Neighboring Group Effects on the Stability of Azaplatinacyclobutane Rings in (2-Aminoethyl)platinum(II) Compounds

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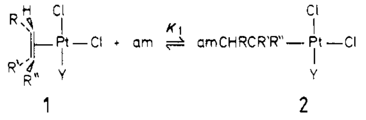
The effect of gem-dialkyl groups and of other bulky substituents on the stability of a four-membered $\overline{\text{NCCPt}}$ ring system has been investigated, cf. the Thorpe–Ingold effect. It is observed that when an amine attacks alkene complexes *cis*-[PtCl$_2$(alkene)Y], cyclic as opposed to acyclic products are more likely to be produced if the amine is secondary and the alkene is substituted.

The small saturated ring compounds of organic chemistry tend to be stabilized by substituents, in particular by gem-dialkyl groups.[1] Thus $Me_2NCH_2CMe_2CH_2Cl$ cyclizes nearly 10 times more quickly than $Me_2NCH_2CH_2CH_2Cl$ to give a four-membered ring,[2] $Me_2NCH_2C(Me\text{ or }H)_2CH_2$. However most investigations on four-membered rings have been made on oxa-, thia-, and azacyclobutanes. This raises the question of the extent to which substituents are important in stabilizing organometallic four-membered ring compounds. Until recently, examples of such compounds were few in number,[3,4] although cases have been discussed, particularly by Shaw and his co-workers, which indicate that cyclometalation is affected by bulky groups.[5] Platinum chemistry provides examples of compounds containing four-membered rings in which in addition to one platinum and two carbons, the fourth atom can be, for example, phosphorous,[6] another carbon,[7] or nitrogen.[8,9]

The last groups of these compounds, the azaplatinacyclobutanes or (2-aminoalkyl)platinum(II) complexes **3**, can often be formed quickly and reversibly by treating a solution of the appropriate η^2-alkene complex **1** with an amine as in reactions 1 and 2. (Abbreviations: acac = acetylacetonate, am = amine, am^{-H} = amine less one N proton, 4-Mepy = 4-methylpyridine, pip = piperidine, py = pyridine.)

These processes can be accompanied by another, competitive, reversible reaction, eq 3, in which an acyclic cationic species **4** is formed. Thus the system as a whole, in particular the tendency for **3** to be produced rather than **2** or **4**, provides an excellent method of studying the stability of a four-membered ring. Earlier work[9–11] has hinted that ring formation is aided by bulky groups in am, in R, and perhaps in Y. Bulky substituents may also be important in determining the reaction pathways of the closely related allene complex *cis*-[PtCl$_2$(η^2-$CH_2{=}C{=}CH_2$)(P-*n*-Pr$_3$)], which can form cyclic complexes,[12] some analogous to the alkene system but others with an eight-membered ring containing two platinum atoms.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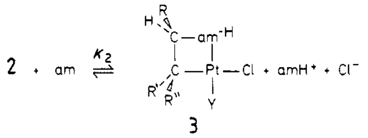
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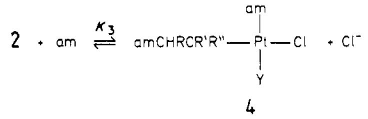
(3)

$$1 + 2\text{am} \overset{K_4}{\rightleftharpoons} 3 + \text{amH}^+ + \text{Cl}^- \qquad (4)$$

$$1 + 2\text{am} \overset{K_5}{\rightleftharpoons} 4 + \text{amH}^+ + \text{Cl}^- \qquad (5)$$

M, Y = 4-Mepy; **N**, Y = NHMe$_2$; **P**, Y = PPh$_3$; **Q**, Y = py; **S**, Y = SOMe$_2$; **a**, R = R′ = R″ = H; **b**, R = Me, R′ = R″ = H; **c**, R = Et, R′ = R″ = H; **d**, R = R′ = Me, R″ = H; **e**, R = R″ = Me, R′ = H

In ring compounds **3** am^{-H} is NMe$_2$ unless stated otherwise. "**3Pc**" is a mixture of **3Pc** and its isomer **3P** (R′ = Et, R = R″ = H).

In the present work we make a more detailed study of the effect of bulky groups on the stability of the cis-dichloro 2-alkylamino ring compounds **3** and attempt some quantification. Several aspects of "stability" are considered: isolation of the compounds as solids that can be

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Table I. ^{1}H NMR Data for Ring Compounds 3[a]

	NC*H*CPt	NCC*H*Pt	*H*$_3$CNPt
3Sa	4.46 (t) (67, 8)	1.4 (t) (96, 8)	2.76 (s) (42.5)
3Sb	4.40 (c)	1.64 (c) (92)	2.72 (s) (44), 2.82 (s) (44)
3Sc	4.05 (c)	1.32–1.88 (c)	2.65 (s) (45), 2.78 (s) (46)
3Sd	3.85 (c)[a]	1.3 (c)	2.56 (s) (46.5), 2.74 (s) (46.5)
3Se	4.41 (c)[b]	2.08 (c)	2.68 (s) (47.5)
3Sa (am = pip)	4.52 (t) (68, 8)	1.36 (t) (98, 8)	
3Pa[c]	4.25 (t) (60, 8)	0.65 (d of t) (88, 8)	2.7 (d) (35)
3Pb	4.20	0.68 (c) (90)	2.68 (d) (38), 2.82 (d) (40)
"**3Pc**"[d]	4.0 (c)	0.35 (c)	
3Mb	4.12 (c)	1.35 (c)	2.82 (d) (46)
3Mc	4.06 (c)	1.26–1.74 (c)	2.78 (d) (50)
3Qc	4.07 (c)	1.04–1.52 (c) (ca. 92)	2.58 (d) (48), 2.85 (d) (48)

[a] δ values with *J*(Pt–H)/Hz and *J*(H–H)/Hz in brackets. In $CDCl_3$ at ca. 25 °C. s = singlet; d = doublet; t = triplet; c = complex; the C*H*C*H* resonances are ABX or AMX systems. [b] Collapses to a doublet with *J* = 7.7 Hz on irradiation of C*H*$_3$C at δ 0.95. [c] Collapses to a doublet with *J* = 8.5 Hz on irradiation of C*H*$_3$C at δ 1.1. [d] Reference 9. [e] Reference 8, see note on "**3Pc**" under eq 1–5.

characterized, the formation in solution of the cyclic species **3** as opposed to the acyclic ones **2** or **4**, the strength of the Pt–N bond in the ring inferred from spectral data, and some semiquantitative equilibrium constants for reaction 2.

Experimental Section

Known Compounds. *cis*-$[PtCl_2(alkene)(SOMe_2)]$,[10,13] *cis*-$[PtCl_2(alkene)(PPh_3)]$,[14] *cis*-$[PtCl_2(alkene)(NHMe_2)]$,[10] *cis*-$[PtCl_2(alkene)(4\text{-}Mepy)]$,[10] $[Cl\overline{Pt(CH_2CH_2N}Me_2)(SOMe_2)]$,[8] and $[Cl\overline{Pt(CH_2CHRN}Me_2)(PPh_3)]$,[8,9] where R is H, Me, or Et, viz., **3Pa**, **3Pb**, or "**3Pc**", were prepared according to the published method indicated.

New Compounds. Four cyclic compounds of type **3S** were prepared from the appropriate amine and the *cis*-$[PtCl_2(alkene)(SOMe_2)]$[10] complex.

$[Cl\overline{PtCH_2CH(Et)N}Me_2(SOMe_2)]$, 3Sc. *cis*-$[PtCl_2(\eta^2\text{-}CH_2{=}CHEt)(SOMe_2)]$ (0.4 g) was dissolved in 10 cm^3 of CH_2Cl_2 at 0 °C, 70 μL of liquid Me_2NH added, and the mixture stirred for about 10 min. KOH (56 mg) dissolved in 3 cm^3 of water was added and the mixture shaken for 20 min. The CH_2Cl_2 layer was washed twice with water. The CH_2Cl_2 was removed under vacuum, giving a white solid that was recrystallized from a toluene/CH_2Cl_2 mixture. Anal. Calcd: C, 23.5; H, 4.95; N, 3.4; Cl, 8.7. Found: C, 23.6; H, 5.1; N, 3.55; Cl, 9.05.

(*E*)- and (*Z*)-$[Cl\overline{PtCH(Me)CH(Me)N}Me_2(SOMe_2)]$. Two geometric isomers are possible because of chirality at the CHMe atoms. It is assumed here that attack of Me_2NH on the *cis*-2-butene ligands is trans to platinum[11,15] as occurs in related systems. The relative rates of cyclization in the two cases support this assumption—see Discussion later. Thus **1Sd** and **1Se** give respectively **3Sd** and **3Se**. The *E* isomer **3Sd** is readily prepared by using the method above from *cis*-$[PtCl_2\{\eta^2\text{-}cis\text{-}CH(Me){=}CH(Me)\}(SOMe_2)]$ and Me_2NH. Anal. Calcd: as for **3Sc** above. Found: C, 23.6; H, 4.7; N, 3.3; Cl, 8.8. The *Z* isomer **3Se** is prepared by treating $[PtCl_2\{\eta^2\text{-}trans\text{-}CH(Me){=}CH(Me)\}(SOMe_2)]$ with Me_2NH as above, allowing the mixture to stand for 2 days at −20 °C, and then proceeding as before. Anal. Calcd: as for **3Sc** above. Found: C, 23.7; H, 4.8; N, 3.3; Cl, 8.8.

$[Cl\overline{PtCH_2CH_2N}C_5H_{10}(SOMe_2)]$, 3Sa (am = pip). This compound derived from piperidine was prepared in a similar way to **3Sc** except that it was found necessary to shake the reacting mixture for a longer period of 30 min. Anal. Calcd: C, 25.7; H, 4.9; N, 3.35. Found: C, 25.9; H, 5.1; N, 3.4.

^{1}H NMR Studies. Observations were made on solutions in $CDCl_3$ at ca. 25 °C except where stated otherwise. Where compounds could be isolated, studies were made immediately on fresh solutions. However several of the cyclic complexes could not be isolated; these were made in situ by adding at least 2 equiv of am to a solution or suspension of **1** and allowing the mixture to stand for about 25 min.

^{1}H NMR Data. Some of the more important data are summarized in Table I. The series **3Sa** to **3Se** illustrates that the peaks for NC*H*CPt and NCC*H*Pt, that is the protons on the β- and α-C (wrt Pt), are completely distinctive in δ value at about δ 4 and between δ 0.3 and 2.1, respectively. These parameters can be affected by substituents, as occurs in relatives of the acyclic species **2**, but the variation is not systematic, cf. **3Sa**, **3Sd**, and **3Se**.

When the ring system is prepared from a starting complex **1** containing a monosubstituted alkene, $RCH = CH_2$, two cyclic isomers could, in principle, be formed with R at either the α- or β-carbon. "**3Pc**" in fact consists of a mixture containing **3P** (R = Et, R′ = R″ = H) and **3P** (R′ = Et, R = R″ = H).[8] However, integration of the regions around 4 and 0.3 to 2.1 show that **3Sb**, **3Sc**, **3Mb**, and **3Mc**, and various other compounds mentioned later, do, as their formulas indicate, contain their Me or Et groups at the β-position (within experimental error of 0.1).

C*H*$_3$N protons are not necessarily inequivalent if R is Me or Et, cf. **3Sd** and **3Se** or **3Me** and **3Qc**.

The values of *J*(C*H*–C*H*) in **3Sd** and **3Se** are not dissimilar to those observed for trans and cis protons, respectively, in organic four-membered ring systems.[16]

Equilibrium Studies. These were made by adding aliquots of amine to solutions of the alkene complexes **1** in $CHCl_3$ at 25.0 °C and recording changes in absorbance at suitable wavelengths in the near ultraviolet. Procedures and formulas have been discussed earlier.[17]

Instrumentation. ^{1}H NMR work was carried out on a 100-MHz JEOL machine. Ultraviolet studies were performed on a Perkin-Elmer 554 spectrophotometer.

Results and Discussion

Isolation of the Ring Compounds 3. Several such complexes have been isolated and characterized,[8,9] namely, **3Pa**, **3Pb**, "**3Pc**", and **3Sa**. We now add **3Sc**, **3Sd**, **3Se**, and **3Sa** (am = pip) to this list. In all of these eight cyclic compounds am is either dimethylamine or piperidine, both secondary amines. All the solids derived from the reaction of primary amines and **1** that have been isolated are either neutral or charged acyclic species,[10] e.g., *cis*-$[PtCl_2(CH_2CH_2NH_2Me)(SOMe_2)]$ and *cis*-$[PtCl(NH_2\text{-}t\text{-}Bu)(CH_2CH_2NH_2\text{-}t\text{-}Bu)(SOMe_2)]^+Cl^-$. None is cyclic. (Tertiary amines and heterocyclic amines like pyridine, which cannot, of course, form ring compounds, also yield acyclic species.) Thus on the basis of the feasibility of isolating

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solids, a gem-dialkyl group on the nitrogen in the $\overline{\mathrm{NCCPt}}$ unit appears to increase stability. The next sections look at the question of stability in solution.

Identification of Ring Compounds in Solution. Two of the compounds just mentioned **3Pa** and **3Sc** and in addition **3Nd** we have identified in solution by using ^{195}Pt NMR and ^{15}N-labeled amine from $^{195}Pt{-}^{15}N$, Pt–N–C, and Pt–N–C–H couplings between the platinum atom and the amine.[9,18] However, a simpler means of detecting a ring compound in solution is provided by the position of the NC*H*CPt resonance.

In these complexes, **3Pa**, **3Sc**, and **3Nd**, and in **3Pb**, "**3Pc**", and **3Sa**, this peak occurs between δ 3.7 and 4.5,[8,9,18] as it does in the new compounds **3Sc**, **3Sd**, **3Se**, and **3Sa** (am = pip); see Table I. In the neutral and cationic acyclic species **2** and **4** respectively, the corresponding NC*H*CPt resonance appears between δ 2.2 and 3.4.[10] The appearance of peaks at δ ca. 4 was used here to detect the possible formation of cyclic compounds by reactions 1 and 2 in situ; an excess of primary or secondary amine was added to a solution or suspension of a particular alkene complex, **1**, in $CDCl_3$ at ca. 25 °C, and ^{1}H NMR spectra were run at intervals.

In such cases where a peak appears at δ ca. 4, the reaction is usually complete within 30 min and often more quickly.

Formation of Cyclic Compounds Containing SOMe$_2$ (3S). The ethene/SOMe$_2$ complex **1Sa** can yield either ring or a cyclic species on the basis of the procedure just mentioned. Peaks between δ 3.0 and 3.3 are produced initially on addition of all the amines tested: *n*- and *i*-PrNH$_2$; *n*-, *i*-, *sec*-, and *t*-BuNH$_2$; $C_5H_9NH_2$; $C_7H_{13}NH_2$; Me$_2$NH; Et$_2$NH; *n*-Pr$_2$NH; *n*-Bu$_2$NH; pip; pyrrolidine; morpholine. However these are replaced by resonances at between δ 4.45 and 4.55 within about 20 min in all the cases in which the amine is secondary as opposed to primary. So far cyclization seems dependent on a gem-dialkyl group. The 1-butene/SOMe$_2$ complex **1Sc** behaves slightly differently. Addition of the secondary amines once again gives the ring-type resonance, now at δ 4.00–4.10, but of the primary amines, *tert*-butylamine does also, with δ 4.58. Thus two vicinal alkyl groups can also bring about cyclization. (The cyclic compounds formed from the 1-butene complex **1Sc** are of **3Sc** type, having the Et group as R rather than R′ or R″; see Experimental Section).

Ring compounds are also produced within minutes when dimethylamine reacts with the analogous propene and *cis*-2-butene complexes **1Sb** and **1Sd**, respectively. The speed of appearance of the peaks at δ ca. 4 indicates an increase in the rate of cyclization of **1Sa** to **3Sa** with change of am: Me$_2$NH < Et$_2$NH < *n*-Pr$_2$NH < *n*-Bu$_2$NH. When the alkene is varied with Me$_2$NH as am, the rate of formation of the ring compound again rises: **3Sa** < **3Sb** < **3Sc** < **3Sd**. Thus in the SOMe$_2$ systems so far discussed the rate of cyclization is increased by bulkiness in am, at the carbon β to Pt and perhaps at the α-C also.

The *trans*-2-butene complex **1Se** is somewhat different kinetically, several hours being required for the formation of **3Se** to reach completion. As was pointed out in the Experimental Section, attack by am on the alkene ligand in a complex like those here is trans to the platinum,[11,15] so that **1Se** gives rise not to **3Sd** but to **3Se**, in which the *C*-methyl groups are eclipsed, at least if the ring is planar. (In $[\mathrm{Cl}\overline{\mathrm{Pt\{C({=}CH_2)CH_2N}}\mathrm{H}\text{-}t\text{-}\mathrm{Bu\}(P\text{-}}n\text{-}\mathrm{Pr_3)}]$, which is similar to the cyclic systems here apart from being derived from an allene complex, the ring only deviates from planarity by 0.06 Å.[12]) Presumably the slowness of formation of the *Z* isomer **3Se** arises from steric retardation.

Like the dichloro complex **1Sa**, *cis*-[PtBr$_2$(η^2-C$_2$H$_4$)(SOMe$_2$)] reacts with dimethylamine to give a ring-type resonance but more rapidly. As chloride is usually a better leaving group than bromide in the platinum(II) substitution process,[19] the faster reaction of the dibromo complexes could arise from a size effect. It has been observed before that a bromide ligand is better than chloride in effecting cyclization.[20]

Cyclic Compounds Containing PPh$_3$. The reaction of **1Pa** and a primary or secondary amine is complete within the time taken to run a conventional ^{1}H NMR spectrum. Secondary amines are known[9] to give peaks at δ ca. 4 characteristic of ring compounds, as does in this case, *tert*-butylamine.[9] Although other primary amines produce ^{1}H NMR spectra with resonances[9] around δ 2.4, which could be due to acyclic species **2P** or **4P**, this assignment is not completely satisfactory since the corresponding UV spectra are unlike those of comparable systems containing other Y groups. The difference in behavior of *tert*-butylamine between the ethene/PPh$_3$ and ethene/SOMe$_2$ systems suggests that the bulkiness of Y is also important in ring formation. PPh$_3$ is certainly larger than SOMe$_2$. While other evidence is less conclusive,[10] we will take the point up again later.

There is another system in which *tert*-butylamine reacts differently from less bulky primary amines with a phosphine complex. When it attacks the allene complex *cis*-[PtCl$_2$(η^2-*C*H$_2$=*C*=CH$_2$)(P-*n*-Pr$_3$)], a four-membered ring compound[12] is produced analogous to those here. The other primary amines lead to the formation of eight-membered rings.[12]

The analogous propene and 1-butene complexes **1Pb** and **1Pc** also react with dimethylamine within manipulation time to give the ^{1}H NMR spectra of the ring compounds **3Pb** and "**3Pc**". **1Pc** is unlike the other 1-butene systems studied here, which give a **3c** type ring, in that it forms an isomeric mixture containing not only **3Pc** (with R = Et) but also **3P** (R′ = Et, R = R″ = H).[8]

Cyclic Compounds in Which Y Is an Amine. Treatment of the ethene/dimethylamine complex **1Na** with dimethylamine gives a peak at δ 2.98, but no resonances are observed around δ 4 even after several hours. In contrast, the propene, 1-butene, and *cis*-2-butene analogues **1Nb**, **1Nc**, and **1Nd**, respectively, on similar treatment do give spectra with peaks at δ 3.82, 3.58, and 3.72, respectively, on standing, the reactions being complete within 30 min. Although products have not been isolated in these three instances, **3Nd** has been identified in solution by multinuclear NMR[18] so that it is reasonable to assume that **3Nb** and **3Nc** are also formed. These experiments show that when Y is NHMe$_2$, the course of the reaction can be altered by the introduction of a substituent at the β-carbon to Pt to give ring compounds, which would otherwise not have been formed. (Integration of peaks shows that **1Nb** and **1Nc** are as designated, with the Me or Et group, respectively, on the β-carbon of the ring. In contrast 3-methyl-1-butene leads to a mixture of two cyclic isomers in which the *i*-Pr is either on the β- or α-carbon.[11]) Similar behavior is also shown when Y is

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Table II. Various IR Peaks (in KBr) and Values of $^3J(PtNCH_3)$ (in $CDCl_3$ at ca. 25 °C) for Ring Compounds 3S (with am = $NHMe_2$)

	ν(Pt–^{14}N)/cm^{-1}			ν(S=O)/cm^{-1}	^3J(Pt-H)/Hz
3Sa	569[a]	444	373	1137	42.5
3Sb	572				44
3Sc	575 (543)[b,c]	446 (446)[b]	375 (375)[b]	1133 (1133)[b]	45.5
3Sd	578	447	379	1130	46.5
3Se	589	449	382	1127	47.5

[a] Refers to 3Sa (am = pip). [b] Values in parentheses refer to ^{15}N. [c] In the ^{15}N system there is also a peak at 554 cm^{-1} for which we are not suggesting an assignment.

4-methylpyridine. On treatment with dimethylamine the ethene/4-Mepy complex **1Ma** produces a peak at δ 2.92 but gives no evidence for the formation of a cyclic compound, but the propene and 1-butene analogues **1Mb** and **1Me** produce ring-type peaks at δ 4.12 and 4.06, respectively.

Earlier, it was pointed out that the different reaction pathways of *tert*-butylamine (as am) with ethene/Y complexes indicate that PPh_3 could be interpreted as being a more bulky Y group than $SOMe_2$ is. Similarly the fact that the attack of dimethylamine on the same system leads to an acyclic product when Y is $NHMe_2$ or 4-Mepy, as opposed to a ring when it is PPh_3 or $SOMe_2$, suggests the possibility of a size effect again. It is perfectly reasonable to regard $NHMe_2$ as being less bulky than $SOMe_2$, and the same could be true of 4-Mepy if it is thought of as two-dimensional.

There is another aspect of the formation of ring compounds when Y is an amine that is curious. Unlike $SOMe_2$ and PPh_3, amines are not trans labilizing so that substitution trans to $NHMe_2$ normally takes several hours in a platinum(II) system.[19] Thus when Y is $NHMe_2$, it ought not to labilize the Cl trans ligand[19] which is displaced during cyclization. Further, amines are not good entering groups in platinum(II) systems[19] so that the rapid formation of the Pt–am bond involved in ring closure cannot be justified on the basis that the $CHCH\mathit{N}HMe_2$ group attacks the Pt readily.

We have also observed that bulky substituents on coordinated alkenes affect the behavior of the corresponding trans isomers *trans*-$[PtCl_2(alkene)(NHMe_2)]$.[11] The ethene complex on treatment with excess $NHMe_2$ gives *trans*-$[PtCl_2(CH_2CH_2NHMe_2)(NHMe_2)]$ as expected but the *cis*-but-2-ene analogue forms **3Sd**, which is the ring compound expected from the cis-dichloro/alkene complex **1Sd**. It was suggested that cyclization involves the formation of a five-coordinate intermediate, square pyramidal in shape, which then undergoes intramolecular rearrangement. It is normally assumed that the intermediate in a substitution process involving platinum(II) is trigonal bipyramidal in shape.[19] However if cyclization involves a different mechanism with square-pyramidal intermediates which rearrange, then an explanation is provided for the anomalous behavior when Y is not trans labilizing. Whether this explanation is correct or not, in the ring closure reactions in which Y is an amine, a substituent on the β-carbon leads to considerable labilization of a bond not normally easily broken.

Strength of the Pt–am^{-H} Bond. The work so far demonstrates that the presence of substituents favors the formation of the four-membered ring. In this and the next sections attempts are made to estimate the stability of these rings more quantitatively.

When ^{14}N is replaced by ^{15}N in **3Sc**, the peak at 575 cm^{-1} is replaced by two, at 554 and 543 cm^{-1}. Hence the absorption at 575 cm^{-1} must be accidentally degenerate, part of it and the peak at 543 cm^{-1} being due to ν(Pt–^{14}N) and ν(Pt–^{15}N), respectively. The corresponding peaks in various other ring compounds, **3S**, apart from **3Sa**, are also degenerate, and frequencies are given in Table II. (Since the position of ν(M–N) in metal amines is somewhat varied and contentious,[21] two other sets of peaks that appear in this general region are also included.) Unfortunately the absorption at ca. 570 cm^{-1} is not clear for **3Sa** when am is $NHMe_2$, the amine involved in all the other compounds discussed in this section; the value in Table II refers to the new complex described in the Experimental Section, **3Sa** (am = pip). ν(Pt–N) rises as the starting alkene becomes more bulky which suggests that substituents on the carbon atoms in the four-membered ring strengthen the Pt–N bond.

The increase in ν(Pt–N) is larger in **3Se**, where the *C*-methyl groups are eclipsed, than in **3Sd**, that is in the *Z* as opposed to the *E* isomer. Yet **3Sd** is formed more quickly than **3Se** from the respective starting alkene complex **1Sd** or **1Se**. Thus if the interpretation of ν(Pt–N) is correct, it appears that neighboring group interaction can effect ring stability in both a thermodynamic and kinetic sense.

Peaks at ca. 1130 cm^{-1} are assigned to ν(S=O);[13] see Table II. There appears to be an inverse correlation between this parameter and the bulkiness of the substituents.

$^3J(PtNCH_3)$ coupling constants are given in Table II for the $SOMe_2$-containing ring compounds just mentioned **3S**. This quantity also appears to be affected by substituents on the carbon atoms of the ring, small but significant increases occurring as bulky group are introduced. This *J* also rises from 35 to 38 Hz between **3Pa** and **"3Pc"** (with $NHMe_2$ as am). While the increases could arise from variations in dihedral angle, in this context it seems plausible to correlate them with shortening of the Pt–N bond[22] as substituents are introduced. Support is provided for the suggestion that ^3J(Pt–H) gives a measure of the strength of the Pt–N bond by the fact that in the ring compounds **3c** (i.e., those based on 1-butene), this coupling constant rises as the trans effect exerted by Y falls, viz., PPh_3, 38 Hz, $SOMe_2$, 45.5 Hz, and 4-Mepy, 50 Hz.

Equilibrium Studies. Reactions 1–3 are reversible (which can be demonstrated by addition of acid to solutions of 3 for example) so that in principle it is possible to measure the equilibrium constants K_1 and K_2. (Equilibrium constants are numbered according to the equation to which they refer, viz., K_1 denotes equilibrium 1. For convenience reaction 4 is introduced.) The changes in absorbances when aliquots of Z are added to X can be used to obtain the equilibrium constant for a system

$$X + nZ \rightleftharpoons XZ_n \qquad (6)$$

by plotting graphs, which should be linear, of either (i) $\{(A_0 - A_x)/(A_x - A_\infty)\}$ against $[Z]^n$ or (ii) $1/|A_0 - A_x|$ against

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(22) Appleton, T. G.; Hall, J. R. *Inorg. Chem.* 1971, *10*, 1717.

Table III. Relative Values of K_4 in $CHCl_3$ at 25.0 °C

am	Sa	Pa
Me_2NH	1[a]	0.5
Et_2NH	1.0	3.5
n-Pr_2NH	0.6	7.1
n-Bu_2NH	1.1	11

[a] Values are quoted relative to Sa (am = $NHMe_2$). On this basis the relative value of K_5 for Sa (am = NH_2-n-Pr) is 1.[10]

$1/[Z]^n$ where A_0, A_x, and A_∞ are absorbances after addition to a solution of X of zero, an aliquot and a large excess of amine, respectively.[17]

In the present systems K_1 is obtainable in principle by using method ii if linear graphs are produced when n is 1 and when [am] < [Pt]. Although linear plots are given on treatment of the ethene/$SOMe_2$ and the ethene/PPh_3 complexes **1Sa** and **1Pa** with various secondary amines, the intercepts are small so that the resulting values of K_1 (which is given by intercept/gradient)[17] are not sufficiently precise for comparative studies to be made.

Application of method i to data for which [am] > [Pt], with n equal to 2, provides a possible means of obtaining K_4. With the concentrations used in this section, equilibrium is established within about 10 min when secondary amines are added to the ethene/$SOMe_2$ complex **1Sa** and almost within mixing time in the case of **1Pa**, the ethene/PPh_3 compound. Good linear graphs are obtained on plotting $\{(A_0 - A_x)/A_x - A_\infty)\}$ vs. $[am]^2$ provided [am] > [Pt]. This appears to indicate a stoichiometry of Pt:am = 1:2 as in reaction 4. However (4) is not equivalent to (6) (with n equal to 2) since more than one entity is produced on the right-hand side in the former but not the latter. However, method i breaks down, if species other than just XY_n are produced on the right-hand side of the equilibrium. Nevertheless better linear graphs are obtained by using method i (with n equal to 2) in its simplest form as above than by introducing modifications to it to allow for the production of species such as Cl^- and amH^+ as in (4). The fact that the simple plots are linear suggests that amH^+ and Cl^- are not formed as entities discrete from the ring compound **3** in $CHCl_3$, the aprotic solvent which was used in these experiments. Evidence to support this supposition is provided by the fact that in some instances a solid can be isolated that analyses as a 1:1 mixture of ring compound plus amH^+Cl^-, e.g., $\{[Cl\overline{PtCH_2CH_2N}Me_2(PPh_3)]\cdot Me_2NH_2Cl\}$.[9]

The values obtained for K_4 using method i for **1Sa** and **1Pa** and various secondary amines are of the order of 10^6 dm^6 mol^{-2}. Unfortunately these figures are far too large[11] to be interpreted as reliable absolute values. However as K_4 is simply the gradient of a linear graph[17] and as gradients can easily be compared quantitatively, it is possible to calculate relative values of K_4 that are reasonably reliable; see Table III.

In the $SOMe_2$ system K_4 hardly changes but it does increase in the PPh_3 case between Me_2NH and n-Bu_2NH. However the more interesting parameter is K_2 which equals K_4/K_1. While K_1 could not be obtained with sufficient reliability for comparative purposes here, as mentioned above, it falls in value with an increase in the bulkiness of am in the analogous reactions between am and *trans*-$[PtCl_2(alkene)am]$[17] and $[PtCl(alkene)(XY)]$.[17,23] (XY are various bidentate ligands such as acetylacetonate, picolinate, and isoquinolinate.) Thus it seems fair to assume that K_1 falls between Me_2NH and n-Bu_2NH in the systems here, from which it follows that K_2 rises correspondingly. Thus ease of ring closure, as estimated by K_2, is increased by the bulkiness of am in both the ethene/$SOMe_2$ and ethene/PPh_3, **Sa** and **Pa**, systems. As K_4 already rises with bulkiness in the phosphine case, the increase in the tendency to cyclize may be greater there. Such an effect would be in keeping with the earlier observation on the reaction of *tert*-butylamine and the ethene systems in which PPh_3 behaved as if it were more bulky than $SOMe_2$.

Conclusion. Neighboring group effects do seem to be important in stabilizing compounds containing the four-membered azaplatinacyclobutane ring in the system $Cl\overline{Pt(CCam}^{-H})(Y)$.

1. It is easier to isolate such compounds if they are derived from dimethylamine or piperidine rather than primary amines.
2. ^1H NMR spectroscopy indicates that they are formed in solution to a greater extent: (a) from secondary as opposed to primary amines; (b) if substituents are present on the β-carbon of the ring (with respect to Pt), viz., Y = $NHMe_2$ or 4-Mepy; (c) if Y is PPh_3 as opposed to $SOMe_2$, viz., am = t-$BuNH_2$; (d) if Y is $SOMe_2$ as opposed to $NHMe_2$ or 4-Mepy, viz., with both carbons unsubstituted.
3. This technique also indicates that they are formed more quickly in solution if there are substituents on the carbon atoms of the ring, viz., the rate of appearance: **3Sa** < **3Sb** < **3Sc** < **3Sd**.
4. ν(Pt–N) stretching frequencies, and maybe ^3J(Pt–N) coupling constants, point to a decrease in the Pt–N bond length as the carbon atoms become more substituted (in the $SOMe_2$ system).
5. Equilibrium constants suggest that ring closure is favored thermodynamically by an increase in the bulkiness of the amine.

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Registry No. **1Ma**, 57918-49-7; **1Mb**, 88244-52-4; **1Me**, 88244-53-5; **1Na**, 88244-54-6; **1Nb**, 88244-55-7; **1Nc**, 88244-56-8; **1Nd**, 75009-40-4; **1Pa**, 38095-87-3; **1Pb**, 39722-83-3; **1Pc**, 39722-84-4; **1Sa**, 39722-87-7; **1Sb**, 39832-16-1; **1Sc**, 39722-88-8; **1Sd**, 61128-89-0; **1Se**, 61176-42-9; **3Mb**, 88200-55-9; **3Mc**, 88200-56-0; **3Nd**, 88244-57-9; **3Pa**, 84924-91-4; **3Pb**, 88244-58-0; **3Pc**, 88244-59-1; 3P(R′ = Et, R = R″ = H), 88200-57-1; **3Qc**, 88200-58-2; **3Sa**, 88244-60-4; **3Sa** (am = pip), 88211-02-3; **3Sb**, 88200-59-3; **3Sc**, 74993-99-0; **3Sd**, 88200-60-6; **3Se**, 88244-61-5; *cis*-$[PtBr_2(\eta^2\text{-}C_2H_4)(SOMe_2)]$, 88200-61-7; n-$PrNH_2$, 107-10-8; i-$PrNH_2$, 75-31-0; n-$BuNH_2$, 109-73-9; i-$BuNH_2$, 78-81-9; *sec*-$BuNH_2$, 13952-84-6; t-$BuNH_2$, 75-64-9; $C_7H_{13}NH_2$, 111-68-2; Me_2NH, 124-40-3; Et_2NH, 109-89-7; n-Pr_2NH, 142-84-7; n-Bu_2NH, 111-92-2; pip, 110-89-4; pyrrolidine, 123-75-1; morpholine, 110-91-8.

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