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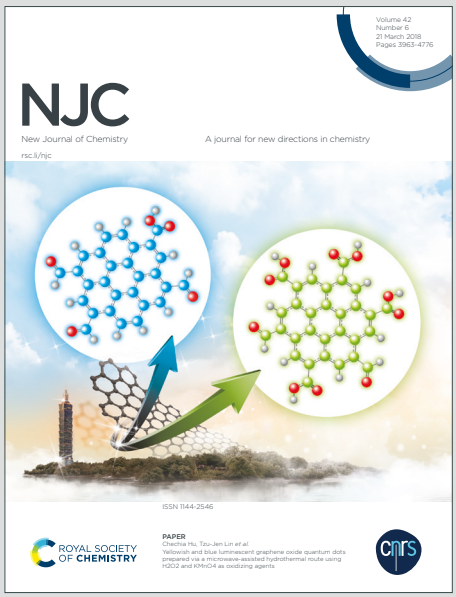

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Reactions of organoplatinum complexes with dimethylamine-borane

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Dedicated to Todd Marder for his outstanding contributions to organometallic chemistry

Abstract

The reactions of dimethylamine-borane with platinum(II) or platinum(IV) triflate complexes gave, not the anticipated σ-complexes, but the respective hydridoplatinum complexes. The reaction with [Pt(OTf)Me_3(NN)], with NN = 2,2'-bipyridine (bipy) and 4,4'-di-*t*-butyl-2,2'-bipyridine (bu_2bipy), gave the rare stable bridging hydridoplatinum(IV) complexes [μ-H{$PtMe_3$(NN)}$_2$][OTf] and the reaction with [Pt(O_2CCF_3)Me(NN)] gave the unstable hydridoplatinum(II) complex [PtHMe(NN)]. The unstable hydridoplatinum(II) complexes could be trapped by reaction with methyl acrylate by forming the insertion products [PtCl(CHMeCO_2Me)(bipy)] and [Pt(CHMeCO_2Me)$_2$(bipy)]. The complex [PtCl(CHMeCO_2Me)(bipy)] reacted with methyl iodide to give [PtClIMe(CHMeCO_2Me)(bipy)], by *cis* oxidative addition, and the presence of two chiral centers in the product platinum(IV) complex allowed a detailed stereochemical pathway to be proposed.

Introduction

The work described in this paper was stimulated by a perusal of the literature of topics of great current interest, namely alkane activation, hydrogen storage and borane chemistry. Todd Marder has made major contributions to all of them.[1]

The activation of C-H bonds is important for functionalization of alkanes, such as in the oxidation of methane to methanol for use as a clean, transportable energy source in fuel cells and for many other applications in the chemical industry.[1-3] The C-H bond activation step can be effected at a platinum(II) center and is thought to occur by formation of a C-H σ-complex, ***A***, followed by oxidative addition and further reactions of the alkyl(hydrido)platinum(IV) intermediate ***B*** (Scheme 1).[1-12] There is good indirect evidence for this mechanism but simple alkane σ-complexes of platinum, ***A***, have proved to be elusive,[4-14] although several are known with other metal centers.[15-21]

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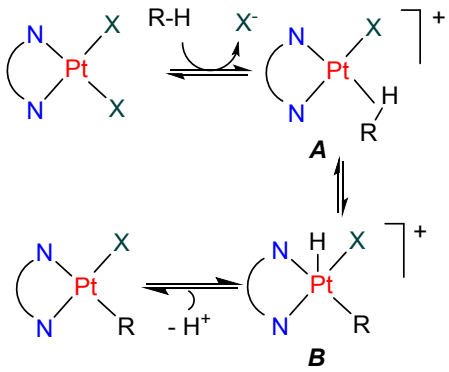

Scheme 1. Activation of alkanes at platinum(II) centers (NN is typically a diamine, bis(pyridyl) or bipyrimidine ligand).

The amine complexes of borane are of interest for hydrogen storage as well as for making boron-nitrogen polymers and materials.[22-26] Thus, for example, the reversible catalytic reaction of dimethylamine-borane to give dihydrogen and $(H_2B\text{-}NMe_2)_2$ can potentially be used for storage and regeneration of dihydrogen for use in fuel cells.[27] The amine-boranes, with more polar BH bonds, form many σ-complexes, including monohapto, ***C***, and dihapto, ***D*** and ***E***, derivatives and the dehydrogenated derivatives can also form σ-complexes, such as ***E*** (Chart 1).[22-26,28-30]

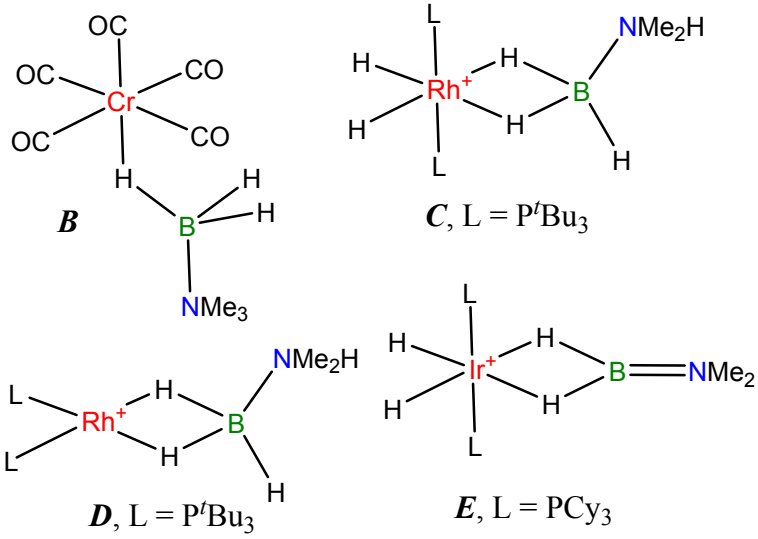

Chart 1. Some borane σ-complexes.

Since amine-boranes and alkanes are isoelectronic, it seemed possible that amine-borane complexes of platinum might be obtained and that they could act as models for the elusive alkane complexes ***A*** (Scheme 1). There is one recent report that a bis(carbene) organoplatinum complex

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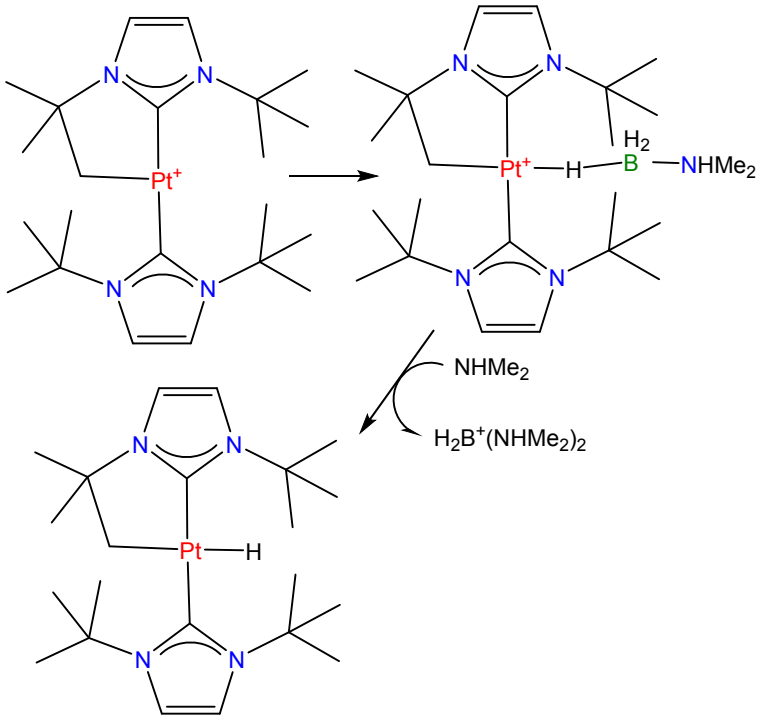
can act as a catalyst for dehydrogenation of dimethylamine-borane by a mechanism involving a σ-complex, and then a platinum hydride and a boronium salt intermediate (Scheme 2).[31]



Scheme 2. Reactions of an organoplatinum complex with dimethylamine-borane.

Results and discussion

The platinum complexes used as reagents in this work are shown in Scheme 3. Most are known compounds,[32-40] but **2a** and **3a** are reported for the first time, and the reactions with dimethylamine-borane are described below. The 2,2'-bipyridine (bipy) and 4,4'-di-*t*-butyl-2,2'-bipyridine (bu_2bipy) ligands were chosen so as to provide a direct analogy with the proposed alkane intermediates of Scheme 1.

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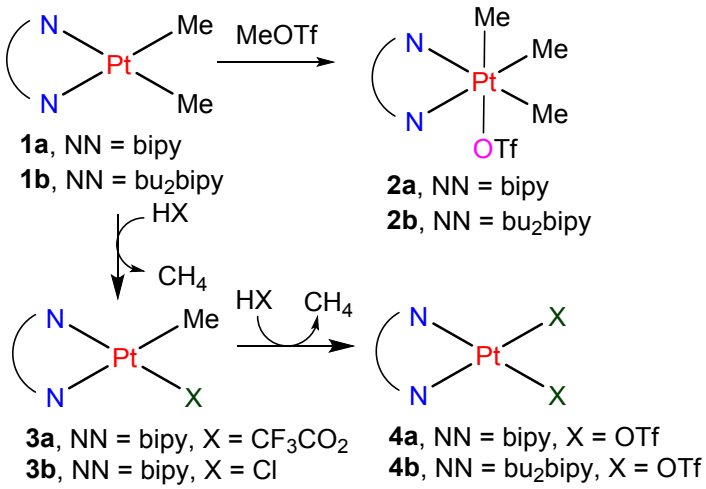

Scheme 3. Synthesis of the platinum complexes (bu_2bipy = 4,4'-di-*t*-butyl-2,2'-bipyridine).

The reactions of the platinum(IV) complexes **2a** and **2b** with $H_3B.NHMe_2$ are shown in Scheme 4. The triflate anion in **2a** or **2b** is easily displaced and the observed products **5** and **6** appear to be formed by a competition between hydride transfer from boron to platinum, presumably to give initially $BH_2(OTf)(NHMe_2)$, and reaction with $NHMe_2$, formed by dissociation from $H_3B.NHMe_2$ or $BH_2(OTf)(NHMe_2)$. Complex **5b** is a known compound, formed by reaction of **2b** with $Na[BH_4]$, and it was readily identified by its characteristic ^1H NMR spectrum.[34,35] It was not possible to separate complexes **5** and **6** and they were identified by comparison of the ^1H NMR spectra with those of authentic samples. Thus, the new complex **5a** was prepared by reaction of **2a** with $Na[BH_4]$, while **6a** and **6b** were prepared by reaction of **2a** and **2b** respectively with $NHMe_2$. In its ^1H NMR spectrum, complex **5a** gave two methylplatinum resonances at δ 0.88 [d, 12H, ^3J(HH) = 1 Hz, ^2J(PtH) = 70 Hz] and 0.13 [d, 6H, ^3J(HH) = 1 Hz, ^2J(PtH) = 65 Hz] for the methylplatinum groups *trans* to nitrogen or hydrogen respectively, each appearing as a barely resolved doublet due to coupling to the bridging hydride. The bridging hydride gave a resonance at δ -11.72 [s, 1H, ^1J(PtH) = 447 Hz], and the appearance as a 1:8:18:8:1 quintet proves the presence of the $Pt_2(\mu$-H) group, as discussed previously for complex **5b**.[35] The ^1H NMR spectrum of complex **6a** contained, as well as the expected resonances for the bipyridine and methylplatinum groups, a broad resonance at δ 3.12 for the NH proton and a doublet resonance at δ 2.06 [^3J(HH) = 6 Hz, ^3J(PtH) = 13 Hz] for the methylnitrogen groups of the coordinated dimethylamine group. The products **5** and **6** (Scheme 4) appear to be formed in competition with each other, and the ratio varied in different

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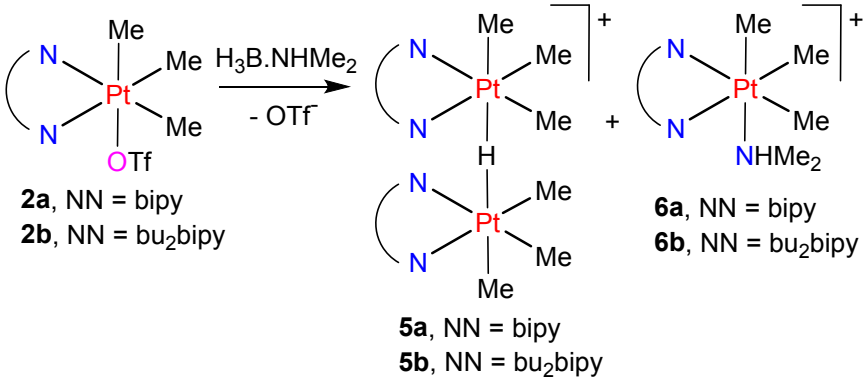
experiments. No σ-complex was detected by NMR during the course of reaction so, if formed, it must be shortlived, and no pure boron product could be identified.



2a, NN = bipy
2b, NN = bu_2bipy

6a, NN = bipy
6b, NN = bu_2bipy

5a, NN = bipy
5b, NN = bu_2bipy

Scheme 4. Reactions of organoplatinum(IV) complexes with $H_3B.NHMe_2$. The products are formed as the triflate salts.

The methylplatinum(II) complex **3a** reacted with dimethylamine-borane in $CDCl_3$ solution to give a mixture of products, including **3b**, platinum black, free 2,2'-bipyridine and methane (Scheme 5). In the early stages of reaction a hydridoplatinum(II) complex identified as [PtHMe(bipy)], **7**, was formed. It was partly characterized by a hydride resonance at δ = -16.5 [^1J(PtH) = 1546 Hz] and a methylplatinum resonance at δ = 0.98 [^2J(PtH) = 80 Hz], with coupling constants in the expected ranges for platinum(II) complexes.[38-41] As complex **7** decayed, resonances for **3b**, methane and free 2,2'-bipyridine were observed. No B-H resonances were observed in the ^{1}H NMR spectrum, so the nature of the boron-containing products is unknown, but free dimethylamine was present. It seems that **7** can either react with chloroform to give **3b** or undergo reductive elimination of methane to give platinum and 2,2'-bipyridine. The analogous complex [PtHMe(bu_2bipy)] has been generated as a shortlived complex by the platinum catalyzed reaction of [PtMe(NHPh)(bu_2bipy)] with dihydrogen. It has similar spectroscopic properties as complex **7** and decomposes in a similar way to give platinum, methane and bu_2bipy.[42]

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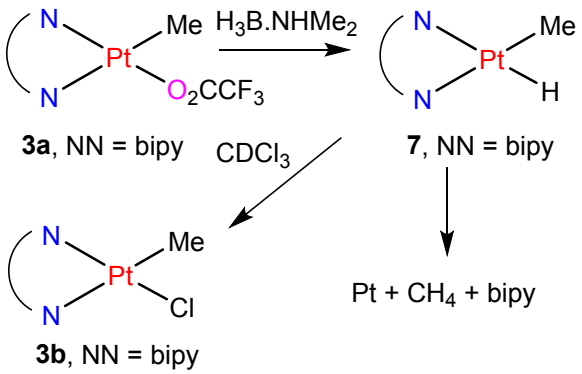

Scheme 5. Reaction of complex **3a** with dimethylamine-borane.

Because the hydride complex **7** was thermally unstable, some reactions in the presence of unsaturated reagents were carried out, with the aim of trapping the hydride as an insertion product. The most successful reactions were with methyl acrylate. An initial reaction of complex **3a** with dimethylamine-borane and methyl acrylate in chloroform solution gave a product mixture containing **3b**, [PtCl(CHMeCO$_2$Me)(bipy)], **8**, as major products along with [Pt(O$_2$CCF$_3$)(CHMeCO$_2$Me)(bipy)], **9**, as minor product (Scheme 6). Complex **9** was converted to **8** by treatment of the mixture with LiCl, and then the products **3b** and **8** were separated by thin layer chromatography. We had expected that the trapping experiment would give [PtMe(CHMeCO$_2$Me)(bipy)] by insertion of methyl acrylate into the Pt-H bond of complex **7**, but no evidence for this complex was found. Methane was identified as a product by its ^{1}H NMR spectrum, and so it seems that further reaction with dimethylamine-borane occurs during the methyl acrylate insertion. Because there is no change in oxidation state of the platinum center, this reaction should involve dihydrogen transfer from dimethylamine-borane to convert the PtMe group to PtH and CH$_4$. The insertion of alkenes into the platinum-hydride bond is known to occur after partial or complete ligand displacement, and it is possible that the methylplatinum bond is cleaved at this stage.[43-48] Complex **8** is characterized in the ^{1}H NMR spectrum by quartet and doublet resonances at δ 4.10 [q, 1H, ^3J(HH) = 7 Hz] and 1.25 [d, 3H, ^3J(HH) = 7 Hz, ^3J(PtH) = 50 Hz, PtC*Me*] for the PtC*H* and PtC*Me* groups, and a singlet at δ 3.64 for the CO$_2$Me group. The PtCHMeCO$_2$Me group is chiral, and so complex **8** exists as a racemic mixture of *R* and *S* enantiomers.

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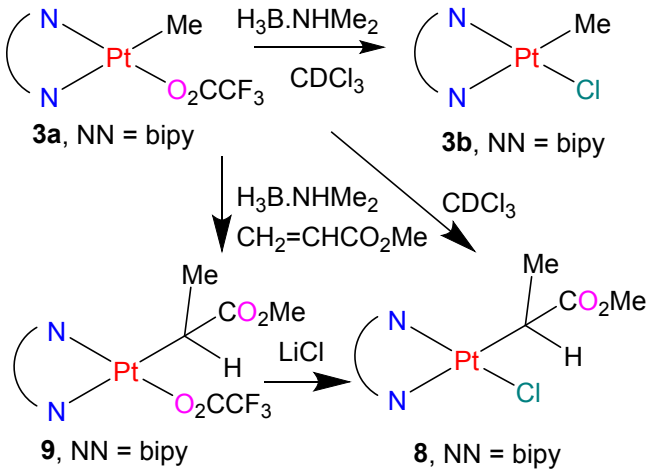

Scheme 6. Trapping with methyl acrylate in $CDCl_3$ solution.

The reactions of Scheme 6 clearly show the involvement of the chlorinated solvent in the products **3b** and **8** and so, to avoid this complication, the reaction was also carried out in benzene solution. In this case, the major product was the double insertion product $[Pt(CHMeCO_2Me)_2(bipy)]$, formed as an almost equimolar mixture of the meso and racemic isomers **10a** and **10b**, which could not be separated by TLC (Scheme 7). Again, none of the anticipated product $[PtMe(CHMeCO_2Me)(bipy)]$ was detected but methane was formed and identified by its ^1H NMR spectrum when the reaction was carried out in C_6D_6. All of the ^1H NMR resonances for the $CHMe(CO_2Me)$ groups of the isomers **10a** and **10b** were resolved, though they could not be assigned to a specific isomer, but only the H^6 resonances of the 2,2'-bipyridine groups were resolved, the chemical shifts for the resonances H^3-H^5 being accidentally degenerate for the *meso* and *rac* diastereomers. The same products **10a** and **10b** were formed by reaction of $[Pt(OTf)_2(bipy)]$, **4a**, with dimethylamine-borane in benzene solution.

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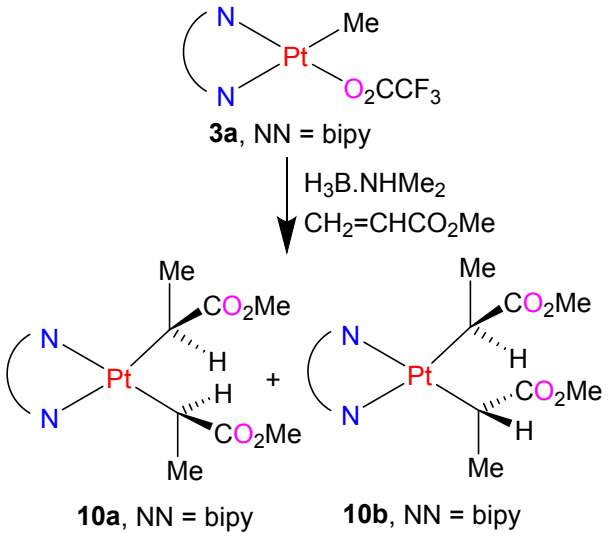

Scheme 7. Trapping in benzene solution, with formation of complexes *meso*-**10a** and *rac*-**10b** (represented as the *S*,*S* enantiomer).

We have not been able to grow crystals of **8** or **10** suitable for structure determination, so platinum(IV) derivatives were studied. The oxidative addition of methyl iodide to complex **8** gave the new platinum(IV) complex [PtClIMe(CHMeCO$_2$Me)(bipy)], **11**, which was formed as a mixture of two diastereomers, suggested to be **11a** and **11b**, in a ratio of approximately 3:2 (Scheme 8). Each diastereomer gave well resolved resonances for the PtCHMeCO$_2$Me protons, and new resonances for the methylplatinum groups of **11a** and **11b** at δ 2.29, ^2J(PtH) = 70 Hz, and 2.44, ^2J(PtH) = 67 Hz, respectively. The diastereomers arise because there are chiral centers at both tetrahedral carbon (*R*,*S*) and octahedral platinum (*C*,*A*) in **11** and so the *R*,*A*/*S*,*C* and *R*,*C*/*S*,*A* isomers, **11a** and **11b** respectively, give different NMR spectra. The downfield shifts of the methylplatinum resonances and upfield shifts of the PtCMe resonances indicate that the MePt groups are equatorial and the PtCHMeCO$_2$Me groups axial with respect to the bipy ligand in both diastereomers, in support of the assigned stereochemistries. The diastereomers were separated by recrystallization and the structure of **11a** was determined crystallographically (Figure 1). The lattice contains both *R*,*A* and *S*,*C* enantiomers, which are related by a crystallographic inversion center (Figure 1).

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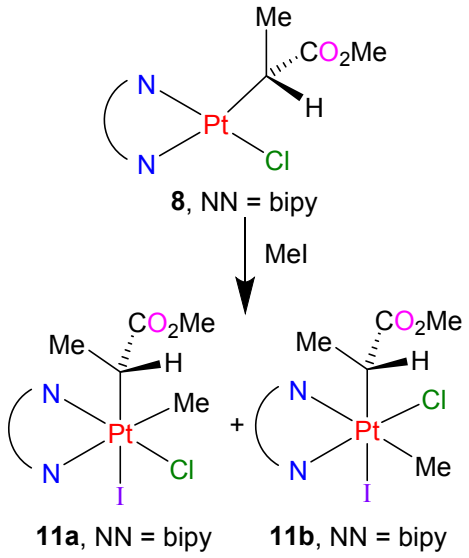

Scheme 8. Oxidative addition of methyl iodide to complex **8**. Complexes **11a** and **11b** are represented as the *R,A* and *R,C* enantiomers respectively.

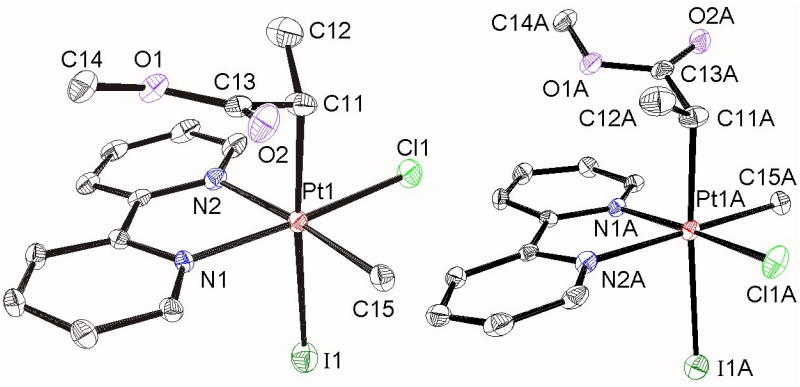

Figure 1. The structure of complex **11a**; left, the *S,C* enantiomer and, right, the *R,A* enantiomer. Selected bond distances: Pt(1)N(1) 2.046(9); Pt(1)N(2) 2.160(10); Pt(1)C(11) 2.132(13); Pt(1)C(15) 2.123(11); Pt(1)Cl(1) 2.295(3); Pt(1)I(1) 2.7284(11) Å. Selected bond angles: N(1)Pt(1)N(2) 78.3(4); C(15)Pt(1)Cl(1) 87.9(3); C(11)Pt(1)I(1) 176.2(4) °.

The bond distances and angles in **11a** are unexceptional, but it is noteworthy that the methyl and iodide ligands are mutually *cis* in **11a** while most oxidative addition reactions of methyl iodide to platinum(II) complexes occur with *trans* stereochemistry.[49-51] In order to understand the reasons for this, DFT calculations (see experimental for details) were carried out on some of the many possible isomers (there are 24 potential isomers counting all diastereomers and enantiomers). The calculated structures of the observed isomers **11a** and **11b** and the expected isomers of *trans* oxidative addition, **11c** and **11d**, along with their relative energies, are

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shown in Figure 2. The isomer **11a**, the one which was structurally characterized (Fig. 1), is calculated to be most stable. The R-Pt-I units (R = $CHMeCO_2Me$) in **11a** and **11b** are calculated to be essentially linear, whereas the MePtI units in **11c** and **11d** are significantly distorted from linearity (Fig. 2). This indicates that the relative stability of the isomers is mostly determined by steric effects, and that **11a** and **11b** are favored because the bulkier ligands $CHMeCO_2Me$ and iodide are in the axial positions and the smaller chloride and methyl ligands equatorial.

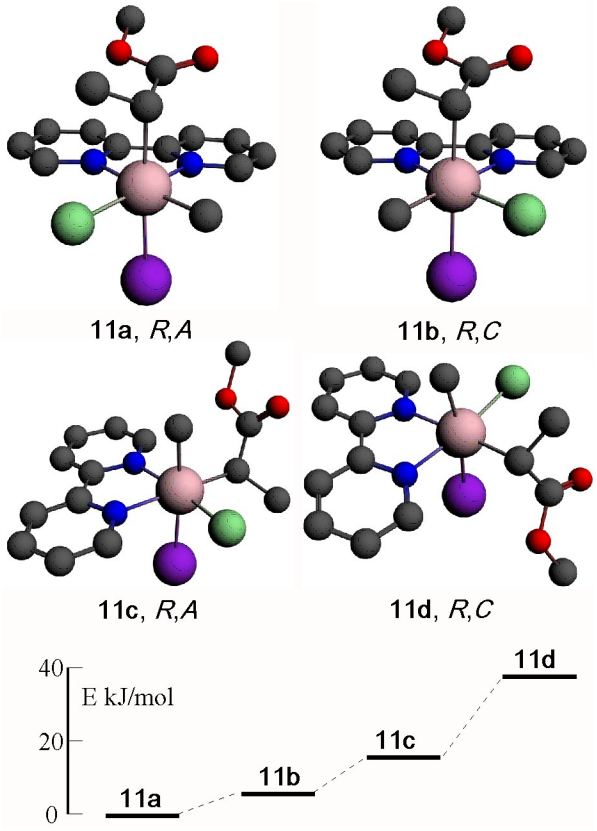

Figure 2. Calculated structures of some isomers of **11** and, below, their relative energies.

The oxidative addition of methyl iodide by the S_N2 mechanism involves a cationic 5-coordinate intermediate $[PtClMe(CHMeCO_2Me)(bipy)]^+I^-$ and calculations were also carried out for some isomers of the cation **12** (Figure 3). In this case, the complexes with the $CHMeCO_2Me$ group in an equatorial site were found to be more stable, in contrast to the octahedral complexes **11** of Figure 2. Now steric effects are lower and the coordinatively unsaturated intermediate is stabilized by weak coordination of the methoxy group of the ester to platinum in the isomers **12c** and **12d**. Coordination of iodide to **12c** and **12d** would give the products of *trans* oxidative addition which are not observed. This can be rationalized in the following way: the ester group in **12c** and **12d** blocks coordination of the iodide anion and so the final products are formed after

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rearrangement to the less stable intermediates **12a** and **12b** (Figure 3). A plausible reaction sequence is shown in Scheme 9. Attack of methyl iodide on the bottom face of **8** gives **12c**, which must then undergo pseudorotation to the less stable isomer **12a** before iodide coordination can occur to give **11a**. Similarly, attack at the top face would give **12d**, which would rearrange to **12b** followed by coordination of iodide to give **11b**.

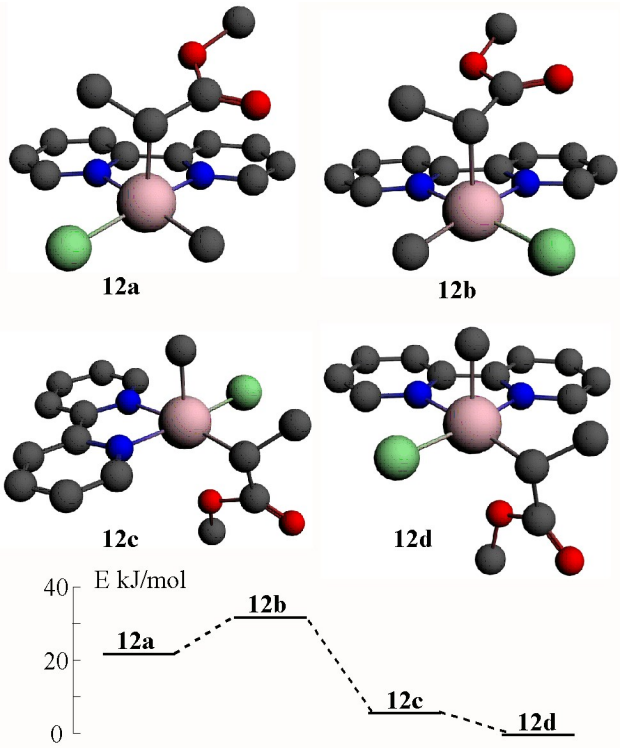

Figure 3. The calculated structures and relative energies of the cationic intermediates $[PtClMe(CHMeCO_2Me)(bipy)]^+$.

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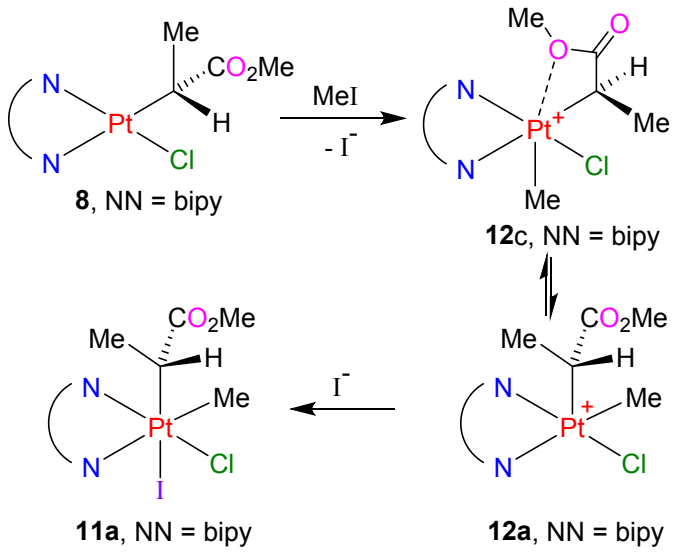

Scheme 9. A likely mechanism for formation of complex **11a**.

Conclusions

The initial aim of this work was to prepare a σ-complex of dimethylamine-borane with platinum(II) or platinum(IV). This was not successful and the main reaction observed was hydride transfer to platinum. This gave the rare stable bridging hydridoplatinum(IV) complexes **5** (Scheme 4) and the unstable hydridoplatinum(II) complex **7** (Scheme 5). The unstable hydridoplatinum(II) complexes could be trapped by reaction with methyl acrylate by forming the insertion products such as [PtCl(CHMeCO$_2$Me)(bipy)], **8**. Finally, the unusual *cis* oxidative addition of methyl iodide was established in the reaction with **8** to give [PtClIMe(CHMeCO$_2$Me)(bipy)], **11**. The presence of two chiral centers in **11** allows a detailed stereochemical pathway to be proposed (Scheme 9).

Experimental

All reactions were carried out under nitrogen, either using Schlenk techniques or in a dry box, unless otherwise specified. NMR spectra were recorded by using Varian Mercury 400 MHz, Varian Inova 400 MHz and 600 MHz spectrometers. ^{1}H and ^{19}F chemical shifts are reported with respect to TMS or CFCl$_3$. The ^{1}H-^{1}H 2D COSY NMR spectra were recorded to confirm multiplet assignments. Solvents were dried and distilled under nitrogen before use. All other reagents were used as received with no further purification. Preparative and analytical TLC separations were carried out by using plates with silica gel support, using UV light (254 nm) to visualize the bands. The platinum complexes [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$], [PtMe$_2$(bipy)],

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[PtClMe(bipy)], [Pt(OTf)$_2$(bipy)], [PtMe$_2$(bu$_2$bipy)], [Pt(OTf)Me$_3$(bu$_2$bipy)] and [Pt$_2$(μ-H)Me$_6$(bu$_2$bipy)$_2$](OTf) were prepared according to the literature.[32-40] DFT calculations were carried out for gas phase structures by using the Amsterdam Density Functional program based on the BLYP functional, with double-zeta basis set and first-order scalar relativistic corrections.[52,53] Minima were confirmed by vibrational analysis.

[Pt(OTf)Me$_3$(bipy)]

Methyl triflate (5.6 μL, 0.05 mmol) was added slowly to a suspension of [PtMe$_2$(bipy)] (19 mg, 0.05 mmol) in dry benzene (10 mL). The reaction mixture was allowed to stir for 30 min., then the white solid product was separated, washed with pentane (3 x 10 mL) and dried under vacuum. Yield: 25 mg, 87 %. Anal. Calc. for $C_{14}H_{17}F_3N_2O_3PtS$: C, 30.83; H, 3.14, N, 5.14. Found: C, 30.52, H, 2.89, N, 5.04%. NMR in acetone-d_6: δ(^{1}H) = 9.07 [br, 2H, H^6]; 8.82 [br, 2H, H^4]; 8.45 [br, 2H, H^3]; 8.00 [br, 2H, H^5]; 1.29 [s, 6H, ^2J(PtH) = 67 Hz, Pt-Me, *trans* py]; 0.75 [s, 3H, ^2J(PtH) = 78 Hz, Pt-Me, *trans* OTf].

[PtMe(O$_2$CCF$_3$)(bpy)]

Trifluoroacetic acid (134 μL, 2 mmol) was added slowly to a suspension of [PtMe$_2$(bpy)] (200 mg, 0.52 mmol) in ether (20 mL) and the mixture was allowed to stir for 1.5 h. The yellow solid product was separated, washed with ether (2 x 5 mL) and dried *in vacuo*. Yield: 210 mg, 83%. It was purified by recrystallization from CH_2Cl_2/pentane. Anal. Calc. for $C_{13}H_{11}F_3N_2O_2Pt$: C, 32.58; H, 2.31, N, 5.84. Found: C, 32.20, H, 2.06, N, 5.49%. NMR in $CDCl_3$: δ(^{1}H) = 9.14 [d, 1H, ^3J(H$^{6'}$H$^{5'}$) = 6 Hz, ^3J(PtH) = 63 Hz, H$^{6'}$]; 8.73 [d, 1H, ^3J(H^{6}H^5) = 6 Hz, ^3J(PtH) = 13 Hz, H^6]; 8.15 [m, 2H, H^4/H$^{4'}$]; 8.07 [d, 1H, ^3J(H$^{4'}$H$^{3'}$) = 7 Hz, H$^{3'}$]; 8.00 [d, 1H, ^3J(H^{4}H^3) = 7 Hz, H^3]; 7.67 [dd, 1H, ^3J(H$^{6'}$H$^{5'}$) = 6 Hz, ^3J(H$^{5'}$H$^{4'}$) = 7 Hz, H$^{5'}$]; 7.44 [dd, 1H, ^3J(H^{6}H^5) = 6 Hz, ^3J(H^{5}H^4) = 7 Hz, H^5]; 1.14 [s, 3H, ^2J(PtH) = 78 Hz, Pt-Me]; δ(^{19}F) = -74.19 [s, CF_3].

[Pt$_2$(μ-H)Me$_6$(bipy)$_2$][OTf]

To a solution of [PtMe$_3$(OTf)(bpy)] (0.10 g, 0.18 mmol) in thf (50 mL) was added NaBH4 (1.5 mg) in thf (25 mL). The mixture was allowed to stir for 3 h., the solvent was evaporated under vacuum, and the residue was extracted with CH_2Cl_2 (2 x 15 mL). This extract was filtered through Celite and the solvent was evaporated to give the product as a yellow solid. Yield 0.05 g, 58%. Anal. Calc. for $C_{27}H_{35}F_3N_4O_3Pt_2S$: C, 34.40; H, 3.74, N, 5.94. Found: C, 33.97, H, 3.76, N, 5.51%. NMR in CD_2Cl_2: δ(^{1}H) = 8.22 [d, 4H, ^3J(H^{6}H^5) = 6 Hz, ^3J(PtH) = 13 Hz, H^6]; 8.13 [d, 4H, ^3J(H^{4}H^3) = 7 Hz, H^3]; 8.10 [t, 4H, ^3J(H^{5}H^4) = ^3J(H^{4}H^3) = 7 Hz, H^4]; 7.46 [dd, 4H,

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$^3J(H^6H^5)$ = 6 Hz, $^3J(H^5H^4)$ = 7 Hz, H^5]; 0.88 [d, 12H, ^3J(HH) = 1 Hz, ^2J(PtH) = 70 Hz, Pt-Me *trans* py]; 0.13 [d, 6H, ^3J(HH) = 1 Hz, ^2J(PtH) = 65 Hz, Pt-Me *trans* H]; -11.72 [s, 1H, ^1J(PtH) = 447 Hz, Pt-H]. ESI-MS: Calc. for $C_{26}H_{35}N_4Pt_2^+$: m/z = 793.21. Found: m/z = 793.2.

[$PtMe_3(NHMe_2)(bipy)$][OTf]

To a solution of [$PtMe_3$(OTf)(bpy)] (0.10 g, 0.18 mmol) in thf (50 mL) was added Me_2NH (1.0 mL, 2M solution in thf). The mixture was stirred for 1 h., then the solvent was evaporated under vacuum to give the product as a pale yellow powder, which was washed with pentane (5 mL) and dried under vacuum. Yield 0.08 g, 62%. Anal. Calc. for $C_{16}H_{24}F_3N_3O_3PtS$: C, 32.54; H, 4.10; N, 7.12. Found: C, 32.81, H, 3.78, N, 7.01%. NMR in CD_2Cl_2: δ(^{1}H) = 8.83 [d, 2H, $^3J(H^6H^5)$ = 6 Hz, ^3J(PtH) = 13 Hz, H^6]; 8.53 [d, 2H, $^3J(H^4H^3)$ = 8 Hz, H^3]; 8.29 [t, 2H, $^3J(H^4H^3)$ = $^3J(H^5H^4)$ = 8 Hz, H^4]; 7.82 [dd, 2H, $^3J(H^6H^5)$ = 6 Hz, $^3J(H^5H^4)$ = 8 Hz, H^5]; 3.12 [br, 1H, Me_2NH]; 2.06 [d, 6H, ^3J(HH) = 6 Hz, ^3J(PtH) = 13 Hz, Me_2NH]; 1.08 [s, 6H, ^2J(PtH) = 67 Hz, Pt-Me *trans* py]; 0.35 [s, 3H, ^2J(PtH) = 69 Hz, Pt-Me *trans* amine]. ESI-MS: Calc. for $C_{15}H_{24}N_3Pt^+$: m/z = 441.16. Found: m/z = 441.1.

[$Pt_2(\mu\text{-}H)Me_6(bipy)_2$][OTf] and [$PtMe_3(NHMe_2)(bipy)$][OTf]

A solution of H_3BNMe_2H (1.1 mg, 0.019 mmol) in acetone (1 mL) was added to a solution of [$PtMe_3$(OTf)(bpy)] (10 mg, 0.018 mmol) in acetone (10 mL). The mixture was allowed to stir for 1 hour and the solvent was removed *in vacuo* to give the product mixture as a yellow oil, which was washed with pentane (3 x 2 mL) and dried under vacuum. NMR analysis (CD_2Cl_2) indicated the ratio [$Pt_2(\mu\text{-}H)Me_6(bipy)_2$][OTf]:[$PtMe_3(NHMe_2)(bipy)$][OTf] = *ca* 2:1.

[$PtMe_3(NHMe_2)(bu_2bipy)$][OTf]

This was prepared from [Pt(OTf)$Me_3(bu_2bipy)$] and Me_2NH in a similar way as the bipy analog. Yield 69%. Anal. Calc. for $C_{16}H_{24}F_3N_3O_3PtS$: C, 32.54; H, 4.10; N, 7.12. Found: C, 32.81, H, 3.78, N, 7.01%. NMR in acetone-d_6: δ(^{1}H) = 8.93 [d, 2H, $^3J(H^6H^5)$ = 6 Hz, ^3J(PtH) = 12 Hz, H^6]; 8.90 [s, 2H, H^3]; 8.01 [d, 2H, $^3J(H^6H^5)$ = 6 Hz, H^5]; 3.81 [br, 1H, Me_2NH]; 2.11 [d, 6H, ^3J(HH) = 6 Hz, ^3J(PtH) = 14 Hz, Me_2NH]; 1.49 [s, 18H, *t*-Bu]; 1.07 [s, 6H, ^2J(PtH) = 68 Hz, Pt-Me, *trans* py]; 0.31 [s, 3H, ^2J(PtH) = 69 Hz, Pt-Me *trans* amine].

[$PtMe_3(NHMe_2)(bu_2bipy)$][OTf] and [$Pt_2(\mu\text{-}H)Me_6(bu_2bipy)_2$][OTf]

A solution of H_3BNMe_2H (1.1 mg, 0.019 mmol) in acetone-d_6 (0.5 mL) was added to a solution of [$PtMe_3$(OTf)(bu_2bipy)] (10 mg, 0.015 mmol) in acetone-d_6 (1 mL). NMR analysis indicated the ratio [$Pt_2(\mu\text{-}H)Me_6(bipy)_2$][OTf]:[$PtMe_3(NHMe_2)(bipy)$][OTf] = *ca* 1:4.

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[PtClMe(bipy)] and [PtCl(CHMeCO$_2$Me)(bipy)]

A solution of H_3BNMe_2H (30 mg, 0.51 mmol) in $CHCl_3$ (10 mL) was added to a mixture of methylacrylate (44 μL, 0.46 mmol) and [PtMe(O_2CCF_3)(bipy)] (0.20 g, 0.42 mmol) in $CHCl_3$ (20 mL). The reaction mixture was stirred for 24 h., LiCl (0.1 g) was added, the solvent was removed *in vacuo*, and the product mixture was separated by TLC using an eluent of MeOH:CH_2Cl_2 at a ratio of 2:98. The pure products [PtMeCl(bipy)] (0.03 g, 14%) and [PtCl(CHMeCO$_2$Me)(bipy)] (0.06 g, 24%) were obtained.

[PtCl(CHMeCO$_2$Me)(bipy)]; Anal. Calc. for $C_{14}H_{15}ClN_2O_2Pt$: C, 35.49; H, 3.19; N, 5.91. Found: C, 34.94, H, 3.38, N, 6.03%. NMR in $CDCl_3$: δ(^{1}H) = 9.77 [d, 1H, ^3J(H$^{6'}$H$^{5'}$) = 6 Hz, H$^{6'}$]; 9.70 [d, 1H, ^3J(H^{6}H^5) = 5 Hz, H^6]; 8.17 [t, 1H, ^3J(H$^{5'}$H$^{4'}$) = ^3J(H$^{4'}$H$^{3'}$) = 8 Hz, H$^{4'}$]; 8.10 [dd, 1H, ^3J(H^{5}H^4) = 8 Hz, ^3J(H^{4}H^3) = 7 Hz, H^4]; 8.03 [d, 1H, ^3J(H$^{4'}$H$^{3'}$) = 8 Hz, H$^{3'}$]; 8.01 [d, 1H, ^3J(H^{4}H^3) = 7 Hz, H^3]; 7.62 [dd, 1H, ^3J(H$^{6'}$H$^{5'}$) = 6 Hz, ^3J(H$^{5'}$H$^{4'}$) = 8 Hz, H$^{5'}$]; 7.59 [dd, 1H, ^3J(H^{6}H^5) = 5 Hz, ^3J(H^{5}H^4) = 8 Hz, H^5]; 4.10 [q, 1H, ^3J(HH) = 7 Hz, PtC*H*]; 3.64 [s, 3H, ^5J(PtH) = 5 Hz, CO_2Me]; 1.25 [d, 3H, ^3J(HH) = 7 Hz, ^3J(PtH) = 50 Hz, PtC*Me*]. ESI-MS: Calc. for $C_{14}H_{15}N_2O_2Pt$+: m/z = 438.08. Found: m/z = 438.1.

[Pt(CHMeCO$_2$Me)$_2$(bipy)]

H_3BNMe_2H (60 mg, 1.0 mmol) was added slowly to a mixture of methylacrylate (88 μL, 0.92 mmol) and [Pt(OTf)$_2$(bipy)] (0.20 g, 0.31 mmol) in C_6H_6 (30 mL). The reaction mixture was stirred for 24 h., the solvent was removed *in vacuo*, and the product mixture was separated by TLC using an eluent of MeOH: C_6H_6 at a ratio of 10:90 to give, after evaporation of the solvent, [Pt(CHMeCO$_2$Me)$_2$(bipy)] as a yellow solid. It was not possible to separate the isomers. Yield = 0.11 g, 64 %. Anal. Calc. for $C_{18}H_{22}N_2O_4Pt$: C, 41.14; H, 4.22; N, 5.33. Found: C, 41.32; H, 4.01; N, 5.53%. NMR in CD_3OD: Isomer a: δ(^{1}H) = 9.53 [d, 2H, ^3J(H^{6}H^5) = 6 Hz, H^6]; 8.41 [d, 2H, ^3J(H^{4}H^3) = 8 Hz, H^3]; 8.26 [dd, 2H, ^3J(H^{6}H^5) = 6 Hz, ^3J(H^{5}H^4) = 8 Hz, H^5]; 7.75 [t, 2H, ^3J(H^{5}H^4) = ^3J(H^{4}H^3) = 8 Hz, H^4];3.53 [s, 6H, CO_2Me]; 3.38 [q, 2H, ^3J(HH) = 7 Hz, PtC*H*]; 1.21 [d, 6H, ^3J(H^{a}H^b) = 7 Hz, ^3J(PtH) = 58 Hz, PtC*Me*]. Isomer b: δ(^{1}H) = 9.47 [d, 2H, ^3J(H^{6}H^5) = 6 Hz, H^6]; 8.41 [d, 2H, ^3J(H^{4}H^3) = 8 Hz, H^3]; 8.26 [dd, 2H, ^3J(H^{6}H^5) = 6 Hz, ^3J(H^{5}H^4) = 8 Hz, H^5]; 7.75 [t, 2H, ^3J(H^{5}H^4) = ^3J(H^{4}H^3) = 8 Hz, H^4]; 3.52 [s, 6H, CO_2Me]; 3.43 [q, 2H, ^3J(HH) = 7 Hz, PtC*H*]; 1.22 [d, 6H, ^3J(HH) = 7 Hz, ^3J(PtH) = 60 Hz, PtC*Me*]. The same product was obtained by the similar reaction of [PtMe(O_2CCF_3)(bipy)] but in lower yield of 14%.

[PtClIMe(CHMeCO$_2$Me)(bipy)]

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To a solution of [PtCl(CHMeCO_2Me)(bipy)] (5 mg, 0.009 mmol) in acetone (3 mL) was added MeI (1.3 mg, 0.009 mmol). The mixture was stirred for 2.5 h., and the solvent was removed *in vacuo* to give the product as a yellow solid. Yield = 4 mg, 70 %. NMR in $CDCl_3$: Isomer **11a**: $\delta(^1H)$ = 9.56 [d, 1H, $^3J(H^6H^5)$ = 5 Hz, ^3J(PtH) = 9 Hz, H^6]; 8.92 [d, 1H, $^3J(H^{6'}H^{5'})$ = 6 Hz, ^3J(PtH) = 39 Hz, $H^{6'}$]; 8.5-7.3 [m, 6H, H^3-H^5, $H^{3'}$-$H^{5'}$]; 3.53 [q, 1H, ^3J(HH) = 7 Hz, PtC*H*]; 2.88 [s, 3H, CO_2Me]; 2.29 [s, 3H, ^2J(PtH) = 70 Hz, Pt-Me *trans* to I]; 0.50 [d, 3H, ^3J(HH) = 7 Hz, ^3J(PtH) = 53 Hz, PtC*Me*]. Isomer **11b**: $\delta(^1H)$ = 9.52 [d, 1H, $^3J(H^6H^5)$ = 5 Hz, ^3J(PtH) = 9 Hz, H^6]; 8.82 [d, 1H, $^3J(H^{6'}H^{5'})$ = 6 Hz, ^3J(PtH) = 39 Hz, $H^{6'}$]; 8.5-7.3 [m, 6H, H^3-H^5, $H^{3'}$-$H^{5'}$]; 3.34 [q, 1H, ^3J(HH) = 7 Hz, PtC*H*]; 3.00 [s, 3H, CO_2Me]; 2.44 [s, 3H, ^2J(PtH) = 67 Hz, Pt-Me *trans* to I]; 0.46 [d, 3H, ^3J(HH) = 7 Hz, ^3J(PtH) = 47 Hz, PtC*Me*].

Structure Determination

A suitable crystal was mounted on a glass fiber and data were collected at 150(2) K by using a Bruker Smart Apex II diffractometer with CCD detector. The unit cell parameters were calculated and refined from the full data set. Crystal data: formula $C_{15}H_{18}ClIN_2O_2Pt$, fw 615.75, T 150 K, λ 0.71073 Å, triclinic, P-1, a = 8.0148(8) Å, b = 9.29899(8) Å, c = 12.1811(12) Å, α = 85.739(6) °, β = 88.707(6) °, γ = 70.069(5) °, V 850.28(14) $Å^3$, Z 2, d(calc) 2.405 Mg/m^3, μ 10.231 mm^{-1}, R [I>2σ(I)] 0.0533, wR^2 (all data) 0.1489. Further details are given in the CIF file (CCDC 1447431).

Conflicts of interest

There are no conflicts to declare.

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Appendix A. Supplementary material

CCDC 1447431 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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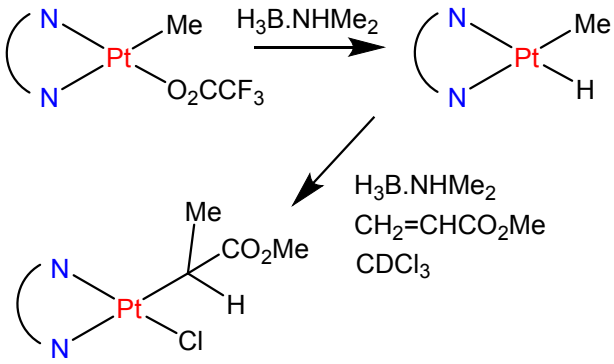
TOC graphic



TOC text

Reactions of organoplatinum complexes with dimethylamineborane are reported.