach to the more hindered side. However, it is also clear that pseudorotation of the 5-coordinate intermediates is competitive with iodide coordination, so the stereoselectivity in the reaction is not high. Complex **12a** is likely to be more thermodynamically stable than **12b** because the larger iodo group is *syn* to the hydrogen and the smaller methyl group is *syn* to the methyl substituent of the CHMe group (Scheme 5). Hence it is possible to rationalize the different selectivities resulting from kinetic or thermodynamic control.



Scheme 5. Proposed mechanism of oxidative addition of CD_3I to complex **2**.

The oxidative addition of the derivatives of benzyl bromide occurred more selectively to give only the isomer **13** from 1,4-$C_6H_4(CF_3)(CH_2Br)$ and **14** from 1,2-$C_6H_4(CF_3)(CH_2Br)$ (Scheme 6). For example, complex **13** gave only one methylplatinum resonance, one $PtCH_2$ resonance, and one set of imidazole resonances. In these reactions, the benzyl group is larger than the bromo group, so the isomer with benzyl group *syn* to the hydrogen atom and bromo group *syn* to the methyl substituent of the CHMe group is favored by both kinetic and thermodynamic control.



Scheme 6. Oxidative addition of benzyl bromide derivatives to complex **2**.

The structure of complex **14** was determined and is shown in Figure 6. It confirms the structure deduced from the ^{1}H NMR spectrum, with the complex formed by selective *trans* oxidative addition to complex **2**. The six-membered chelate ring is in the boat conformation with the C-Me group *syn* to the bromo ligand. The bite angle of the chelate ligand, N(1)-Pt(1)-N(3) 86.6(1)°, is similar to that in complex **6a** (86.1(2)°, Figure 4).

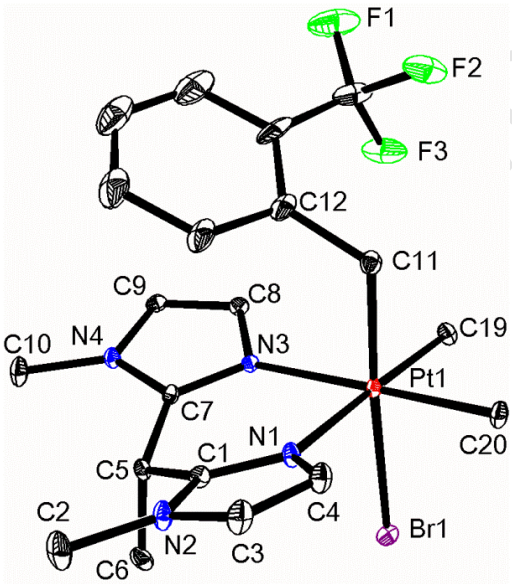


Figure 6. The structure of [PtBrMe$_2$(CH$_2$-2-C$_6$H$_4$CF$_3$){(mim)$_2$CHMe}], **14**. Selected bond parameters: Pt(1)-Br(1) 2.5951(6); Pt(1)-N(1) 2.152(4); Pt(1)-N(3) 2.152(4) ; Pt(1)-C(11) 2.086(5); Pt(1)-C(19) 2.044(4); Pt(1)-C(20) 2.051(4) Å; N(1)-Pt(1)-N(3) 86.6(1)^{o}.

3. Computational Studies and Conclusions

The dimethylplatinum(II) complexes [PtMe$_2$\{(mim)$_2$C=CH$_2$\}], **1**, and [PtMe$_2$\{(mim)$_2$CHMe\}], **2**, are very reactive towards oxidative addition chemistry. The

reactivity towards dichloromethane and also to oxidation by air is higher than for [$PtMe_2$(bipy)] [41], consistent with the greater donor power of the imidazolyl compared to pyridyl subsituents [24]. In most oxidative addition reactions, the platinum(II) center is the nucleophile using its $5d_{z^2}$ orbital (Figure 7). The calculated energy of the HOMO and the calculated Hirshfeld charge on platinum for related complexes are shown in Table 1. It can be seen that the calculated energy of the HOMO is higher and the calculated positive charge on platinum is lower for complexes **1** and **2** than for pyridyl analogs, consistent with the high reactivity of complexes **1** and **2** [24]. We note that the methyl substituent in **2** is close to platinum, and can hinder reaction at that face, but this close proximity does not lead to C-H or C-C bond activation analogous to the known reactions of ligands such as ***D*** [4,38,46].

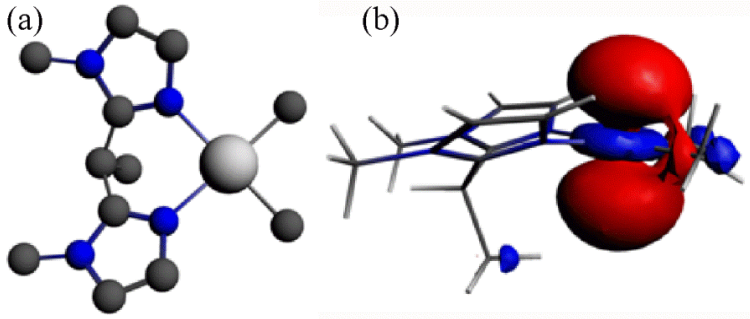


Figure 7. (a) The DFT calculated structure of complex **2** and (b) the calculated HOMO (mostly Pt $5d_{z^2}$) of complex **2**.

Table 1. Calculated energies (eV) of the HOMO and Hirshfeld charges, Q(Pt), on platinum [47].

	Complex **1**	Complex **2**	[$PtMe_2$(bipy)]	[$PtMe_2$(2-py_2CHMe)]
E(HOMO)	-3.93	-3.78	-4.88	-4.59
Q(Pt)	0.139	0.136	0.186	0.191

The ligand $(mim)_2C{=}CH_2$ forms platinum(IV) complexes in which the PtN2C3 chelate ring is in the boat conformation with the $=CH_2$ group *syn* to the halide ligand in complexes **3**, **4a**, **6a** and **7a** (Figures 1,3,4,5). DFT calculations were carried on complex **3** in different conformations, as illustrated in Figure 8. The experimentally observed conformation **3**-*syn* was calculated to be more stable than **3**-*anti* by 5 kJ mol^{-1}, and they could interconvert by way of the conformation **3**-planar (Fig. 8), with a significant barrier of 49 kJ mol^{-1} predicted.

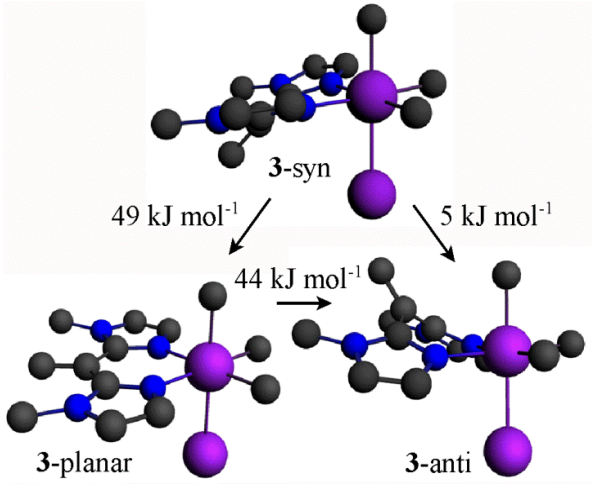


Figure 8. The calculated structures and relative energies of complex **3** in different conformations.

In contrast, the interconversion of isomeric complexes **12a** and **12b** requires dissociation of the iodide ligand at an intermediate stage (Scheme 5). The DFT calculation predicts that **12a** and **12b** have almost equal energy (Figure 9), consistent with the observation of both isomers at equilibrium, as established by NMR spectroscopy.

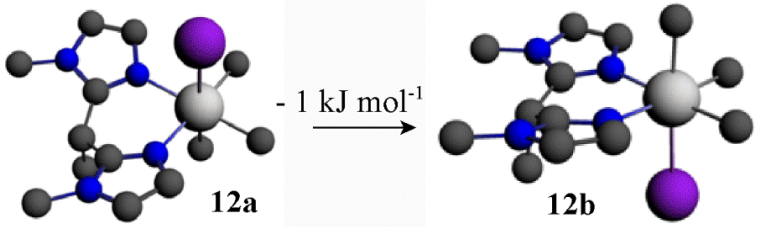


Figure 9. The calculated structures and relative energies of complexes **12a** and **12b**.

The calculated structures and energies of the most stable *trans* and *cis* isomers of $[PtBrMe_2(CH_2Ph)\{(mim)_2C{=}CH_2\}]$, **4a** and **4b**, are shown in Figure 10. The illustrated conformers with the bromo ligand *syn* to the $C{=}CH_2$ group are preferred in each case. Several conformations of the benzyl ligand were tested, and the preferred orientation in **4a** was close to that observed crystallographically (Figure 3), with the benzyl group above one of the imidazole rings. The preferred conformation of the benzyl group in **4b** was found to be towards an imidazole group, and this conformer of **4b** was calculated to be only 3 kJ mol^{-1} higher in energy than **4a**, consistent with the observation of both isomers in equilibrium.

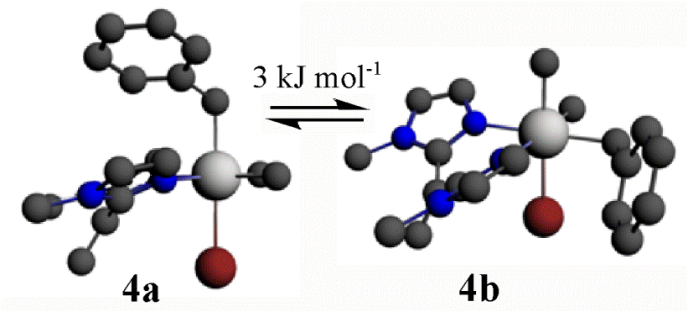


Figure 10. Calculated structures and relative energies of **4a** and **4b**.

The calculated structures and energies of isomers of [PtBrMe$_2$(CH$_2$Ph){(mim)$_2$CHMe}], as a model for complexes **13** and **14**, are shown in Figure 11. The *trans-syn* isomer, analogous to the observed structures of the derivatives **13** and **14**, is predicted to be most stable. The next in energy is the *cis-syn* isomer (Figure 11), which is calculated to be 9 kJ mol^{-1} higher in energy than the *trans-syn* isomer. Although the difference is not huge, if other factors such as solvation effects are equal, it would lead to an equilibrium constant of *ca*. 5 x 10^{-3}, whereas the analogous value for **4** (Figure 10) would be 0.2. Thus, the predictions of the DFT calculations are consistent with the experimental observations. For reasons outlined above, the *trans-syn* isomer (Figure 11) is also expected to be the product of kinetic control, so it is not surprising that it is the only isomer detected in formation of complexes **13** and **14**.

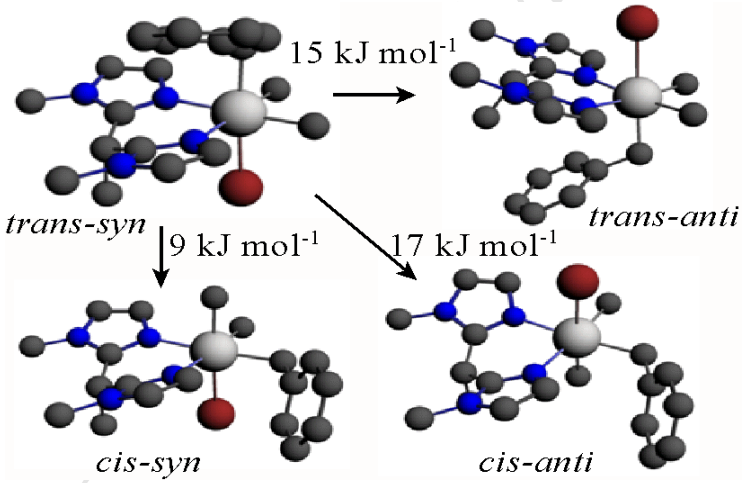


Figure 11. Calculated structures of isomers of the model complex [PtBrMe$_2$(CH$_2$Ph){(mim)$_2$CHMe}].

In conclusion, both the high reactivity of the complexes **1** and **2** towards oxidative addition, and differences in selectivity of the stereochemistry of oxidative addition between complexes **1** and **2**, can be understood in terms of a combination of electronic and differential steric effects.

4. Experimental

All reactions were carried out under nitrogen, either using Schlenk techniques or in a dry box, unless otherwise specified. NMR spectra were recorded using an Inova 400, Inova 600 or Mercury 400 spectrometer. Mass spectrometry studies were carried out using an electrospray PE-Sciex Mass Spectrometer (ESI MS), and a high resolution Finnigan MAT 8200 instrument. The complex $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ and ligands were prepared according to the literature [24,34]. DFT calculations were carried out using the ADF software, with the Becke-Perdew gradient-corrected exchange-correlation functional, double zeta basis set, and scalar relativistic correction. The calculations refer to the gas phase only, with no symmetry constraints used [47].

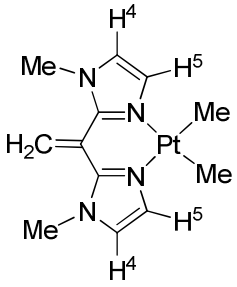


Chart 2. NMR labeling scheme

$[PtMe_2\{(mim)_2C{=}CH_2\}]$, 1. $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (0.4 g, 0.70 mmol) was added to a stirring solution of $(mim)_2C{=}CH_2$ (0.262 g, 1.40 mmol) in ether (15 mL). The product precipitated from solution as a light yellow solid. After 12 h. at 0°C, the mixture was filtered, and the product was washed with ether (6 mL) and pentane (6 mL), and then dried under high vacuum. It was purified by dissolution in the minimum volume of acetone, followed immediately by precipitation with pentane, then the product was separated and dried as above. Yield 81%. NMR in acetone-d_6: $\delta(^1H)$ = 0.53 (s, 6H, $^2J_{PtH}$ = 86 Hz, PtMe), 3.91 (s, 6H, NMe), 6.18 (s, 2H, $=CH_2$), 7.19 (d, 2H, $^3J_{HH}$ = 1 Hz, $^3J_{PtH}$ = 13 Hz, H^5), 7.23 (d, 2H, $^3J_{HH}$ = 1 Hz, H^4). Anal. Calcd. for $C_{12}H_{18}N_4Pt$: C, 34.87; H, 4.39; N, 13.55. Found: C, 34.51; H 4.46; N, 13.19%.

$[PtMe_2\{(mim)_2CHMe\}]$, 2. This was prepared similarly, and isolated as a yellow solid. Yield 83%. NMR in acetone-d_6: $\delta(^1H)$ = 0.49 (s, 6H, $^2J_{PtH}$ = 88 Hz, PtMe), 1.66 (d, 3H, $^3J_{HH}$ = 7 Hz, CMe), 3.82 (s, 6H, NMe), 4.64 (q, 1H, $^3J_{HH}$ = 7 Hz, CH), 7.03 (d, 2H, $^3J_{HH}$ = 2 Hz, H^4), 7.08 (d, 2H, $^3J_{HH}$ = 2 Hz, $^3J_{PtH}$ = 14 Hz, H^5). Anal. Calcd. for $C_{12}H_{20}N_4Pt$: C, 34.70; H, 4.85; N, 13.49. Found: C, 34.48; H, 5.02; N, 13.29%.

$[PtIMe_3\{(mim)_2C{=}CH_2\}]$, 3. To a solution of $[PtMe_2\{(mim)_2C{=}CH_2\}]$, **1**, (0.1 g, 0.24 mmol) in ether (10 mL) was added MeI (0.015 mL, 0.24 mmol). There was an immediate color change from yellow to white. The mixture was stirred for 4 h., then the white solid product which precipitated was separated, washed with pentane (3 x 1 mL) and ether (3 x 1 mL) and dried under high vacuum. Yield 65 %. NMR in CD_2Cl_2: $\delta(^1H)$ = 0.89 (s, 3H, $^2J_{PtH}$ = 74 Hz, PtMe), 1.30 (s, 6H, $^2J_{PtH}$ = 71 Hz, PtMe), 3.83 (s, 6H, NMe), 6.08 (s, 2H, $=CH_2$), 7.09 (d, 2H, $^3J_{HH}$ = 1 Hz, H^4), 7.41 (d, 2H, $^3J_{HH}$ = 1 Hz, $^3J_{PtH}$ = 9 Hz, H^5). Anal. Calcd. for $C_{13}H_{21}IN_4Pt$: C, 28.12; H, 3.81; N, 10.09. Found: C, 28.19; H, 4.15; N, 9.44%.

$[PtBr(CH_2Ph)Me_2\{(mim)_2C{=}CH_2\}]$, 4. To a solution of complex **1** (0.1 g, 0.24 mmol) in acetone (15 mL) was added benzyl bromide (0.04 g, 0.24 mmol). The mixture was stirred for 3 h., then the volume was reduced to 1 mL, and pentane (5 mL) was added to

precipitate the product as a white solid, which was separated, washed with ether and pentane (1 x 2 mL), and dried under high vacuum. Yield 82%. NMR in CD_2Cl_2: **4a**; $\delta(^1H)$ = 1.19 (s, 6H, $^2J_{PtH}$ = 71 Hz, PtMe), 2.99 (s, 2H, $^2J_{PtH}$ = 99 Hz, $PtCH_2$), 3.79 (s, 6H, NMe), 5.98 (s, 2H, $=CH_2$), 6.56 (d, 2H, $^3J_{HH}$ = 7 Hz, $^4J_{PtH}$ = 11 Hz, H^o), 6.81 (t, 2H, $^3J_{HH}$ = 7 Hz, H^m), 6.92 (t, 1H, $^3J_{HH}$ = 7 Hz, H^p), 6.94 (d, 2H, $^3J_{HH}$ = 2 Hz, H^4), 7.04 (d, 2H, $^3J_{HH}$ = 2 Hz, $^3J_{PtH}$ = 9 Hz, H^5); **4b**; δ = 0.79 (s, 3H, $^2J_{PtH}$ = 76 Hz, PtMe), 1.05 (s, 3H, $^2J_{PtH}$ = 71 Hz, PtMe), 3.61 (br, 2H, $^2J_{PtH}$ = 104 Hz, $PtCH_2$), 3.76 (s, 3H, NMe), 3.78 (s, 3H, NMe), 6.05, 6.06 (m, each 1H, $=CH_2$), 6.90-6.92 (m, 2H, H^4 and $H^{4'}$), 7.06-7.07 (m, 2H, H^5 and $H^{5'}$), 7.08 (d, 2H, $^3J_{HH}$ = 8 Hz, $^4J_{PtH}$ = 11 Hz, H^o), 7.30 (m, 3H, H^m, H^p). Anal. Calcd. for $C_{19}H_{25}BrN_4Pt$: C, 39.05; H, 4.31; N, 9.59. Found: C, 39.27; H, 4.37; N, 9.49%.

[PtBr($CH_2C_6H_4$-4-CF_3)Me_2{(mim)$_2$C=CH_2}], 5. This was prepared similarly and isolated as a white solid. Yield 80%. NMR in CD_2Cl_2: **5a**; $\delta(^1H)$ = 1.22 (s, 6H, $^2J_{PtH}$ = 70 Hz, PtMe), 3.03 (s, 2H, $^2J_{PtH}$ = 100 Hz, $PtCH_2$), 3.80 (s, 6H, NMe), 5.99 (s, 2H, $=CH_2$), 6.62 (d, 2H, $^3J_{HH}$ = 8 Hz, $^4J_{Pt\text{-}H}$ = 11 Hz, H^o), 6.95 (d, 2H, $^3J_{HH}$ = 1 Hz, H^4), 7.02 (d, 2H, $^3J_{HH}$ = 1 Hz, $^3J_{Pt\text{-}H}$ = 8 Hz, H^5), 7.07 (d, 2H, $^3J_{HH}$ = 8 Hz, H^m); **5b**; δ = 0.79 (s, 3H, $^2J_{PtH}$ = 74 Hz, PtMe), 1.00 (s, 3H, $^2J_{PtH}$ = 70 Hz, PtMe), 3.59 (d, 1H, $^2J_{HH}$ = 9 Hz, $^2J_{PtH}$ = 100 Hz, $PtCH_2$), 3.86 (d, 1H, $^2J_{HH}$ = 9 Hz, $^2J_{PtH}$ = 84 Hz, $PtCH_2$), 3.78 (s, 3H, NMe), 3.82 (s, 3H, NMe), 6.08, 6.09 (m, each 1H, $=CH_2$), 6.94-6.98 (m, 2H, H^4, $H^{4'}$), 7.04-7.07 (m, 2H, H^5, $H^{5'}$), 7.34 (d, 2H, $^3J_{HH}$ = 8 Hz, H^m), 7.43 (d, 2H, $^3J_{HH}$ = 8 Hz, $^4J_{PtH}$ = 11 Hz, H^o). Anal. Calcd. for $C_{20}H_{24}BrF_3N_4Pt$: C, 36.82; H, 3.71; N, 8.59. Found: C, 36.59; H, 3.60; N, 8.78%.

[PtBr($CH_2C_6H_4$-2-CF_3)Me_2{(mim)$_2$C=CH_2}], 6. This was prepared similarly and isolated as a white solid. Yield 81%. NMR in CD_2Cl_2: **6a**; $\delta(^1H)$ = 1.28 (s, 6H, $^2J_{PtH}$ = 70 Hz, PtMe), 3.25 (s, 2H, $^2J_{PtH}$ = 108 Hz, $PtCH_2$), 3.77 (s, 6H, NMe), 5.79 (s, 2H, $=CH_2$), 6.96 (d, 1H, $^3J_{HH}$ = 6 Hz, $^4J_{PtH}$ = 13 Hz, H^o), 6.99 (d, 2H, $^3J_{HH}$ = 1 Hz, H^4), 7.11 (d, 2H, $^3J_{HH}$ = 1 Hz, $^3J_{PtH}$ = 8 Hz, H^5), 7.15-7.18 (m, 3H, H^m, H^p); **6b**; δ = 0.76 (s, 3H, $^2J_{PtH}$ = 74 Hz, PtMe), 1.15 (s, 3H, $^2J_{PtH}$ = 70 Hz, PtMe), 3.69-3.70 (m, 2H, $PtCH_2$), 3.78 (s, 3H, NMe), 3.80 (s, 3H, NMe), 6.08, 6.10 (m, each 1H, $=CH_2$), 7.05-7.08 (m, 4H, H^4, $H^{4'}$, H^5, $H^{5'}$), 7.19-7.43 (m, 4H, C_6H_4). Anal. Calcd. for $C_{20}H_{24}BrF_3N_4Pt$: C, 36.82; H, 3.71; N, 8.59. Found: C, 36.93; H, 3.74; N, 8.55%.

[PtBr($CH_2C_6H_3$-3,5-*t*-Bu_2)Me_2{(mim)$_2$C=CH_2}], 7. This was prepared similarly and isolated as a white solid. Yield 83%. NMR in CD_2Cl_2: **7a**; $\delta(^1H)$ = 1.07 (s, 18H, *t*-Bu), 1.26 (s, 6H, $^2J_{PtH}$ = 71 Hz, PtMe), 2.99 (s, 2H, $^2J_{PtH}$ = 93 Hz, $PtCH_2$), 3.75 (s, 6H, NMe), 6.01 (s, 2H, $=CH_2$), 6.26 (d, 2H, $^4J_{HH}$ = 2 Hz, $^4J_{PtH}$ = 10 Hz, H^o), 6.87 (d, 2H, $^3J_{HH}$ = 2 Hz, H^4), 6.90 (t, 1H, $^4J_{HH}$ = 2 Hz, H^p), 6.95 (d, 2H, $^3J_{HH}$ = 2 Hz, $^3J_{PtH}$ = 7 Hz, H^5); **7b**; δ = 0.80 (s, 3H, $^2J_{PtH}$ = 76 Hz, PtMe), 1.06 (s, 18H, *t*-Bu), 1.14 (s, 3H, $^2J_{PtH}$ = 71 Hz, PtMe), 3.67 (b, 2H, Pt-CH_2), 3.74 (s, 3H, NMe), 3.79 (s, 3H, NMe), 6.03, 6.05 (m, each 1H, $=CH_2$), 7.04-7.11 (m, 4H, H^4, $H^{4'}$, H^5, $H^{5'}$), 7.18 (s, 2H, $^4J_{PtH}$ = 11 Hz, H^o), 7.29 (m, 1H, H^p). Anal. Calcd. for $C_{27}H_{41}BrN_4Pt$: C, 46.55; H, 5.93; N, 8.04. Found: C, 46.79; H, 5.71; N, 7.85%.

[Pt(OH)$_2$Me$_2${(mim)$_2$C=CH_2}], 8. To a solution of complex **1** (0.01 g, 0.02 mmol) in acetone (2 mL) was added excess H_2O_2 (0.1 mL). The product was isolated as a white solid by evaporation of the solvent, and was purified by precipitation from solution in minimum CH_2Cl_2 by addition of pentane. Yield: 45%. NMR in acetone-d_6: $\delta(^1H)$ = 1.36 (s, 6H, $^2J_{PtH}$ = 73 Hz, PtMe), 2.99 (br, 2H, OH), 3.98 (s, 6H, NMe), 6.21 (s, 2H, $=CH_2$),

7.25 (d, 2H, $^3J_{HH}$ = 1 Hz, H^4), 7.30 (d, 2H, $^3J_{HH}$ = 1 Hz, $^3J_{PtH}$ = 14 Hz, H^5). Anal. Calcd. for $C_{12}H_{20}N_4O_2Pt$: C, 32.22; H, 4.51; N, 12.52. Found: C, 32.07; H, 4.72; N, 12.28%.

[PtCl(CH$_2$Cl)Me$_2${(mim)$_2$C=CH$_2$}], 9. A solution of [PtMe$_2${(mim)$_2$C=CH$_2$}], **1** (0.05 g, 0.12 mmol) in CH_2Cl_2 (2 mL) was stirred for 2 days. The white product was obtained by precipitation with pentane, then separated, washed with pentane, and dried under high vacuum. Yield 78 %. NMR in CD_2Cl_2: **9a**; δ(^{1}H) = 1.12 (s, 6H, $^2J_{PtH}$ = 70 Hz, PtMe), 3.72 (s, 2H, $^2J_{PtH}$ = 56 Hz, PtCH$_2$), 3.84 (s, 6H, NMe), 6.11 (s, 2H, =CH$_2$), 7.15 (d, 2H, $^3J_{HH}$ = 2 Hz, $^3J_{PtH}$ = 9 Hz, H^5), 7.20 (d, 2H, $^3J_{HH}$ = 2 Hz, H^4); **9b**; δ = 0.89 (s, 3H, $^2J_{PtH}$ = 74 Hz, PtMe), 1.13 (s, 3H, $^2J_{PtH}$ = 69 Hz, PtMe), 3.80 (s, 3H, NMe), 3.81 (s, 3H, NMe), 4.13 (m, 1H, $^2J_{PtH}$ = 45 Hz, PtCH$_2$Cl), 4.60 (m, 1H, $^2J_{PtH}$ = 88 Hz, PtCH$_2$Cl), 6.09, 6.10 (m, each 1H, =CH$_2$), 7.07 (br, 2H, H^4, $H^{4'}$), 7.27 (d, 1H, $^3J_{HH}$ = 2 Hz, $^3J_{PtH}$ = 12 Hz, H^5), 7.50 (d, 1H, $^3J_{HH}$ = 2 Hz, $^3J_{PtH}$ = 6 Hz, $H^{5'}$). Anal. Calcd. for $C_{13}H_{20}Cl_2N_4Pt$: C, 29.25; H, 3.90; N, 10.25. Found: C, 29.24; H, 3.86; N, 10.23%.

[PtI$_2$Me$_2${(mim)$_2$CHMe}], 10. To a solution of [PtMe$_2${(mim)$_2$CHMe}], (0.14 g, 3.3 mmol) in acetone (10 mL) was added iodine (0.085 g) dissolved in acetone (5 mL). After 30 min., the solvent was removed and the orange product was purified by precipitation from minimum CH_2Cl_2 by addition of pentane, then separated, washed with pentane, and dried under vacuum. Yield 63%. NMR in CD_2Cl_2: δ(^{1}H) = 1.89 (d, 3H, $^3J_{HH}$ = 7 Hz, CMe), 2.32 (s, 6H, $^2J_{PtH}$ = 71 Hz, PtMe), 3.87 (s, 6H, NMe), 4.64 (q, 1H, $^3J_{HH}$ = 7 Hz, CH), 7.08 (d, 2H, $^3J_{HH}$ = 2 Hz, H^4), 7.26 (d, 2H, $^3J_{HH}$ = 2 Hz, $^3J_{PtH}$ = 9 Hz, H^5). Anal. Calcd. for $C_{12}H_{20}I_2N_4Pt$: C, 21.54; H, 3.01; N, 8.37. Found: C, 21.21; H, 2.96; N, 8.05%.

[Pt(OH)$_2$Me$_2${(mim)$_2$CHMe}], 11. This was prepared in a similar way as complex **8**, but using complex **2**. Yield 55%. NMR in acetone-d_6: δ(^{1}H) = 1.37 (s, 6H, $^2J_{PtH}$ = 73 Hz, PtMe), 1.80 (d, 3H, $^3J_{HH}$ = 7 Hz, CMe), 3.92 (s, 6H, NMe), 4.80 (q, 1H, $^3J_{HH}$ = 7 Hz, CH), 7.17 (d, 2H, $^3J_{HH}$ = 2 Hz, $^3J_{PtH}$ = 10 Hz, H^5), 7.19 (d, 2H, $^3J_{HH}$ = 2 Hz, H^4). Anal. Calcd. for $C_{12}H_{22}N_4O_2Pt$: C, 32.07; H, 4.93; N, 12.47. Found: C, 32.28; H, 4.69; N, 12.25%.

[PtIMe$_3${(mim)$_2$CHMe}], 12, This was prepared similarly to complex **3** but using complex **2**, and isolated as a white solid. Yield 79%. ^{1}H-NMR in CD_2Cl_2: (**4.13a**) δ = 0.93 (s, 3H, $^2J_{Pt\text{-}H}$ = 75 Hz, Pt-CH$_3$), 1.32 (s, 6H, $^2J_{Pt\text{-}H}$ = 70 Hz, Pt-CH$_3$), 1.55 (d, 3H, $^3J_{H\text{-}H}$ = 8 Hz, CCH$_3$), 3.75 (s, 6H, N-CH$_3$), 4.45 (q, 1H, $^3J_{H\text{-}H}$ = 8 Hz, C-H), 7.01 (d, 2H, $^3J_{H\text{-}H}$ = 2 Hz, Im{H^2 and $H^{2'}$}), 7.38 (d, 2H, $^3J_{H\text{-}H}$ = 2 Hz, $^3J_{Pt\text{-}H}$ = 10 Hz, Im{H^1 and $H^{1'}$}); (**4.13b**) δ = 0.70 (s, 3H, $^2J_{Pt\text{-}H}$ = 74 Hz, Pt-CH$_3$), 1.37 (s, 6H, $^2J_{Pt\text{-}H}$ = 70 Hz, Pt-CH$_3$), 1.94 (d, 3H, $^3J_{H\text{-}H}$ = 7 Hz, CCH$_3$), 3.74 (s, 6H, N-CH$_3$), 4.49 (q, 1H, $^3J_{H\text{-}H}$ = 7 Hz, C-H), 6.99 (d, 2H, $^3J_{H\text{-}H}$ = 2 Hz, Im{H^2 and $H^{2'}$}), 7.20 (d, 2H, $^3J_{H\text{-}H}$ = 2 Hz, $^3J_{Pt\text{-}H}$ = 11 Hz, Im{H^1 and $H^{1'}$}). Anal. Calcd. for $C_{13}H_{23}IN_4Pt$ (%): C, 28.02; H, 4.16; N, 10.05. Found: C, 28.29; H, 3.97; N, 9.77%.

[PtBr(CH$_2$C$_6$H$_4$-4-CF$_3$)Me$_2${(mim)$_2$CHMe}], 13. This was prepared similarly to complex **5** but using complex **2**, and isolated as a white solid. Yield 79 %. NMR CD_2Cl_2: δ(^{1}H) = 1.34 (s, 6H, $^2J_{PtH}$ = 69 Hz, PtMe), 1.73 (d, 3H, $^3J_{HH}$ = 8 Hz, CMe), 2.87 (s, 2H, $^2J_{PtH}$ = 97 Hz, Pt-CH$_2$), 3.66 (s, 6H, NMe), 4.18 (q, 1H, $^3J_{HH}$ = 8 Hz, CH), 6.36 (d, 2H, $^3J_{HH}$ = 8 Hz, $^4J_{PtH}$ = 11 Hz, H^o), 6.84 (d, 2H, $^3J_{HH}$ = 2 Hz, H^4), 6.93 (d, 2H, $^3J_{HH}$ = 8 Hz, H^m), 7.02 (d, 2H, $^3J_{HH}$ = 2 Hz, $^3J_{PtH}$ = 7 Hz, H^5). Anal. Calcd. for $C_{20}H_{26}BrF_3N_4Pt$: C, 36.71; H, 4.00; N, 8.56. Found: C, 36.65; H, 3.84; N, 8.31%.

[PtBr(CH$_2$C$_6$H$_4$-2-CF$_3$)Me$_2${(mim)$_2$CHMe}], 14. This was prepared similarly to complex **6** but using complex **2**, and isolated as a white solid. Yield 81%. NMR in

CD_2Cl_2: δ(^{1}H) = 1.34 (s, 6H, $^2J_{PtH}$ = 69 Hz, PtMe), 1.86 (d, 3H, $^3J_{HH}$ = 7 Hz, CMe), 3.11 (s, 2H, $^2J_{PtH}$ = 104 Hz, $PtCH_2$), 3.69 (s, 6H, NMe), 4.32 (q, 1H, $^3J_{HH}$ = 7 Hz, CH), 6.71 (m, 1H, H^o), 6.78 (d, 2H, $^3J_{HH}$ = 1 Hz, H^4), 6.81 (d, 2H, $^3J_{HH}$ = 1 Hz, $^3J_{PtH}$ = 7 Hz, H^5), 7.01-7.08 (m, 3H, H^mH^p). Anal. Calcd. for $C_{20}H_{26}BrF_3N_4Pt$: C, 36.71; H, 4.00; N, 8.56. Found: C, 36.54; H, 3.73; N, 8.81%.

X-ray Structure Determinations: In a typical experiment, a sample was mounted on a Mitegen polyimide micromount with Paratone N oil. All X-ray measurements were made using a Bruker Kappa Axis Apex2 diffractometer at a temperature of 150 K. The structure was solved by direct methods. The hydrogen atoms for the main molecule were introduced at idealized positions and were allowed to refine isotropically. The structural model was fit to the data using full matrix least-squares based on F^2. The structure was refined using SHELXL [48]. Data are given in Table 2 and in the CIF files (CCDC 984275-984279). Complex **3** contained a dichloromethane solvate molecule which appeared to be disordered, but this disorder could not be resolved. Complex **7** contained a solvent accessible void of 487 $Å^3$, but the solvent molecules were poorly defined, and the electron density was modelled by using SQUEEZE; there was also some unresolved disorder of the benzyl substituents.

Table 2. Crystal and refinement data for the complexes.

Complex	$\mathbf{3}_2.CH_2Cl_2$	$\mathbf{4}.0.5CH_2Cl_2$	**6**	**7**	**14**
Formula	$C_{27}H_{44}Cl_2I_2N_8Pt_2$	$C_{19.5}H_{26}BrClN_4Pt$	$C_{20}H_{24}BrF_3N_4Pt$	$C_{27}H_{41}BrN_4Pt$	$C_{20}H_{26}BrF_3N_4Pt$
fw	1195.58	626.89	652.43	696.62	654.45
λ / Å	0.71073	0.71073	0.71073	0.71073	0.71073
T / K	150	150	150	150	150
Cryst.syst.	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
Sp.gp.	$P2_1/m$	C2/c	$P2_1/c$	Pbcn	$P2_1/c$
a / Å	16.424(1)	21.034(1)	10.8308(4)	30.038(2)	10.6274(7)
b / Å	13.052(1)	16.738(1)	16.8547(5)	16.554(1)	16.5446(1)
c / Å	16.649(1)	12.754(1)	12.5852(4)	12.574(1)	12.9666(9)
α /°	90	90	90	90	90
β /°	96.088(2)	110.303(3)	105.87(1)	90	105.737(2)
γ /°	90	90	90	90	90
V / $Å^3$	3548.9(3)	4211.2(4)	2209.9(1)	6252.4(8)	2194.4(3)
Z	4	8	4	8	4
$d_{c.}$ /Mg m^{-3}	2.238	1.978	1.961	1.585	1.981
μ / mm^{-1}	9.796	8.700	8.196	5.802	8.254
$R_1(I>2\sigma I)$	0.0504	0.0499	0.0350	0.0514	0.0310
wR_2(all)	0.1154	0.1241	0.0900	0.0867	0.0579

Supporting Materials

X-ray data in electronic CIF format (CCDC 984275-984279).

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References

[1] L.M. Rendina, R.J. Puddephatt, Chem. Rev. 97 (1997) 1735.

[2] M. Lersch, M. Tilset, Chem. Rev. 105 (2005) 2471.

[3] F. Zhang, C.W. Kirby, D.W. Hairsine, M.C. Jennings, R.J. Puddephatt, J. Am. Chem. Soc. 127 (2005) 14190.
[4] F. Zhang, M.E. Broczkowski, M.C. Jennings, R.J. Puddephatt, Canad. J. Chem. 83 (2005) 595.
[5] A.J. Hickman, J.M. Villalobos, M.S. Sanford, Organometallics 28 (2009) 5316.
[6] B.A. McKeown, H.E. Gonzalez, M.R. Friedfeld, T.B. Gunnoe, T.R. Cundari, M. Sabat, J. Am. Chem. Soc. 133 (2011) 19131.
[7] B.A. McKeown, H.E. Gonzalez, T.B. Gunnoe, T.R. Cundari, M. Sabat, A.C.S. Catalysis 3 (2013) 1165.
[8] B.A. McKeown, H.E. Gonzalez, T. Michaelos, T.B. Gunnoe, T.R. Cundari, R.H. Crabtree, M. Sabat, Organometallics 32 (2013) 3903.
[9] F. Zhang, E.M. Prokopchuk, M.E. Broczkowski, M.C. Jennings, R.J. Puddephatt, Organometallics 25 (2006) 1583.
[10] S. Achar, R.J. Puddephatt, Angew. Chem. Int. Ed. Engl. 33 (1994) 847.
[11] J. Kuyper, Inorg. Chem. 17 (1978) 1458.
[12] R.P. Hughes, R.B. Laritchev, L.N. Zakharov, A.L. Rheingold, Organometallics 24 (2005) 4845.
[13] M.A. Safa, A. Abo-Amer, A. Borecki, B.F.T. Cooper, R.J. Puddephatt, Organometallics 31 (2012) 2675.
[14] M. Crespo, Organometallics 31 (2012) 1216.
[15] B.Z. Momeni, M. Rashidi, M.M. Jafari, B.O. Patrick, A.S. Abd-el-Aziz, J. Organomet. Chem. 700 (2012) 83.
[16] R.J. Puddephatt, Coord. Chem. Rev. 219 (2001) 157.
[17] A.J. Canty, M.G. Gardiner, R.C. Jones, T. Rodemann, M. Sharma, J. Am. Chem. Soc. 131 (2009) 7236.
[18] S.M. Nabavizadeh, F.N. Hosseini, N. Nejabat, Z. Parsat, Inorg. Chem. 52 (2013) 13480.
[19] H.C. Clark, R.J. Puddephatt, Inorg. Chem. 10 (1971) 18.
[20] M.D. Aseman, M. Rashidi, S.M. Nabavizadeh, R.J. Puddephatt, Organometallics 32 (2013) 2593.
[21] E. Traversa, J.L. Templeton, H.Y. Cheng, M.M. Beromi, P.S. White, N.M. West, Organometallics 32 (2013) 1938.
[22] P.K. Monaghan, R.J. Puddephatt, J. Chem. Soc. Dalton Trans. (1988) 595.
[23] K.-T. Aye, A.J. Canty, M. Crespo, R.J. Puddephatt, J.D. Scott, A.A. Watson, Organometallics 8 (1989) 1518.
[24] P.K. Byers, A.J. Canty, Organometallics, 9 (1990) 210.
[25] X.-Y. Zhang, K. Ding, H.-B. Song, L.-F. Tang, Chinese J. Inorg. Chem. 26 (2010) 1.
[26] M.P. Batten, A.J. Canty, K.J. Cavell, T. Ruther, B.W. Skelton, A.H. White, Inorg. Chim. Acta 359 (2006) 1710.
[27] C.T. Burns, H. Shen, R.F. Jordan, J. Organomet. Chem. 683 (2003) 240.
[28] B.A. Messerle, V.A. Tolhurst, P. Turner, Eur. J. Inorg. Chem. (2003) 293.
[29] S. Elgafi, L.D. Field, B.A. Messerle, P. Turner, T.W. Hambley, J. Organomet. Chem. 588 (1999) 69.
[30] S. Elgafi, L.D. Field, B.A. Messerle, T.W. Hambley, P. Turner, J. Chem. Soc. Dalton Trans. (1997) 2341.
[31] A.J. Canty, P.R. Traill, B.W. Skelton, A.H. White, Inorg. Chim. Acta 255 (1997) 117.
[32] H.J. Korte, B. Krebs, C.G. van Kralingen, A.T.M. Marcelis, J. Reedijk, Inorg.

Chim. Acta 52 (1981) 61.
[33] A.T.M. Marcelis, C.G. van Kralingen, J. Opschoor, J. Reedijk, Rec. Trav. Chim. Pays Bas 99 (1980) 198.
[34] J.D. Scott, R.J. Puddephatt, Organometallics 2 (1983) 1643.
[35] M. Crespo, R.J. Puddephatt, Organometallics 6 (1987) 2548.
[36] M. Rashidi, S.M. Nabavizadeh, A. Akbari, S. Habibzadeh, Organometallics 24 (2005) 2528.
[37] K.T. Aye, J.J. Vittal, R.J. Puddephatt, J. Chem. Soc., Dalton Trans., (1993) 1835.
[38] K. Thorshaug, I. Fjeldahl, C. Romming, M. Tilset, J. Chem. Soc., Dalton Trans., (2003) 4051.
[39] E.M. Prokopchuk, R.J. Puddephatt, Canad. J. Chem. 81 (2003) 476.
[40] K.R. Pellarin, M.S. McCready, R.J. Puddephatt, Organometallics 31 (2012) 6388.
[41] A. Abo-Amer, M.S. McCready, F. Zhang, R.J. Puddephatt, Canad. J. Chem. 90 (2012) 46.
[42] A.G. Algarra, P. Braunstein, S.A. Macgregor, Dalton Trans. 42 (2013) 4208.
[43] 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.
[44] K.A. Grice, M.L. Scheuermann, K.I. Goldberg, Topics Organomet. Chem. 35 (2011) 1.
[45] R.J. Puddephatt, Angew. Chem. Int. Ed. 41 (2002) 261.
[46] M. Safa, M.C. Jennings, R.J. Puddephatt, Organometallics 31 (2012) 3539.
[47] 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.
[48] G.M. Sheldrick, Acta Cryst. A64 (2008) 112.

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Synopsis

The bis(N-methylimidazol-2-yl) ligands, $(mim)_2C=CH_2$ or $(mim)_2CHMe$, promote oxidative addition chemistry in their dimethylplatinum(II) complexes.

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