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Aiding Factors in the Formation of Azaplatinacyclobutane Rings – X-ray and Crystal Structure of [Pt{CH(Ph)$CH_2$$NEt_2$-κC,κN}(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)]$^+$ and of Its Open-Chain Precursor

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The addition products **2** of a secondary amine to a coordinated olefin, in the cationic complexes [PtCl(η^2-CH_2=CHR)(tmeda)]$^+$ (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine; R = Me, **1a**; Ph, **1b**, H, **1c**), undergo in basic medium an intramolecular nucleophilic substitution with elimination of the chlorido ligand and formation of an azaplatinacyclobutane ring **3**. The ring-closing process occurs notwithstanding the absence of a labilizing ligand *trans* to the leaving chlorido ligand and of bulky substituents on the amino–ethanide chain. If the addition product **2** is a mixture of Markovnikov and anti-Markovnikov isomers, the ring-closing reaction is faster for the anti-Markovnikov form, and this leads to an increase of the relative amount of the anti-Markovnikov isomer in the cyclized species **3**. The difference in the rate of formation of the azaplatinacyclobutane ring between the two isomers has been interpreted on the basis of a more favorable stereochemistry in the case of the anti-Markovnikov form. The X-ray crystal structures of [Pt{CH(Ph)$CH_2$$NEt_2$-κC,κN}(tmeda)]$^+$ (**3bn**) and of its open-chain precursor, [PtCl{CH(Ph)$CH_2$$NHEt_2$}(tmeda)]$^+$ (**2bn**) fully support this hypothesis.

Introduction

A number of azametallacyclobutanes have been reported in the literature; in some cases they have been isolated and fully characterized, while in other cases they have only been detected in solution, or proposed as key intermediates in catalytic processes concerned with the hydroamination of olefins and allenes.[1–8]

The reaction sequence leading to their formation is very much dependent upon the nature of the metal involved. In the case of early transition metals, the azametallacyclobutanes are generated by [2+2] cycloaddition of an olefin to a metalla-imido moiety (M=NR).[1] The reaction is generally reversible, and in the specific case of [Cp_2(THF)Zr(=*N*-*t*Bu)] reacting with norbornene, the formed azazirconacyclobutane was also structurally characterized.[1b]

A different and more complex reaction pathway was proposed for the formation of an azatungstacyclobutane. The allenyl precursor, $Cp(CO)_3W$–CH=C=CH_2, underwent methylamine addition both at a carbonyl ligand (which was transformed into a carbamoyl group) and at the β-carbon atom of the allenyl ligand (across the terminal double bond), accompanied by a regiospecific coupling of the amido group with the α-carbon atom of the allenyl ligand and the coordination of the amine to the tungsten metal center.[2]

Also in the case of late transition metals, several procedures have been reported to lead to the formation of azametallacyclobutanes. For instance, in the iridium-catalyzed hydroamination of norbornene, reported by Calabrese et al., a very reactive 14-electron iridium complex first undergoes oxidative addition with aniline followed by [2+2] cycloaddition of the formed metalla-amido moiety to norbornene to form an azairidacyclobutane complex.[3] An azairidacyclobutane is also formed by a ring-closing reaction (with elimination of HCl) of an iridium 2-aminoethanide complex obtained by the photolysis of an iridium hydride species in the presence of *tert*-butylamine.[4]

More recently, Puddephatt has reported a platinum(IV) complex containing an azaplatinacyclobutane ring obtained through oxidative addition of a protonated tethered imine group present on a platinum(II)-coordinated amine (the azaplatinacyclobutane ring resulting from the coordination of the imine carbon and the nitrogen atom of a 2-pyridyl substituent present on the imine carbon atom to the platinum atom).[5]

More often, 2-aminoethanide species are formed through nucleophilic addition of an amine to a coordinated olefin followed by a ring-closing process.[6–8] By this procedure stable azaplatinacyclobutane complexes have been prepared since the early 1980's. Their isolation was strictly dependent

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upon the nature of the ancillary ligands and the presence of substituents on the metal-coordinated olefin and on the attacking amine.[6,7] Starting from a complex such as *cis*-[$PtCl_2(L)(\eta^2$-alkene/allene)], the addition to the olefin of a secondary amine leads to a zwitterionic species (formal negative charge on the platinum atom and positive charge on the nitrogen ammonium group), which can eliminate HCl and form an azaplatinacyclobutane ring. The reaction occurs readily when L is a *trans*-labilizer (phosphorus or sulfur donor ligand).[6,7] When L is a N-donor ligand, the ring-closing reaction is observed only in the case of olefins bearing substituents on the α and/or β carbon atoms.[7] Azaplatinacyclobutanes formed in the case of L = triphenylphosphane have also been characterized by X-ray crystallography.[6]

We have recently reconsidered the amination reaction of platinum-coordinated olefins in some cationic complexes and observed a facile ring closing of the 2-ammonium ethanide species obtained therefrom, with the ready formation of azaplatinacyclobutane rings. The results, hereafter described, have allowed us to gain new insights into factors governing this reaction (for a preliminary account see ref.[10]).

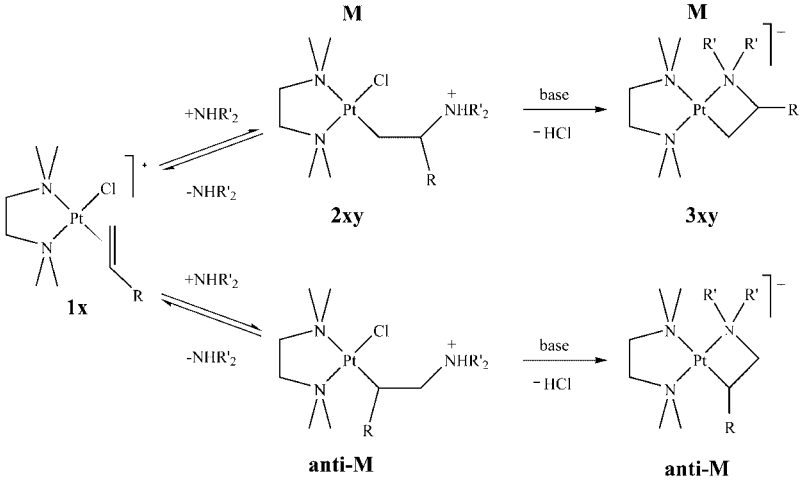
Results and Discussion

The cationic complexes [$PtCl(\eta^2$-olefin)(tmeda)]$^+$ (**1**)[9] (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine; olefin = alkyl or aryl-substituted ethene such as propene, **1a**, or styrene, **1b**) react quickly and smoothly with secondary amines (such as dimethylamine, **m**, and diethylamine, **n**) to give the corresponding η^1-2-ammonium ethanide species **2** (see Scheme 1). Species of type **2** exist as equilibrium mixtures of Markovnikov (**M**) and anti-Markovnikov (**anti-M**) forms; the interconversion process most likely requires the detachment and re-addition of the amine as illustrated in Scheme 1. The thermodynamically determined isomeric ratio is largely in favor of the Markovnikov form in the case of **2an** and in favor of the anti-Markovnikov isomer in the case of **2bm**,**n**.[10]

Under basic conditions, the product of amination (**2** in Scheme 1) undergoes deprotonation followed by displacement of the *cis* chlorido ligand by the amine nitrogen atom and formation of an azaplatinacyclobutane species (**3** in Scheme 1). We have found that the **M/anti-M** ratio decreases on going from the linear addition product to the ring-closed species. Therefore, the linear addition product **2an**, containing at equilibrium a **M/anti-M** ratio of 95:5, yields, upon ring-closing, compound **3an**, in which the **M/anti-M** ratio decreases to 75:25. Similarly, the linear addition product **2bm**, in which at equilibrium the **M/anti-M** ratio was 30:70, gives, after the ring-closing process, compound **3bm**, in which the anti-Markovnikov isomer is the exclusive form. This behavior can be explained with a greater propensity of the linear anti-Markovnikov addition product to undergo the ring-closing reaction.

The cyclization reaction of **2an** and **2bm** (leading to **3an** and **3bm**, respectively), performed in an NMR tube under basic conditions, did show the formation of trace amounts of byproducts that were probably due to the reaction of species **1a** and **1b**, which are intermediates in the Markovnikov/anti-Markovnikov isomerization of **2a** and **2b**, with the base.[11] However, by operating on millimolar quantities and after work-up procedures, the species of type **3** were obtained in almost pure form (> 95%).

The structures of species **3** could be unequivocally determined by NMR techniques (1D and 2D ^1H, $^1H/^{13}C$, APT). The Markovnikov and anti-Markovnikov isomers could be easily distinguished through the different patterns of connectivities in the metallacyclobutane ring. The separation of the Markovnikov and anti-Markovnikov isomers of **3an** (**3bm**,**n** are essentially formed as the **anti-M** isomer)[13] has not been attempted at this stage of the work.



x = **a** (R = CH_3), **b** (R = C_6H_5), **c** (R = H); **y** = **m** (R' = CH_3), **n** (R' = CH_2CH_3)

M = Markovnikov; **anti-M** = anti-Markovnikov

Scheme 1.

Some significant differences can be observed between the NMR parameters of the open-chain species **2** and the ring-closed species **3**. In particular, Cα is more shielded in **3** than in **2** while Cβ is more shielded in **2** than in **3** [for the pairs of compounds: **M-2an/M-3an**, **anti-M-2bm/anti-M-3bm**, and **anti-M-2bn/anti-M-3bn**; $\Delta\delta$(Cα) and $\Delta\delta$(Cβ) values are –17.8 and +6.3, –22.7 and +15.6, and –22.1 and +13.7 ppm, respectively]. Similarly to the carbon atom, the protons on the β carbon are also considerably less shielded in the cyclized species **3** than in the linear addition product **2** ($\Delta\delta$ in the range 0.6–1.9 ppm). The deshielding of the β protons was taken by Green et al. as an indicator for the occurrence of the ring-closing process[7] (although in that work the reaction stereochemistry and the possible formation of Markovnikov and anti-Markovnikov isomers were not discussed in detail). Another highly distinctive NMR feature of species **3** is the value of $^{3}J_{Pt,H}$ for the β protons, which can nearly reach 100 Hz, well above the observed values for the corresponding coupling in the linear compounds. It is worth noting that in the **anti-M** isomer, where there are two β protons, these protons are diastereotopic with a dispersion which can be as large as 1 ppm. Moreover, only for one of these protons (that at lower field), the $^{3}J_{Pt,H}$ is very high (78, 99, and 95 Hz for **anti-M-3an**, **anti-M-3bm**, and **anti-M-3bn**, respectively), while for the other proton (that at higher field) the $^{3}J_{Pt,H}$ is much smaller and ill-defined. Finally we have found that, on going form **2** to **3**, the resonance of the ^{195}Pt nucleus shifts downfield by more than 300 ppm ($\Delta\delta$ = +354.4 and +415.7 ppm for **M-2an/M-3an** and **anti-M-2bn/anti-M-3bn**, respectively).

Crystals suitable for X-ray analysis were obtained for the **anti-M** isomers of **2bn** and **3bn**. The structures of **2bn** and **3bn**, together with the numbering scheme, are depicted in Figure 1 (bond lengths and angles are in Table 1). In both cases, the coordination around the platinum atom is roughly square planar, considering the four metal-linked atoms: the tmeda nitrogen atoms, the carbon, and the chlorine (**2bn**) or the nitrogen atom of the four-membered chelate (**3bn**). The maximum deviation from the mean plane through the four donor atoms applies to N1 in **2bn** and to C8 in **3bn** [–0.019(6) and –0.026(4) Å, respectively]; moreover, the displacement exhibited by the platinum atom is 0.0141(2) and –0.0214(1) Å for **2bn** and **3bn**, respectively. Bond lengths for Pt–C8, Pt–N1, and Pt–N2 fall in the usual range. A significant difference (0.09 and 0.12 Å, for **2bn** and **3bn**, respectively) is found between the two Pt–N bonds pertaining to the tmeda ligand, as a result of the stronger *trans* influence of the carbon atom with respect to the chlorine or nitrogen donor atoms. The penta-atomic ring, resulting from chelation of the tmeda ligand to the platinum atom, is puckered with displacements of the C1 and C2 carbon atoms on opposite sides of the plane defined by Pt, N1, and N2 [–0.44(1) and 0.24(1) Å for **2bn** and 0.398(6) and –0.310(6) Å for **3bn**].[14] In **2bn**, the C9–C8–C7–N3 torsion angle of –172.5(4)° indicates an antiperiplanar disposition of the phenyl and amine substituents on the ethanide chain. This brings the amine group in a synclinal disposition with respect to the platinum atom with a Pt–C8–C7–N3 torsion angle of –45.9(5)°. The proximity of the amine group to the chlorido ligand sets the nitrogen in a suitable position to undergo chlorido substitution and ring-closing reaction.

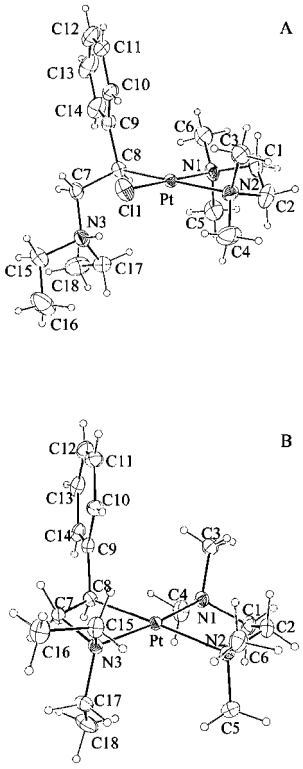


Figure 1. (A) ORTEP drawing of the complex cation [PtCl{CH(Ph)CH_2NHEt_2}(tmeda)]$^+$; the ellipsoids enclose 20% probability. (B) ORTEP drawing of the complex cation [Pt{CH(Ph)CH_2NEt_2-κC,κN}(tmeda)]$^+$; the ellipsoids enclose 20% probability.

Table 1. Selected bond lengths [Å] and angles [°] for **2bn** and **3bn**.

	2bn	**3bn**
Pt–C8	2.062(4)	2.053(4)
Pt–N1	2.081(6)	2.084(3)
Pt–N2	2.174(4)	2.209(3)
Pt–N3		2.085(3)
Pt–Cl1	2.312(2)	
N3–C7		1.516(5)
C7–C8		1.522(6)
C8–Pt–N1	91.5(2)	100.3(2)
C8–Pt–N3		70.4(2)
N1–Pt–N2	85.2(2)	83.3(2)
N3–Pt–N2		106.0(2)
N3–C7–C8		103.5(3)
C8–Pt–Cl1	93.1(1)	
N2–Pt–Cl1	90.1(2)	
C7–C8–Pt		93.1(2)

In **3bn**, the cyclobutane metallacycle is rather strained and "quasi" planar; as a consequence, the substituents on adjacent atoms of the aminoethanide chain are placed in eclipsed positions. Notwithstanding the large deviation from theoretical values of bond angles, bond lengths within the four-member metallacycle are rather normal and in agreement with values found in the analogous

[Pt($CH_2CH_2NMe_2$-κC,κN)Cl(PPh_3)] complex, in which, however, the ethanide chain had no substituents and the Pt–N bond was *ca*. 0.04 Å longer because of the *trans* influence of phosphane.[6] The steric interaction between substituents on *cis* ligands [particularly C9···C3 = 3.426(8) and C6···C15 = 3.548(8) Å] can fully explain the pyramidal distortion of the platinum coordination center. Moreover, it can be noted that, in both compounds (**2bn** and **3bn**), the phenyl ring angle centered on the *ipso* carbon is smaller than all the others [C10–C9–C14 = 117.3(5)° and 117.3(4)° for **2bn** and **3bn**, respectively]. The distortion of benzene rings has been the object of careful studies by Domenicano et al., who have rationalized the deviations from a regular geometry in terms of electronegativity, resonance, and steric effects of the substituent. An angle that is less than 120° is indicative of the accumulation of negative charge on the *ipso* carbon induced by an electron-donor substituent (electron-withdrawing substituents produce the opposite effect).[15] Therefore, the platinum-bonded carbon atom behaves like an electron donor towards the *ipso* carbon atom of the phenyl ring, and the electronic characteristics of this carbon atom are rather similar for the two compounds.

Azaplatinacyclobutanes, analogous to those here described,[6,7] were already reported in the literature; however, all of them were characterized by the presence of a labilizing ligand *trans* to the ligand displaced in the ring-closing process (usually a chlorido), and/or by having substituents on the ethanide chain (the Thorpe–Ingold effect of these substituents promoting the chelate ring formation).[12] However, the ring-closing reaction readily occurs in our systems notwithstanding the absence of a labilizing ligand *trans* to the leaving chlorido ligand. Moreover, although compounds **2an** and **2bm**,**n** contain a substituent (a methyl and a phenyl, respectively) on the ethanide chain, we could prove that compound [PtCl(η^1-$CH_2CH_2NHEt_2$)(tmeda)](ClO_4), **2cn**, which has no substituents on the ethanide chain, can also easily undergo a ring-closing process. In particular, **2cn** in chloroform solution, treated with a slight excess of $NHEt_2$, affords a new complex species that is characterized, with respect to the NMR parameters of **2cn**, by a considerable downfield shift of the ^{195}Pt resonance ($\Delta\delta$ = +440 ppm), a shielding of the C and H atoms in the α position ($\Delta\delta$ = –20 and –0.6 ppm, respectively), and a deshielding of the C and H atoms in the β position ($\Delta\delta$ = +10 and +1.3 ppm, respectively). All these features are characteristic of a ring-closed species. Moreover, the ESI mass spectrum of the reaction solution did show, besides a peak at 447.9, due to residual **2cn**, another intense peak at 411.5 corresponding to the elimination of HCl from **2cn** (the absence of chlorine was also confirmed by the peak isotopic pattern).

The cyclized species **3** of this work are closely related to the metallacycles proposed by Hartwig for the rhodium-catalyzed **anti-M** amination of vinylarenes.[16] Our findings prove that the formation of such intermediates is very likely, and the greater propensity of the **anti-M** isomer to undergo a ring-closing reaction may be the reason for the **anti-M** selectivity observed in the Hartwig reaction.

It can also be noted that, in spite of its strained structure, compound **3** appears to have considerable stability. To account for such stability, the concept of geometrical rigidity (steric constraints disfavor the reorganization of the metal orbital, which is necessary for a reaction pattern to take place) can be invoked. The same concept has been proposed by Zetterberg for justifying the lack of β-hydrogen elimination in azapalladacyclobutane species.[8c]

Conclusions

In the systems under consideration, neither the *trans*-labilization of the ligand to be displaced by the entering nitrogen, nor the presence of substituents on the ethanide chain (which facilitates cyclization by the Thorpe–Ingold effect) are necessary for the ring-closing reaction to take place. The main difference between our substrates and those previously investigated[6,7] is the absence of a formal negative charge on the aminoethanide compound undergoing cyclization (deprotonated **2**). Therefore, a greater electrophilicity of the metal center (which is deprived of formal negative charge) could be the aiding factor promoting the ring-closing process.

Another outcome of the present investigation is the greater propensity of the anti-Markovnikov isomer of **2**, as compared with the Markovnikov one, to undergo ring-closing reaction. The **anti-M** isomer of **2** differs from the **M** isomer in that it has the two substituents (the methyl or phenyl group and the amine) on different carbon atoms of the ethanide chain. Steric repulsion between the two substituents will set them in an antiperiplanar conformation. As a consequence, the amine group is brought in a synclinal conformation with respect to the platinum atom and therefore in a suitable position to undergo chlorido substitution and ring-closing. This aiding effect is not present in the Markovnikov isomer, for which the hydrocarbon and the amine substituents are on the same carbon atom of the ethanide chain. The X-ray structure of compound **2bn** has fully confirmed this prevision. The phenyl ring and the amine substituents on the ethanide chain are in antiperiplanar disposition, which brings the amine group in a synclinal position with respect to the platinum atom and close to the chlorido ligand, which can therefore be easily displaced.

Experimental Section

General Methods: All reagent-grade chemicals were purchased from Aldrich and used without purification. Elemental analyses were performed by using an Elemental Analyzer 1106 Carlo Erba instrument. ^{1}H NMR spectra were recorded with a DPX300 Advance Bruker instrument equipped with a probe for inverse detection and with *z* gradient for gradient-accelerated spectroscopy. ^{1}H and ^{13}C spectra were referenced to TMS; the residual proton signal of the solvent was used as internal standard. For ^{195}Pt spectra K_2PtCl_4 was used as external standard (–1643.00 ppm). ^{1}H/^{13}C inversely detected gradient-sensitivity-enhanced heterocorrelated 2D NMR spectra for normal coupling (INVIEAGSSI) were acquired by

using standard Bruker automation programs and pulse sequences. APT spectra were recorded on a 300-MHz Mercury Varian instrument equipped with *z* gradient. All spectra were acquired in $CDCl_3$ and at 298 K. ESI mass spectra were obtained through a direct injection (10 μL/min) of micromolar methanol solutions of all the compounds into an Agilent 1100 Series LC-MSD Trap System VL instrument.

Synthesis

Alkene complexes [PtCl(η^2-CH_2=CHX)(tmeda)](ClO_4) (X = CH_3, **1a**. C_6H_5, **1b**) were prepared by ethene exchange on the cationic complex [PtCl(η^2-C_2H_4)(tmeda)](ClO_4) (**1c**) by following a reported procedure.[17]

Amine addition compounds **2xy** were prepared by reaction of the alkene complex **1** (0.4 mmol), suspended in dichloromethane (8 mL), with a slight excess of the amine ($NHMe_2$, **m**; $NHEt_2$, **n**; 1.2-fold the stoichiometric amount). After stirring for 3 h at room temperature, complete dissolution of the solid was observed. The solution was filtered, the solvent evaporated under reduced pressure, and the oily residue, after trituration with diethyl ether, afforded a white solid which was identified as the amine addition product. The isolated yield, referred to platinum, was ca. 95% for all the compounds.

2an(ClO_4): $C_{13}H_{33}Cl_2N_3O_4Pt$ (561.40): calcd. C 27.81, H 5.92, N 7.48; found C 27.62, H 5.81, N 7.38. NMR (tmeda signals are given first) **M-2an:** ^{1}H NMR δ = 2.65 (s, 3 H), 2.67 (s, 3 H), 2.81 (s, 3 H), and 2.87 (s, 3 H), CH_3N; 2.56 (1 H) and 2.73 (1 H), 2.82 (1 H) and 3.02 (1 H), -CH_2N; 1.26 (d, 1 H), Pt-CH_2CH(CH_3)-NH(CH_2CH_3)$_2$; 1.46 (dd, 1 H) and 1.59 (dd, 1 H), Pt-CH_2CH-(CH_3)NH(CH_2CH_3)$_2$; 3.59 (m, 1 H), Pt-CH_2C*H*(CH_3)NH-(CH_2CH_3)$_2$; 1.43 (m, 3 H) and 1.49 (m, 3 H), Pt-CH_2CH(CH_3)NH-(CH_2CH_3)$_2$; 2.77 (m, 1 H) and 3.34 (m, 1 H), 3.05 (m, 1 H) and 3.28 (m, 1 H), Pt-CH_2CH(CH_3)NH(CH_2CH_3)$_2$ ppm. ^{13}C NMR δ = 47.4, 49.1, 51.1, and 52.2, *C*H_3N; 59.9 and 66.1, -*C*H_2N; 1.0, Pt-*C*H_2CH(CH_3)NH(CH_2CH_3)$_2$; 15.5, Pt-CH_2CH(*C*H_3)NH-(CH_2CH_3)$_2$; 62.6, Pt-CH_2*C*H(CH_3)NH(CH_2CH_3)$_2$; 10.9 and 10.6, Pt-CH_2CH(CH_3)NH(CH_2*C*H_3)$_2$; 42.8 and 46.8, Pt-CH_2CH(CH_3)-NH(*C*H_2CH_3)$_2$ ppm. ^{195}Pt NMR δ = –3384.0 ppm. **anti-M-2an:** ^{1}H NMR δ = 0.95 (d, 3 H), Pt-CH(CH_3)CH_2NH(CH_2CH_3)$_2$; 1.39 (m, 1 H), Pt-C*H*(CH_3)CH_2NH(CH_2CH_3)$_2$; 2.34 (dd, 1 H) and 3.21 (dd, 1 H), Pt-CH(CH_3)CH_2NH(CH_2CH_3)$_2$ ppm.

2bm(ClO_4): $C_{16}H_{31}Cl_2N_3O_4Pt$ (595.42): calcd. C 32.27, H 5.25, N 7.06; found C 32.03, H 5.11, N 6.98. NMR (tmeda signals are given first) **anti-M-2bm:** ^{1}H NMR δ = 2.46 (s, 3 H), 2.69 (s, 3 H), 2.85 (s, 3 H), and 2.98 (s, 3 H), CH_3N; 2.48 (1 H), 2.68 (2 H), and 2.98 (1 H), -CH_2N; 2.76 (dd, $^2J_{Pt,H}$ = 76.2, 1 H), Pt-C*H*(Ph)CH_2NH-(CH_3)$_2$; 2.32 (1 H) and 3.79 (1 H), Pt-CH(Ph)CH_2NH(CH_3)$_2$; 3.02 (3 H) and 3.12 (3 H), Pt-CH(Ph)CH_2NH(CH_3)$_2$; 7.12 (1 H, *para*), 7.19 (2 H, *meta*), and 7.40 (2 H, *ortho*), Pt-CH(*Ph*)CH_2NH(CH_3)$_2$ ppm. ^{13}C NMR δ = 48.9, 49.0, and 52.0, *C*H_3N; 59.8 and 66.8, -*C*H_2N; 16.5 ($^1J_{Pt,C}$ = 846 Hz), Pt-*C*H(Ph)CH_2NH(CH_3)$_2$; 67.6, Pt-CH(Ph)*C*H_2NH(CH_3)$_2$; 42.7 and 45.2, Pt-CH(Ph)CH_2NH(*C*H_3)$_2$; 125.3 (*para*), 128.4 (*meta*), and 129.2 (*ortho*), Pt-CH(*Ph*)-CH_2NH(CH_3)$_2$ ppm. **M-2bm:** ^{1}H NMR δ = 1.77 (dd, 1 H) and 2.08 (dd, 1 H), Pt-CH_2CH(Ph)NH(CH_3)$_2$; 4.64 (1 H), Pt-CH_2C*H*(Ph)-NH(CH_3)$_2$; 7.40 (3 H, *meta* and *para*) and 7.57 (2 H, *ortho*), Pt-CH_2CH(*Ph*)NH(CH_3)$_2$ ppm. ^{13}C NMR δ = –0.6, Pt-*C*H_2CH(Ph)-NH(CH_3)$_2$; 74.5, Pt-CH_2*C*H(Ph)NH(CH_3)$_2$; 129.0 (*meta* and *para*) and 129.6 (*ortho*), Pt-CH_2CH(*Ph*)NH(CH_3)$_2$ ppm.

2bn(ClO_4): $C_{18}H_{35}Cl_2N_3O_4Pt$ (623.47): calcd. C 34.68, H 5.66, N 6.74; found C 34.39, H 5.56, N 6.84. NMR (tmeda signals are given first) **anti-M-2bn:** ^{1}H NMR δ = 2.42 (s, 3 H), 2.68 (s, 3 H), 2.78 (s, 3 H), and 2.94 (s, 3 H), CH_3N; 2.47 (1 H), 2.62 (1 H), 2.64 (1 H), and 3.02 (1 H), -CH_2N; 2.85 (dd, 1 H), Pt-C*H*(Ph)CH_2NH-(CH_2CH_3)$_2$; 2.52 (1 H) and 3.46 (1 H), Pt-CH(Ph)CH_2NH-(CH_2CH_3)$_2$; 1.36 (3 H) and 1.38 (3 H), Pt-CH(Ph)CH_2NH-(CH_2CH_3)$_2$; 3.23 (4 H), 3.49 (2 H), and 3.63 (2 H), Pt-CH(Ph)-CH_2NH(CH_2CH_3)$_2$; 7.13 (1 H, *para*), 7.21 (2 H, *meta*), and 7.59 (2 H, *ortho*), Pt-CH(*Ph*)CH_2NH(CH_2CH_3)$_2$ ppm. ^{13}C NMR δ = 48.9 and 51.8, *C*H_3N; 59.8 and 66.6, -*C*H_2N; 14.8, Pt-*C*H(Ph)-CH_2NH(CH_2CH_3)$_2$; 61.1, Pt-CH(Ph)*C*H_2NH(CH_2CH_3)$_2$; 7.8 and 9.5, Pt-CH(Ph)CH_2NH(CH_2*C*H_3)$_2$; 44.2 and 48.3, Pt-CH(Ph)-CH_2NH(*C*H_2CH_3)$_2$; 125.9 (*para*), 128.2 (*meta*), and 129.0 (*ortho*), Pt-CH(*Ph*)CH_2NH(CH_2CH_3)$_2$ ppm. ^{195}Pt NMR δ = –3294.4 ppm. **M-2bn:** ^{1}H NMR δ = 1.69 (dd, 1 H) and 2.25 (dd, 1 H), Pt-CH_2CH(Ph)NH(CH_2CH_3)$_2$; 4.66 (1 H), Pt-CH_2C*H*(Ph)NH-(CH_2CH_3)$_2$ ppm.

Azaplatinacyclobutane complexes **3xy** were prepared by treatment of a dichloromethane solution of the amine addition product **2xy** (0.2 mmol in 0.4 mL solvent) with a water solution of KOH (1.2 times the stoichiometric amount in 0.4 mL solvent). The mixture was kept under vigorous stirring for 48 h at room temperature. The organic phase was then removed, washed twice with water (1 mL), dried with Na_2SO_4, and submitted to solvent evaporation under vacuum. The oily residue, triturated with diethyl ether, afforded a white solid, which was separated by filtration of the solvent and dried. It was identified as the azaplatinacyclobutane complex. The isolated yield, referred to platinum, was ca. 90% for all compounds.

3an(ClO_4): $C_{13}H_{32}ClN_3O_4Pt$ (524.94): calcd. C 29.74, H 6.14, N 8.00; found C 29.44, H 6.03, N 7.92. NMR (tmeda signals are given first) **M-3an:** ^{1}H NMR δ = 2.79 (s, 6 H), 2.80 (s, 6 H), CH_3N; 2.35–3.30 (m, 4 H), -CH_2N; 1.04 (d, 3 H), Pt{CH_2CH(CH_3)-N(CH_2CH_3)$_2$-κC,κN}; 0.71 (dd, $^2J_{Pt,H}$ = 87.8 Hz, 1 H) and 1.23 (dd, 1 H), Pt{CH_2CH(CH_3)N(CH_2CH_3)$_2$-κC,κN}; 4.35 (m, 1 H), Pt{CH_2C*H*(CH_3)N(CH_2CH_3)$_2$-κC,κN}; 1.26 (t, 3 H) and 1.64 (t, 3 H), Pt{CH_2CH(CH_3)N(CH_2CH_3)$_2$-κC,κN}; 2.58 (m, 1 H) and 2.79 (m, 1 H), 2.92 (m, 1 H) and 3.08 (m, 1 H), Pt{CH_2CH(CH_3)-N(CH_2CH_3)$_2$-κC,κN} ppm. ^{13}C NMR δ = 50.1 and 52.7, *C*H_3N; –16.08 ($^1J_{Pt,c}$ = 583.7 Hz), Pt{*C*H_2CH(CH_3)N(CH_2CH_3)$_2$-κC,κN}; 21.8, Pt{CH_2CH(*C*H_3)N(CH_2CH_3)$_2$-κC,κN}; 73.5, Pt{CH_2*C*H-(CH_3)N(CH_2CH_3)$_2$-κC,κN}; 11.7 and 16.2, Pt{CH_2CH(CH_3)-N(CH_2*C*H_3)$_2$-κC,κN}; 57.4 and 57.6, Pt{CH_2CH(CH_3)-N(*C*H_2CH_3)$_2$-κC,κN} ppm. ^{195}Pt NMR δ = –3029.6 ppm. **anti-M-3an:** ^{1}H NMR δ = 0.63 (d, $^3J_{Pt,H}$ = 64.4 Hz, 3 H), Pt{CH(CH_3)-CH_2N(CH_2CH_3)$_2$-κC,κN}; 1.39 (m, 1 H), Pt{C*H*(CH_3)-CH_2N(CH_2CH_3)$_2$-κC,κN}; 3.79 (dd, 1 H) and 4.71 (dd, $^3J_{Pt,H}$ = 78.0 Hz, 1 H), Pt{CH(CH_3)CH_2N(CH_2CH_3)$_2$-κC,κN} ppm.

3bm(ClO_4): $C_{16}H_{30}ClN_3O_4Pt$ (558.96): calcd. C 34.38, H 5.41, N 7.52; found C 34.13, H 5.49, N 7.44. NMR (tmeda signals are given first) **anti-M-3bm:** ^{1}H NMR δ = 1.90 (s, 3 H), 2.69 (s, 3 H), 2.82 (s, 3 H), and 2.84 (s, 3 H), CH_3N; 2.43 (1 H), 2.56 (1 H), 2.64 (1 H), and 2.80 (1 H), -CH_2N; 2.85 (dd, $^2J_{Pt,H}$ = 105.4 Hz, 1 H), Pt{C*H*(Ph)CH_2N(CH_3)$_2$-κC,κN}; 4.24 (1 H) and 5.21 ($^3J_{Pt,H}$ = 99.4 Hz, 1 H), Pt{CH(Ph)CH_2N(CH_3)$_2$-κC,κN}; 2.85 (3 H) and 2.89 (3 H), Pt{CH(Ph)CH_2N(CH_3)$_2$-κC,κN}; 7.14 (1 H, *para*), 7.20 (2 H, *meta*), and 7.44 (2 H, *ortho*), Pt{CH(*Ph*)CH_2N(CH_3)$_2$-κC,κN} ppm. ^{13}C NMR δ = 49.8, 50.5, 51.1, and 53.2, *C*H_3N; 60.5 and 64.8, -*C*H_2N; –6.2 ($^1J_{Pt,C}$ = 564.4 Hz), Pt{*C*H(Ph)CH_2-N(CH_3)$_2$-κC,κN}; 83.2 ($^2J_{Pt,C}$ = 188.2 Hz), Pt{CH(Ph)*C*H_2-N(CH_3)$_2$-κC,κN}; 53.0 and 52.4, Pt{CH(Ph)CH_2N(*C*H_3)$_2$-κC,κN}; 124.6 (*para*), 128.4 (*meta*), and 127.8 (*ortho*), Pt{CH(*Ph*)-CH_2N(CH_3)$_2$-κC,κN} ppm. **M-3bm:** (not isolated in the solid state but detected in solution by performing the ring-closing reaction in an NMR tube) ^{1}H NMR δ = 1.44 (dd, 1 H) and 1.65 (dd, 1 H),

Pt{CH_2CH(Ph)N(CH_3)$_2$-κC, κN}; 5.20 (1 H), Pt{CH_2CH(Ph)N(CH_3)$_2$-κC,κN} ppm.

3bn(ClO$_4$): $C_{18}H_{34}ClN_3O_4Pt$ (587.01): calcd. C 36.83, H 5.83, N 7.16; found C 36.54, H 5.73, N 7.08. NMR (tmeda signals are given first) **anti-M-3bn:** ^{1}H NMR δ = 1.91 (s, 3 H), 2.68 (s, 3 H), 2.80 (s, 3 H), and 2.83 (s, 3 H), CH_3N; 2.48 (1 H), 2.56 (1 H), 2.62 (1 H), and 2.80 (1 H), -CH_2N; 2.57 (dd, $^2J_{Pt,H}$ = 98.0 Hz, 1 H), Pt{CH(Ph)CH$_2$N(CH$_2$CH$_3$)$_2$-κC,κN}; 4.28 (1 H) and 5.09 ($^3J_{Pt,H}$ = 94.8 Hz, 1 H), Pt{CH(Ph)CH_2N(CH$_2$CH$_3$)$_2$-κC,κN}; 1.49 (3 H) and 1.75 (3 H), Pt{CH(Ph)CH$_2$N(CH$_2$CH_3)$_2$-κC,κN}; 2.62 (1 H), 2.89 (1 H), 2.90 (1 H), and 3.34 (1 H), Pt{CH(Ph)CH$_2$N-(CH_2CH$_3$)$_2$-κC,κN}; 7.13 (1 H, *para*), 7.19 (2 H, *meta*), and 7.42 (2 H, *ortho*), Pt{CH(*Ph*)CH$_2$N(CH$_2$CH$_3$)$_2$-κC,κN} ppm. ^{13}C NMR δ = 49.9, 50.8, 51.2, and 52.7, *C*H$_3$N; 60.7 and 65.1, -*C*H$_2$N; –7.2 ($^1J_{Pt,C}$ = 564.4 Hz), Pt{*C*H(Ph)CH$_2$N(CH$_2$CH$_3$)$_2$-κC,κN}; 74.8 ($^2J_{Pt,C}$ = 188.2 Hz), Pt{CH(Ph)*C*H$_2$N(CH$_2$CH$_3$)$_2$-κC,κN}; 11.1 and 13.8, Pt{CH(Ph)CH$_2$N(CH$_2$*C*H$_3$)$_2$-κC,κN}; 56.4 and 57.7, Pt{CH(Ph)CH$_2$N(*C*H$_2$CH$_3$)$_2$-κC,κN}; 124.8 (*para*), 127.8 (*ortho*), and 128.7 (*meta*), Pt{CH(*Ph*)CH$_2$N(CH$_2$CH$_3$)$_2$-κC,κN} ppm. ^{195}Pt NMR δ = –2878.7 ppm.

In the case of unsubstituted ethene compounds **2cn/3cn**, the reaction was only performed in an NMR tube, and the species were identified and characterized by ESI-MS and NMR spectroscopy. NMR (tmeda signals are given first) **2cn:** ^{1}H NMR δ = 2.72 (s, 6 H) and 2.93 (s, 6 H), CH_3N; 2.59 (2 H) and 2.84 (2 H), -CH_2N; 1.62 (m, $^2J_{Pt,H}$ = 93.6 Hz, 2 H), Pt-CH_2CH$_2$NH(CH$_2$CH$_3$)$_2$; 3.13 (m, 2 H), Pt-CH$_2$CH_2NH(CH$_2$CH$_3$)$_2$; 1.32 (t, 6 H), Pt-CH$_2$CH$_2$NH(CH$_2$CH_3)$_2$; 3.18 (q, 4 H), Pt-CH$_2$CH$_2$NH-(CH_2CH$_3$)$_2$ ppm. ^{13}C NMR δ = 48.8 and 52.5, *C*H$_3$N; 59.9 and 66.1, -*C*H$_2$N; –9.3 ($^1J_{Pt,C}$ = 752.5 Hz), Pt-*C*H$_2$CH$_2$NH(CH$_2$CH$_3$)$_2$; 57.4, Pt-CH$_2$*C*H$_2$NH(CH$_2$CH$_3$)$_2$; 8.8, Pt-CH$_2$CH$_2$NH(CH$_2$*C*H$_3$)$_2$; 44.9, Pt-CH$_2$CH$_2$NH(*C*H$_2$CH$_3$)$_2$ ppm. ^{195}Pt NMR δ = –3336.0 ppm. **3cn:** ^{1}H NMR δ = 2.80 (s, 6 H) and 2.81 (s, 6 H), CH_3N; 2.68 (2 H) and 2.73 (2 H), -CH_2N; 0.98 (m, $^2J_{Pt,H}$ = 91.2 Hz, 2 H), Pt{CH_2CH$_2$N(CH$_2$CH$_3$)$_2$-κC,κN}; 4.46 (m, $^3J_{Pt,H}$ = 58.4 Hz, 2 H), Pt{CH$_2$CH_2N(CH$_2$CH$_3$)$_2$-κC,κN}; 1.49 (t, 6 H), Pt{CH$_2$CH$_2$N-(CH$_2$CH_3)$_2$-κC,κN}; 2.60 (m, 2 H) and 2.90 (m, 2 H), Pt{CH$_2$CH$_2$N(CH_2CH$_3$)$_2$-κC,κN} ppm. ^{13}C NMR δ = 50.5 and 52.4, *C*H$_3$N; 61.0 and 64.1, -*C*H$_2$N; –29.2 ($^1J_{Pt,C}$ = 517.4 Hz), Pt{*C*H$_2$CH$_2$N(CH$_2$CH$_3$)$_2$-κC,κN}; 67.4 ($^2J_{Pt,C}$ = 188.1 Hz), Pt{CH$_2$*C*H$_2$N(CH$_2$CH$_3$)$_2$-κC,κN}; 12.5, Pt{CH$_2$CH$_2$N(CH$_2$-*C*H$_3$)$_2$-κC,κN}; 56.7, Pt{CH$_2$CH$_2$N(*C*H$_2$CH$_3$)$_2$-κC,κN} ppm. ^{195}Pt NMR δ = –2895.3 ppm.

X-ray Crystallography

X-ray data were collected for the crystals **2bn**(ClO$_4$) and **3bn**(ClO$_4$) with a Bruker AXS X8 APEX CCD system equipped with a four-circle Kappa goniometer and a 4-K CCD detector (Mo-K_α radiation). The crystal-to-detector distance was 40 mm. The SAINT-IRIX package was employed for data reduction and unit-cell refinement.[18] All reflections were indexed, integrated, and corrected for Lorentz, polarization, and absorption effects by using the program SADABS.[19]

For compound **2bn**(ClO$_4$), which was crystallized from CHCl$_3$/pentane, a total of 33622 reflections (Θ_{max} = 37.00°) were collected. The number of independent reflections was 11082. The unit-cell dimensions were calculated from all reflections. The structure was solved by direct methods in the *Cc* space group. The model was refined by full-matrix least-squares methods. Anisotropic thermal parameters were applied for all non-hydrogen atoms. H atoms were located in difference maps, and were included in the full-matrix least-squares cycles with isotropic thermal parameters (U) fixed at 1.2 and 1.5 (for methyl group) times the values of U of the corresponding carbon atoms. The perchlorate counterion is disordered. The final difference-Fourier map showed electron-density peaks (up to 1.839 e Å^{-3}) lying near the Pt atoms.

For compound **3bn**(ClO$_4$), also crystallized from CHCl$_3$/pentane, a total of 25934 reflections (Θ_{max} = 41.00°) were collected. The number of independent reflections was 12990. The unit-cell dimensions were calculated from all reflections. The structure was solved by direct methods in the $P2_1/c$ space group. The model was refined by full-matrix least-squares methods. Anisotropic thermal parameters were applied for all non-hydrogen atoms. H atoms were located in difference maps, and the parameters were freely refined. The final difference-Fourier map showed electron-density peaks (up to 3.432 e Å^{-3}) lying near the Pt atoms.

The crystallographic data are listed in Table 2. All calculations and molecular graphics were carried out by using the SIR2004,[20] SHELXL97,[21] PARST97,[22] WinGX,[23] or ORTEP-3 for Windows packages.[24] CCDC-624564 (**2bn**) and CCDC-269917 (**3bn**) contain 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.

Table 2. Crystal data and structure refinement parameters for **2bn**(ClO$_4$) and **3bn**(ClO$_4$).

	2bn(ClO$_4$)	**3bn**(ClO$_4$)
Empirical formula	$C_{18}H_{35}Cl_2N_3O_4Pt$	$C_{18}H_{34}ClN_3O_4Pt$
Formula weight	623.48	587.02
Crystal system	monoclinic	monoclinic
Space group	*Cc*	$P2_1/c$
a [Å]	13.4927(3)	10.1870(5)
b [Å]	13.7925(3)	15.6315(7)
c [Å]	13.1851(3)	14.1576(7)
β [°]	97.424(1)	95.348(1)
V [Å^3]	2433.2(1)	2244.6(2)
Z	4	4
ρ_{calc}[g cm^{-3}]	1.702	1.737
μ[mm^{-1}]	6.013	6.397
F(000)	1232	1160
θ Range	7.11–36.84	1.95–41.21
Reflections collected	33622	25934
Data/restraints/parameters	11082/2/263	12990/0/380
Goodness-of-fit on F^2	1.029	1.041
R_1, wR_2[$F^2 > 2\sigma(F^2)$]	0.0311, 0.0682	0.0471, 0.0914
R_1, wR_2 (all data)	0.0452, 0.0732	0.0888, 0.1080

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