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Olefin strain energies and platinum complexes of highly pyramidalised alkenes

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Dedicated to the memory of Professor Michael Dewar on the 50th anniversary of the publication of his paper ‘A Review of the π-Complex Theory’

Abstract

Density functional theory has been used to investigate the platinum complexes of a series of 16 highly pyramidalised alkenes. Olefin pyramidalisation strain energies (OPSE) were calculated at the B3LYP level for the free alkenes. The geometries and binding energies of the platinum complexes are reported. The charge decomposition analysis procedure was used to quantitatively investigate the nature of the bonding in these complexes. This showed that the metal–alkene bond in 14 of the complexes could be interpreted in terms of the Dewar model of donation and back donation. For two series of alkenes, the back donation becomes more important as the degree of pyramidalisation increases. For these two series of alkenes, it was found that a useful correlation exists between the binding energies of the platinum complexes and either the donation/back donation ratio, the pyramidalisation angle, or the OPSE of the free alkene.

Keywords: Molecular orbital; Density functional; Alkene complexes; Strain energies

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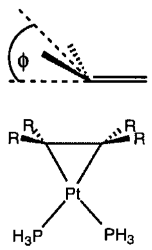
1. Introduction

In a previous paper [1] we examined in some detail the nature of the metal–alkene bond in the platinum complexes of a series of increasingly pyramidalised alkenes. In that work we investigated the relationship between the calculated binding energies and various orbital analyses, measures of donation and back donation, and olefin strain energies (OSE) (the OSE is a measure of the extra strain introduced into a system by the alkene bond) [2]. We found an excellent correlation between the OSE for the free alkene and the binding energy of the complex for the series of five complexes that we studied. On this basis we predicted the likely binding energy in three, as yet, unstudied complexes. The purpose of this paper is to investigate this relationship further, obtain calculated binding energies for the three predicted compounds, and survey a wider range of pyramidalised alkenes and their platinum(0) complexes.

Pyramidalised alkenes [3–5] are compounds where the substituents on the C=C bond are bent out of the usual plane. The pyramidalisation angle, ϕ, is a measure of this distortion as shown below. The platinum complexes of such alkenes that we have studied are represented by the general picture shown here. The nature of the metal–alkene bonding in the simplest case where R = H has been investigated by many authors [1,6–34] and has included detailed analyses of the donation and back donation effects as a function of pyramidalisation of the ethylene fragment.



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Although we have shown that the OSE provides perhaps the best correlation with binding energies, complementary ideas have been put forward in the past. For example, Godleski et al. [35]. have explained that a strained alkene will benefit from rehybridisation, whether it be by hydrogenation or metal complexation. And nearly 30 years ago Herberhold [36] noted that a rough correlation existed between ΔH(hydrogenation) and K(complexation).

In our earlier work, we carried out charge decomposition analyses (CDA) [37] which allowed us to investigate the platinum–alkene bond in terms of donation and back-donation contributions. The standard model to describe this sort of bonding in metal–alkene complexes is of course that due to Dewar [38] and Chatt and Duncanson [39]. Dewar first outlined the idea of his model in his paper published 50 years ago. In an answer to a question from Bartlett, he is reported as saying “The d-electrons in heavy metals… have the correct symmetry to interact with the antibonding π-MO of an olefine”. And thus he introduced the concept of the second dative bond from the metal to the alkene which gives rise to the back donation effect. His insight and explanations have guided many in the interpretation of donor–acceptor bonds since that time. In this paper I will use the CDA once again to probe the nature of the bonding in these platinum complexes of highly pyramidalised alkenes.

As mentioned, the OSE of an alkene is defined as the extra strain introduced into a molecule by the presence of the double bond. So perhaps the simplest way of calculating it is as the difference between the strain energy of the alkene and the strain energy of the corresponding alkane. This could be done, for example, by using molecular mechanics to calculate the strain energies [2]. An alternative approach suggested by Borden [40] is to calculate it as the difference between the hydrogenation energy of the strained alkene and the hydrogenation energy of the unstrained alkene. This latter approach is more amenable to quantum chemical calculations. Borden has also suggested [40] that in the case of pyramidalised alkenes it makes sense to consider the strain energy as arising from two sources: one is the presence of the double bond, and the other is the extra strain caused by pyramidalisation of the alkene bond. This latter contribution is termed the olefin pyramidalisation strain energy (OPSE).

In this paper I report my studies of 12 new platinum(0) complexes of pyramidalised alkenes. Binding energies, charge decomposition energies, and OSE and OSPE values will be presented.

2. Theoretical methods

Structures of all the hydrocarbons were initially prepared in PCModel [41] and then minimised and their strain energies calculated with the MM3 program [42]. In some cases involving cyclopropene rings a few of the MM3 parameters were estimated. The details of these parameters are listed in the supporting information [43]. Conformational searching was carried out for all of the hydrocarbon systems via the Saunders stochastic search algorithm [44] implemented within MM3. Although many systems had little flexibility, this nevertheless ensured that the global minimum of each system was selected. Full geometry optimisations for all the structures, including the platinum complexes of the alkenes, were then carried out with the use of the B3LYP [45–47] density functional level of theory and the standard ‘Basis Set II’ [31] of Frenking and co-workers. This basis set incorporates the Hay and Wadt [48] small-core relativistic effective core potential and double-zeta valence basis sets (441/2111/21) on platinum, and 6-31G(d) [49–51] on the other atoms. Sets of five d-functions were used in the basis sets throughout these calculations. Optimisations were for the most part carried out in C_1 symmetry and thus one can be confident that they correspond to true minima. In our previous paper on similar systems [1] we showed that carrying out the optimisations with several other density functionals leads to negligible changes in the geometries. Several recent studies [52,53] have also considered the use of TCSCF and MP2 methods for the study of highly pyramidalised alkenes and have shown that the B3LYP method gives equivalent or superior results. In two previous papers [1,34] we also carried out high-level CCSD(T) calculations on five platinum complexes of alkenes. There we found that there was good correlation between the CCSD(T) relative energies and the B3LYP values (in fact, we were able to use this relationship to estimate CCSD(T) values using the isostructural reaction approach [54]). In this study I wish to evaluate 12 complexes for which the CCSD(T) method would prove rather challenging from a practical point of view. Given the reasonable correlation between B3LYP and CCSD(T), the fact that the trends are more interesting than the absolute values, and the computational difficulty of carrying out CCSD(T) for these systems, I have limited myself to the B3LYP approach in this paper. Since this is the same level of theory that we used previously, this enables a direct comparison with our previous results. These molecular orbital calculations were performed with the GAUSSIAN 98 [55] program.

As mentioned in the introduction, olefin strain energies may be calculated in two ways:

$$\text{OSE} = \text{strain energy(alkene)} - \text{strain energy(alkene–H}_2\text{)} \quad (1)$$

$$\text{OSE} = \Delta H_{\text{hydrog}}(\text{strained alkene}) - \Delta H_{\text{hydrog}}(\text{unstrained alkene}) \quad (2)$$

In addition, the olefin pyramidalisation strain energy suggested by Borden [40] can be evaluated as:

$$\mathrm{OPSE} = \Delta H_{\mathrm{hydrog}}(\text{pyramidalised alkene}) - \Delta H_{\mathrm{hydrog}}(\text{unpyramidalised alkene}) \qquad (3)$$

In this paper results obtained using Eqs. (1) and (3) are presented.

A CDA for each system was carried out with the CDA [37] program. In the CDA method the (canonical, natural or Kohn–Sham) molecular orbitals of the complex are expressed in terms of the MOs of appropriately chosen fragments. In the present case, the Kohn–Sham orbitals of the complexes are constructed in the CDA calculation as a linear combination of the orbitals of the fragments, e.g. the alkene ligand and the metal fragment. Thus, three single-point calculations are involved for each system: one on the optimised geometry of the complex, and one on each of the fragments frozen at their geometries in the complex. The orbital contributions to the charge distributions are divided into four parts: (i) the mixing of the occupied orbitals of the alkene and the unoccupied MOs of the metal fragment (alkene → Pt donation *d*); (ii) the mixing of the unoccupied orbitals of the alkene and the occupied MOs of the metal fragment (alkene ← Pt back donation *b*); (iii) the mixing of the occupied orbitals of the alkene and the occupied orbitals of the metal fragment (alkene ↔ Pt repulsive polarisation *r*); and (iv) the mixing of the unoccupied orbitals of the alkene and the unoccupied orbitals of the metal fragment (residual term Δ). The residual term Δ should be ~ 0 for true donor–acceptor complexes [56]. A more detailed description of the method and the interpretation of the results can be found in the literature [37,56–65].

The structures of all the species studied in the current work are presented in Figs. 1 and 2. In my system of numbering, I have used ‘E’ to designate the alkene, ‘A’ to designate the corresponding hydrogenated structure, and ‘RE’ and ‘RA’ to designate the reference alkenes and alkanes for the OPSE calculations. Later on I will use ‘PtE’ to designate the platinum complexes of the pyramidalised alkenes. Total energies and complete sets of cartesian coordinates for the optimised geometries are available from the author [43].

3. Results and discussion

3.1. Pyramidalised alkenes

Several reviews on pyramidalised alkenes have been published [3–5] and there is still much recent interest in

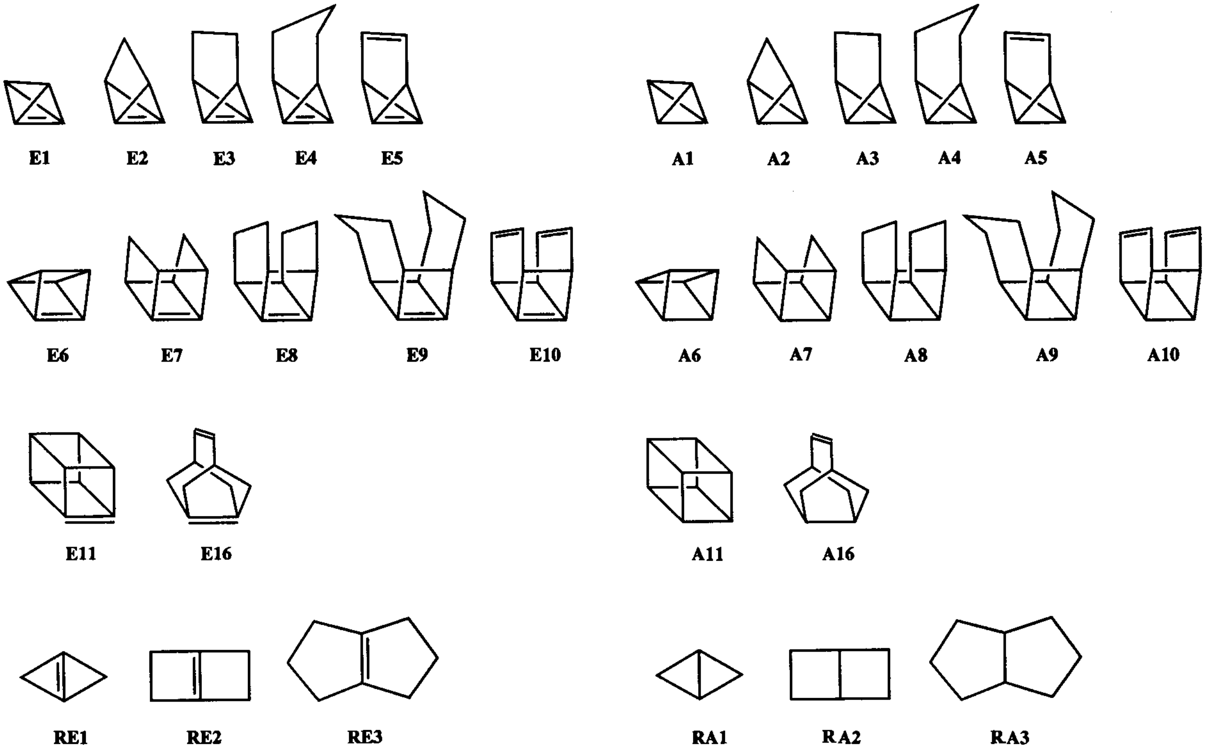
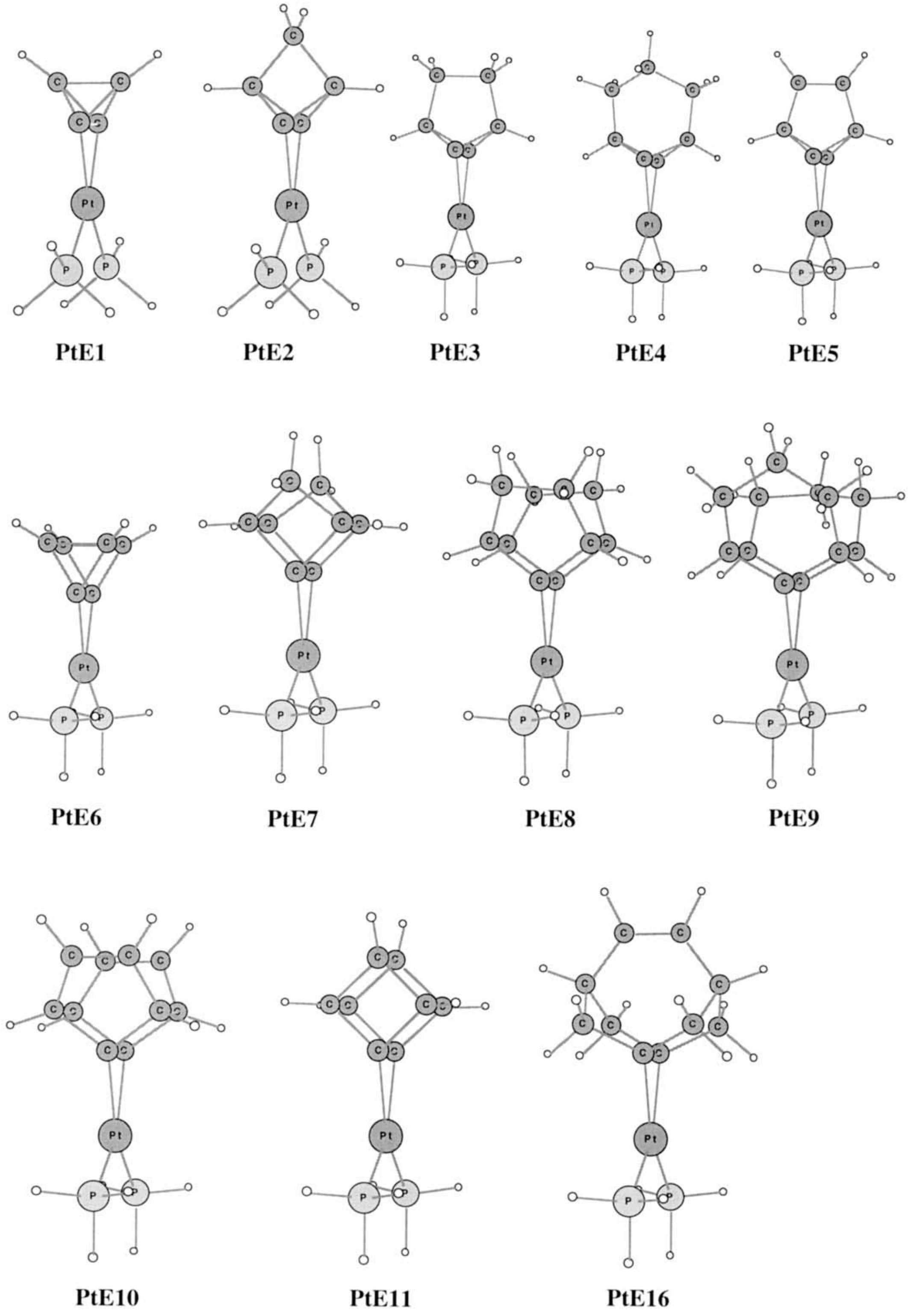


Fig. 1. Alkenes and alkanes investigated in this work.



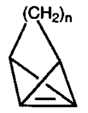
PtE1 **PtE2** **PtE3** **PtE4** **PtE5**

PtE6 **PtE7** **PtE8** **PtE9**

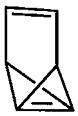
PtE10 **PtE11** **PtE16**

Fig. 2. Platinum complexes investigated in this work.

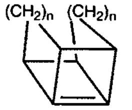
the field today [53,66,67]. To complement our earlier work I have chosen two series of pyramidalised alkenes incorporating the bicyclo[1.1.0]butene fragment (structures **E1**–**E5**) and the bicyclo[2.2.0]hexene fragment (structures **E6**–**E11**).



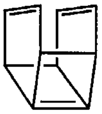
E1-E4 (n=0-3)



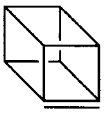
E5



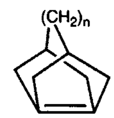
E6-E9 (n=0-3)



E10



E11

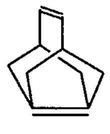


E12-E15 (n=0-3)

Table 1
Pyramidalisation angles, butterfly angles (°) and C=C bond distances (Å) in the pyramidalised alkenes

Alkene	Pyramidalisation angle (ϕ)	Butterfly angle (ω)	C=C bond distance
E1	56.3	52.0	1.373
E2	54.5	42.7	1.344
E3	47.7	33.6	1.358
E4	42.5 [a]	27.8	1.366
E5	52.6	37.5	1.337
E6	89.4	56.1	1.470
E7	85.6	43.3	1.384
E8	83.2	32.9	1.357
E9	81.3 [a]	23.7	1.342
E10	80.6	33.4	1.349
E11	87.9	40.6	1.393
E12	61.9	36.2	1.380
E13	53.7	27.8	1.362
E14	42.2 [a]	19.4	1.349
E15	27.9 [a]	11.6	1.342
E16	43.4	20.2	1.350
RE1	35.6	21.8	1.375
RE2	0	0	1.320
RE3	5.8	2.5	1.337

[a] Average of the two values in this alkene.

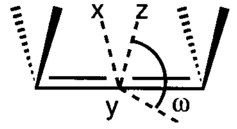


E16

The results for these compounds are compared with our earlier results for structures **E12**–**E15** which incorporate the bicyclo[3.3.0]octene fragment. Structure **E16**, which we did not study earlier, is included for completeness. Some of these pyramidalised alkenes (**E1**–**E5** and **E12**–**E16**) have been studied very thoroughly by Borden [4,40] while cubene has of course been studied theoretically by a number of groups [40,66,68]. The three series of alkenes described here (based on 3-, 4-, and 5-membered rings) provide a good basis for investigating the binding energies of the platinum complexes and comparing the trends as the degree of pyramidalisation increases. In addition, in our previous paper [1] we made predictions about the likely platinum binding energies of **E3**, **E11** and **E16**, so it will be important to test out those predictions in this work.

3.1.1. Geometries

All the alkenes had the expected geometries. Most of them were fairly symmetric, but it was found that **E8** underwent a slight distortion into C_1 symmetry. The calculated pyramidalisation angles and C=C bond distances are shown in Table 1. (Complete geometry specifications are available in the supporting information.) For the species containing the bicyclobutene fragment the angles reported are actually the supplement of the pyramidalisation angle defined in the introduction (following the suggestion of Borden [40]). However, the pyramidalisation angles for the bicyclobutene and bicyclohexene containing species do not provide a meaningful measure of their degree of non-planarity. For example, a deviation from planarity of the CH_2 carbon atoms in bicyclohexene by a mere 0.1 Å leads to a pyramidalisation angle of 35°. For symmetric alkenes, I propose an alternative definition as shown below:



This butterfly angle, ω, is orthogonal to the previously defined pyramidalisation angle. Since the dashed line in the hypothetical plane is not easily defined, in practice I have calculated this angle as the complement of half the folding angle between the rings, i.e.

butterfly angle, $\omega = 90° - XYZ/2$

For a planar alkene this angle would be zero, and would rise towards a maximum of 90° in very highly pyramidalised alkenes. The calculated butterfly angles

Table 2
Heats of hydrogenation, olefin strain energies and olefin pyramidalisation strain energies (kJ mol^{-1})

Alkene	Heat of hydrogenation [a]	OSE [b]	OPSE [a]
E1	623.1	136.8	239.3
E2	453.9	107.4	70.1
E3	415.9	198.5	32.1
E4	377.4	253.6	−6.3
E5	287.2	364.5	−96.5
E6	409.5	–	130.1
E7	381.4	1.3	101.9
E8	403.8	18.6	124.3
E9	342.5	56.4	63.0
E10	398.5	3.9	119.1
E11	353.3	5.2	73.8
E12	260.8 [c]	125.1 [c]	304.6 [c]
E13	175.2 [c]	102.5 [c]	218.8 [c]
E14	–	76.1 [c]	156.5 [c]
E15	–	41.0 [c]	74.1 [c]
E16	280.8	87.4	144.0
RE1	383.8	184.3	0
RE2	279.5	74.1	0
RE3	136.8	3.2	0

[a] B3LYP/6-31G(d) values (with five d polarisation functions).

[b] From molecular mechanics strain energies.

[c] From Hrovat and Borden [38].

for the alkenes in this study are shown in Table 1. In each series there is a regular decrease in ω corresponding to a gradual decrease in the out-of-plane deformation of the alkene. It may be noted that ω is much lower in the series of structures containing the bicyclooctene fragment; in other words, there is considerably less out-of-plane deformation of the alkene bond in these structures. If the pairs of structures **E3**/**E5**, **E8**/**E10** and **E14**/**E16** are considered, then it can be seen from Table 1 that adding the extra double bond to the structure leads to an increase in pyramidalisation of the alkene bond. However this change in ω is only moderate for the first pair (an increase of 3.9°) and very small for the other two (0.5° and 0.8°, respectively).

The C=C bond distances in Table 1 show the expected regular increase in the length of the formal double bond as the degree of pyramidalisation increases for the series of structures incorporating the bicyclohexene and bicyclooctene fragments. The C=C bond in **E6** is longer than would have been predicted on the basis of the series of compounds **E9** → **E6**. **E6** corresponds to the more highly strained isomer of prismene [69,70] and it has been shown previously that the triplet state of this isomer lies only about 60 kJ mol^{-1} above the singlet ground state [69]. The trend in C=C bond lengths in the series of structures incorporating the bicyclobutene fragment is not so regular. The bond length *decreases* as the pyramidalisation increases for **E4** → **E2**, but then increases again for **E1**. If the pairs of structures **E3**/**E5** and **E8**/**E10** are considered again, it can be seen that adding the extra double bond leads to a shortening of the pyramidalised alkene bond.

3.1.2. Energies

All of the alkenes and alkanes employed in the calculation of the olefin strain energies are shown in Fig. 1. Heats of hydrogenation, olefin strain energies and olefin pyramidalisation strain energies are listed in Table 2. The calculation of the OSE from molecular mechanics strain energies is straightforward. However in calculating the OPSE an unpyramidalised reference alkene needs to be chosen. I have used **RE1** as the reference alkene for structures **E1**–**E5**, **RE2** for structures **E6**–**E11**, and **RE3** for structures **E12**–**E16**. The choice of reference alkene is not always clear and this has been discussed previously in relation to cubene [40,52]. In addition, Borden has pointed out [40] that **RE1** is not planar and that this will affect the OPSE calculation. In this work the non-planar ground state of **RE1** has been used as the reference (it lies 39.4 kJ mol^{-1} lower than the planar structure at the B3LYP/6-31G(d) level of theory used here).

The OSE values calculated from molecular mechanics are on the whole not very good. This is no doubt due in some cases to a poor choice of ancillary parameters on my part. However no extra parameters were used in the case of cubene, yet its OSE is calculated to be very small. On the other hand, the trend for the OSEs of **E12**–**E15** as calculated by Borden [40] with the MM2 force field appears reasonable. The results presented here suggest that **E16** should have a similar OSE to that of **E14**, which agrees with the result of Schleyer [2] who used the MM1 force field.

OPSE values have been previously calculated by Borden [40] for **E3** (33.9 kJ mol^{-1}) and **E11** (79.1 kJ mol^{-1}) at the TCSCF/6-31G(d) level. The present results in Table 1 obtained at the B3LYP/6-31G(d) level of theory are in good agreement. (Borden also obtained OPSEs for **E12**–**E15** and those calculations are not repeated here.) The present results obtained for cubene, **E11**, are also consistent with two other calculations of the olefin strain energy for this system [52,68]. The OPSE values in Table 1 show a definite trend towards smaller amounts of strain as the pyramidalisation decreases in **E1** → **E4** and **E12** → **E15**. This is not surprising. However, what may be unexpected is the negative OPSE calculated for **E4**. This suggests that there is less strain in this alkene than the reference alkene, bicyclo[1.1.0]butene, **RE1**. The butterfly angle, ω, in **RE1** is 21.8°, so indeed it has a very similar degree of non-planarity to **E4**. Tethering the three-membered rings together by a three-carbon bridge has very little affect on the shape of the bicyclobutene fragment. The trend in OPSE values for **E6** → **E9** is rather mixed up. Although the OPSE does decrease over all for this series, it is higher than expected for **E8**. The extra strain in **E8** may be caused by the eclipsed nature of the CH_2 groups on opposite bridges. Certainly the molecule is distorted into C_1 symmetry as if to minimise this H...H repulsion. If the pairs of structures **E3**/**E5**, **E8**/**E10** and **E14**/**E16** are considered, then it is found that the structure with the extra double bond has a lower OPSE in each case. However while **E14** and **E16** have fairly similar OPSEs, **E5** is 130 kJ mol^{-1} lower than **E3**. Once again, this very negative OPSE seems to indicate that **E5** has considerably less strain than the reference alkene, **RE1**. This is difficult to explain since the degree of pyramidalisation increases on going from **RE1** to **E5**.

3.2. Platinum complexes

The structures of all the platinum complexes investigated in this current study are shown in Fig. 2 [71]. All the structures appear to be quite reasonable. For the platinum fragment I have used $Pt(PH_3)_2$ as in our earlier paper [1]. This allows direct comparison of the results with our earlier work. In previous work, we have also investigated the effect on the predicted binding energies of using more realistic phosphine ligands [34] and showed that the PH_3 approximation is well-suited to the purpose of understanding the trends in platinum–alkene bonds.

3.2.1. Geometries

Pyramidalisation angles and C=C bond distances for the platinum complexes are shown in Table 3. For comparison, the corresponding values for the four complexes we studied in our earlier work have also been included. All the alkenes become (slightly) more pyramidal and the C=C bonds lengthen upon complexation with the platinum fragment. However when comparing the butterfly angles in Tables 1 and 3 it may be seen that there is in fact very little change in the degree of pyramidalisation in structures **1**–**4**. For the other structures, the increase in ω is greatest for those with the least strain. On the other hand, for **1**–**5** and **12**–**16** the degree of C=C bond lengthening upon complexation increases as the degree of pyramidalisation increases. This degree of C=C bond lengthening is most pronounced for structures **1**–**5** incorporating the bicyclobutene fragment. The largest effect is seen on going from **E1** to **PtE1** where the C=C bond lengthens by 0.289 Å; this results in a very long C–C bond. This complex is also seen to have the shortest Pt–C distance which may indicate that it is not a true donor–acceptor complex. When considering the pairs of structures **PtE3**/**PtE5**, **PtE8**/**PtE10** and **PtE14**/**PtE16** it can be seen that the behaviour upon complexation is very similar.

3.2.2. Binding energies

The binding energies for the complexes with respect to the free alkene and the $Pt(PH_3)_2$ fragment are also shown in Table 3. Clearly better levels of theory (such as the CCSD(T)) method would be required to obtain accurate binding energies, but these results are sufficient to establish the trends. In our earlier work [1], we showed that the B3LYP method consistently underestimated the approximate CCSD(T) binding energy by about 80 kJ mol^{-1} for complexes **PtE12**–**PtE15**. The binding energies in Table 3 correlate well with the expected strain and pyramidalisation changes in the alkenes for **PtE1**–**PtE5** and **PtE12**–**PtE16**. For the middle series of complexes, **PtE6**–**PtE11**, the numbers do not show the same pattern, which may indicate that there is a combination of factors at work in these

Table 3
Pyramidalisation angles, butterfly angles (°), C=C and Pt–C bond distances (Å) and binding energies (kJ mol^{-1}) for the platinum complexes [a]

Complex	Pyramidalisation angle (ϕ)	Butterfly angle (ω)	C=C bond distance	Pt–C bond distance	Binding energies
PtE1	49.0	51.7	1.662	2.077	388.6
PtE2	48.9	41.6	1.530	2.084	253.6
PtE3	43.8	33.8	1.520	2.107	213.7
PtE4	40.3	28.7	1.510	2.123	176.8
PtE5	47.7	36.4	1.470	2.121	129.8
PtE6	90.0	58.4	1.536	2.101	156.6
PtE7	87.6	45.2	1.475	2.106	155.9
PtE8	86.3	36.0	1.465	2.111	161.8
PtE9	84.5 [b]	30.5	1.447	2.134	121.1
PtE10	84.3	36.3	1.453	2.106	165.8
PtE11	87.8	42.8	1.491	2.109	151.2
PtE12	66.6	38.5	1.513	2.098	217.4
PtE13	60.2	31.4	1.480	2.118	160.2
PtE14	53.9 [b]	26.3	1.460	2.135	115.5
PtE15	48.4 [b]	22.0	1.446	2.152	59.6
PtE16	54.4	26.5	1.462	2.134	114.6

[a] All results obtained with B3LYP/Basis set II optimised geometries and energies.

[b] Average of the two values in this complex.

Table 4
Charge decomposition analyses [a] calculated at B3LYP/II

Complex	d	b	d/b	r	Δ
PtE1	0.433	−0.096	−4.51	0.186	0.175
PtE2	0.664	0.480	1.38	−0.410	−0.056
PtE3	0.666	0.465	1.43	−0.394	−0.069
PtE4	0.654	0.443	1.48	−0.400	−0.071
PtE5	0.626	0.426	1.47	−0.403	−0.061
PtE6	0.477	0.447	1.07	−0.436	−0.043
PtE7	0.494	0.462	1.07	−0.444	−0.035
PtE8	0.481	0.465	1.03	−0.448	−0.040
PtE9	0.474	0.431	1.10	−0.451	−0.042
PtE10	0.474	0.473	1.00	−0.446	−0.037
PtE11	−1.049	0.453	−2.32	−0.438	−0.155
PtE12	0.517	0.500	1.03	−0.444	−0.041
PtE13	0.504	0.460	1.10	−0.445	−0.038
PtE14	0.498	0.429	1.16	−0.460	−0.036
PtE15	0.477	0.396	1.20	−0.464	−0.034
PtE16	0.503	0.427	1.18	−0.463	−0.036

[a] Donation d, back donation b, repulsive part r, and residual term Δ.

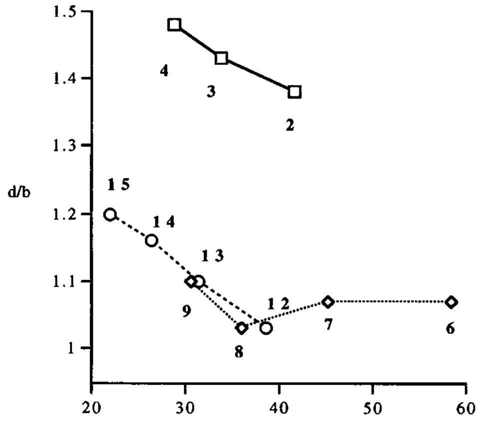


Fig. 3. CDA d/b value plotted against butterfly angle for platinum complexes.

complexes. The greatest binding energy is, as expected, for **PtE1**. In general, the binding energies for the bicyclobutene based systems is nearly twice that of the bicyclooctene based systems. In our earlier paper [1] we made some bold predictions about the likely binding energies of **PtE3**, **PtE11** and **PtE16**. If the 80 kJ mol^{-1} underestimation by B3LYP is taken into account, then the results in Table 3 suggest that the approximate CCSD(T) binding energies of these three complexes are 294, 231 and 195 kJ mol^{-1}, respectively. These values compare very favourably with our predictions of 275, 250 and 200 kJ mol^{-1}.

3.2.3. Charge decomposition analyses

The results for the CDA are displayed in Table 4. For all the complexes except **PtE1** and **PtE11**, the residual term (Δ) is very small which indicates that it is appropriate to consider these structures as donor–acceptor complexes and to interpret their bonding in terms of the Dewar–Chatt–Duncanson model. For the two exceptions, d or b is negative which is physically unreasonable and is another indication that these species are not donor–acceptor complexes [56]. In the case of **PtE1**, the CDA results are supported by the geometry of the molecule which indicates that the ligand double bond has disappeared in the complex and two quite strong covalent Pt–C bonds have been formed. Thus it is more appropriate to consider this compound as containing a platinacyclopropane ring. As for **PtE11**, the platinum complex with cubene, there does not appear to be strong evidence from the geometry that this is *not* a donor–acceptor complex, however the CDA method has been shown to be a reliable indicator and so I conclude that the metal–alkene bonding in this too cannot be considered as a Dewar–Chatt–Duncanson interaction.

Apart from these two exceptions, in the rest of the complexes studied here a single molecular orbital dominates each of the donation and back donation interactions. As we found in our earlier study [1], in each case, the dominant orbital in the alkene → Pt donation interaction involves the C=C π system and the s, d_{z^2} and $d_{x^2-y^2}$ on platinum. The dominant orbital in each of the alkene ← Pt back donation interactions involves the platinum d_{xz} and the C=C π* system. Once again, these results provide a beautiful confirmation of the theory originally put forward by Dewar. In contrast, as expected, in **PtE1** and **PtE11** the CDA results indicate that quite a mixture of orbitals contribute to the interaction and these will not be discussed further.

The d/b value is plotted against the butterfly angle, ω, in Fig. 3. This clearly shows that there is a decrease in the d/b ratio as the degree of pyramidalisation increases in the first and third series of compounds studied. In other words, back donation in the platinum complex becomes more important relative to donation as the alkene becomes more pyramidal.

3.3. Correlations

The binding energies for the complexes are plotted against d/b, ω and OPSE in Fig. 4. The graphs appear to show quite reasonable relationships between these quantities, except for the series of compounds incorporating the bicyclohexene fragment (structures **6**–**11**). All three measures used here give reasonably linear correlations with the binding energies. We had found similar correlations previously [1] but the results presented here now show that these correlations can be extended to other alkenes. Although Fig. 4b seems to indicate that compounds **2**–**4** and **12**–**15** lie on a continuum, Fig. 4a and c show that with respect to d/b and OPSE they form a set of parallel series. These correlations need to be tested further but it appears that for some related systems they will allow the prediction of approximate binding energies.

4. Concluding remarks

A series of pyramidalised alkenes and their platinum complexes have been investigated. The results show that in most cases the bonding in the complexes can be considered as a Dewar–Chatt–Duncanson interaction. The CDA is a useful tool for quantitatively analysing the nature of the bonding in such complexes. The degree of pyramidalisation, the ratio of donation to back donation, and the olefin pyramidalisation strain energy all provide a useful correlation with binding energy for some of the complexes studied here. However, there appear to be competing factors involved in the series of compounds incorporating the bicyclohexene fragment and these systems deserve a more thorough investigation.

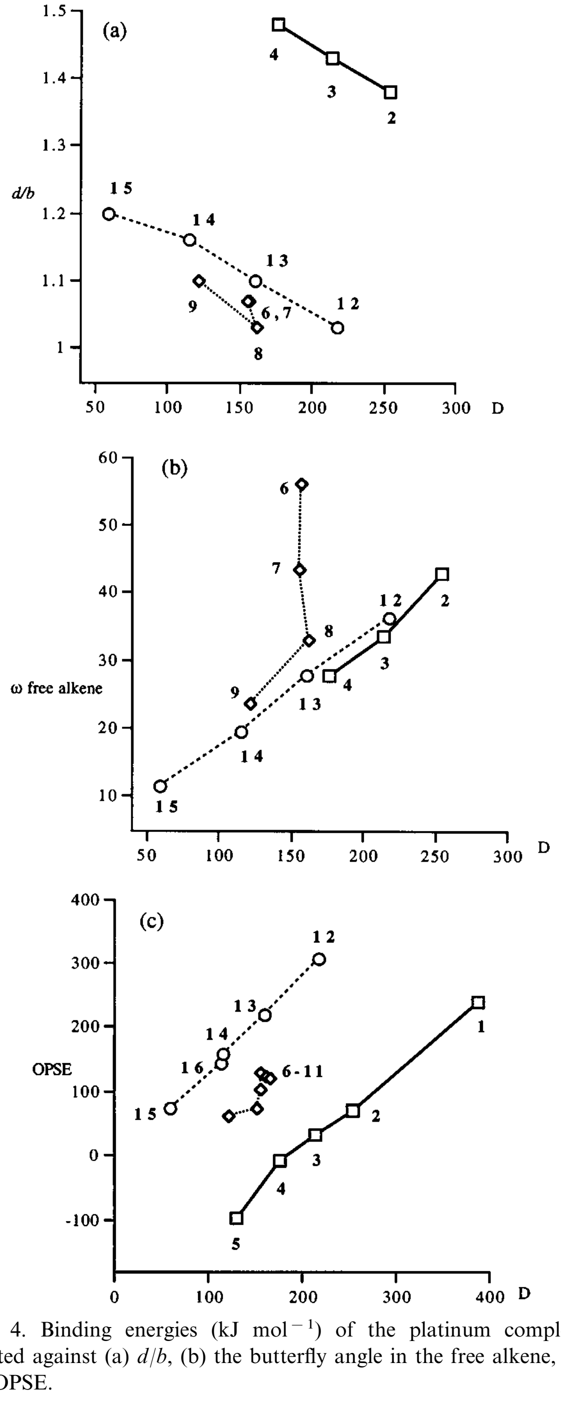
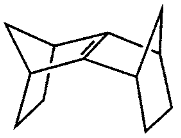


Fig. 4. Binding energies (kJ mol^{-1}) of the platinum complexes plotted against (a) d/b, (b) the butterfly angle in the free alkene, and (c) OPSE.



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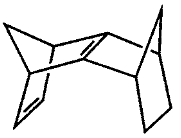

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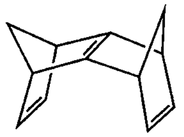

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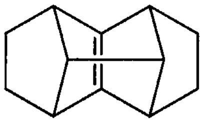

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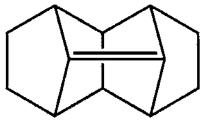

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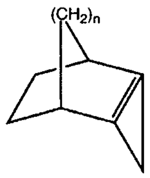

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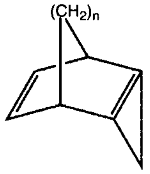

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It will be interesting to test the relationships developed here on a wider range of somewhat larger pyramidalised alkenes. In his detailed and thorough review, Borden [4] has considered a wealth of interesting alkenes including the series of compounds **17**–**19**. Another pair of pyramidalised alkenes which have attracted the attention of experimentalists are **20** [69] and **21** [52]. Recently, Warrener and co-workers [53] have described a further series of pyramidalised alkenes involving the cyclopropene fragment, **22**–**23**. It would also be interesting to look at more simple cyclopropene systems and strained (but not necessarily pyramidalised) alkenes. This work will form the subject of another paper.

Finally, I have restricted myself to a very simple platinum fragment in this work and I have not considered the influence of this fragment on the metal–alkene bond. It would be useful to carry out a parallel investigation of the Ni(0) and Pd(0) complexes and to take into account the orbital energies of the metal fragments. This will also form the basis of a future project.

5. Supplementary material

Supporting information is available. Details of the extra MM3 parameters used, and geometries and total energies of all the structures optimised at the B3LYP/II level of theory are available from the author or can be downloaded from http://www.chem.utas.edu.au/staff/yatesb/pt_pyr.html.

Acknowledgements

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