Olefin Rotation in Platinum(II) Olefin Complexes. Part IV.[1] Energies of Activities for Rotation of Substituted Olefins in Square-planar $PtCl_2(L)$(olefin) and PtCl(acac)(olefin) Complexes

By **John Ashley-Smith, Zacci Douek, Brian F. G. Johnson,** and **Jack Lewis,*** University Chemical Laboratory, Lensfield Road, Cambridge

The energy barriers to rotation of the olefin in the complexes *cis*-$PtCl_2L$(olefin) and PtCl(acac)(olefin) have been measured by variable-temperature n.m.r. spectroscopic techniques (L = tertiary arsine or phosphine; olefin = a series of monosubstituted, 1,1-disubstituted, *cis*- and *trans*-1,2-disubstituted, and trisubstituted ethylenes). The measured $\Delta G^{\ddagger}_{T_c}$ values are dependent on both the bulk and electronegativity of the substituents and on the symmetry of the olefin. The orientation of the olefin in the ground state, as deduced from a study of platinum–proton coupling constants, is strongly influenced by steric factors. There is evidence for a rotational distortion of the co-ordinated olefin about the carbon–carbon axis in the complex PtCl(acac)($Bu^tCH{=}CH_2$).

CO-ORDINATED olefins in some transition-metal complexes are non-rigid and rotate, presumably with the co-ordination bond as axis. The rate of this rotation has been shown to be temperature dependent by n.m.r. spectroscopic techniques [2] and the probable sources of the energy barrier to rotation have been discussed.[1-6] Cramer has demonstrated that increasing the electron-withdrawing properties of other ligands around the metal in rhodium–olefin complexes lowers the barrier to rotation,[5,6] and that a perfluorinated olefin co-ordinated to rhodium does not rotate. A change in central metal ion from rhodium to iridium without apparently changing the steric interactions of the ligands increases the barrier significantly.[7] In the previous paper in this series [1] it was shown that a bulky group *cis* to the olefin on a square planar platinum(II) complex increased the energy barrier, even when an increase in rate would have been predicted on electronic grounds.

Much of the previous work has concerned unsubstituted ethylene and no general study of the effect of olefinic substitution on the barrier to rotation has been undertaken. A number of n.m.r. studies of the geometry and orientation of substituted ethylenes co-ordinated to platinum(II) have been published but the authors have not been in agreement about the interpretation of chemical shift and platinum–proton coupling constant data.[8-10] This paper contains the results of a systematic study of the free energies of activation of the rotation of substituted olefins in square planar platinum(II) complexes of the type *cis*-$PtCl_2(L)$(olefin) and PtCl(acac)(olefin) (where L is a tertiary phosphine or arsine), and a discussion of the orientation and geometry of the co-ordinated olefin in terms of the n.m.r. parameters.

It is not experimentally possible to examine the steric and electronic factors independently. However, the theoretical effect of varying one without affecting the other can be discussed qualitatively.

Electronic Contribution.—If we assume the Dewar–Chatt model for olefin–metal bonding the energy of rotation may be considered as being composed of two contributions namely (i) the rotation about the σ-metal–olefin bond and (ii) rotation about the π component of the metal–olefin bond. The first of these will be mainly controlled by steric factors whilst the second will have contributions from both electronic and steric effects. The qualitative molecular orbital description for a platinum(II) olefin system may be represented by Figure 1. The barrier to rotation will depend on the *difference* in bond energy of the in- and out-of-plane-π-bonds. If these π-orbitals were of equal energy this would correspond to a cylindrical electron distribution about the metal–olefin bond and a zero energy barrier to rotation other than from steric factors. Any disparity

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[1] Part III, J. Ashley-Smith, I. Douek, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1972, 1776.

[2] R. Cramer, *J. Amer. Chem. Soc.*, 1964, **86**, 217.

[3] C. E. Holloway, G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc.* (*A*), 1969, 53.

[4] C. E. Holloway, G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc.* (*A*), 1970, 1653.

[5] R. Cramer and J. J. Mrowca, *Inorg. Chim. Acta*, 1971, 528.

[6] R. Cramer, J. B. Kline, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1969, **91**, 2519.

[7] K. Moseley, J. W. Kang, and P. M. Maitlis, *J. Chem. Soc.* (*A*), 1970, 2875.

[8] R. Lazzaroni and C. A. Veracini, *J. Organometallic Chem.*, 1971, **33**, 131.

[9] H. P. Fritz, K. E. Schwartzhans, and D. Sellman, *J. Organometallic Chem.*, 1966, **6**, 551.

[10] T. Kinugasa, M. Nakamura, H. Vamada, and A. Saika, *J. Amer. Chem. Soc.*, 1968, **90**, 2649.

in the energies of these two orbital sets will therefore be reflected in an increase in the rotational barrier. The bond energy of the π-orbital is proportional to the square of the overlap integral S between the appropriate orbitals of the metal and the anti-bonding orbitals of the olefin, and inversely proportional to the orbital energy separation ΔE, *i.e.* $S^2/\Delta E$, and thus the π-bond energy difference between the in- and out-of-plane bonding may be related to $\left(\frac{S_1^2}{\Delta E_1} - \frac{S_2^2}{\Delta E_2}\right)$, where ΔE_1 and ΔE_2 are the energy separation shown and S_1 and S_2 the respective overlap integrals. As the overlap integral S will be approximately the same for d_{xy} and d_{xz} orbitals the value of this expression will increase as ΔE_1 and ΔE_2 decrease and conversely approach zero as ΔE_1 and ΔE_2 become large. Thus, the difference in energy of the two π-orbitals is dependent on the initial energy separation of the d_{xy} and d_{xz} orbitals and on the relative separation of the ligand π^* and metal d orbitals. The electronic contribution to the rotational barrier will be dependent therefore on the atomic number and oxidation state of the metal, the ligand-field splitting of the co-ordinated groups and on the electronegativity of substituents on the olefin.

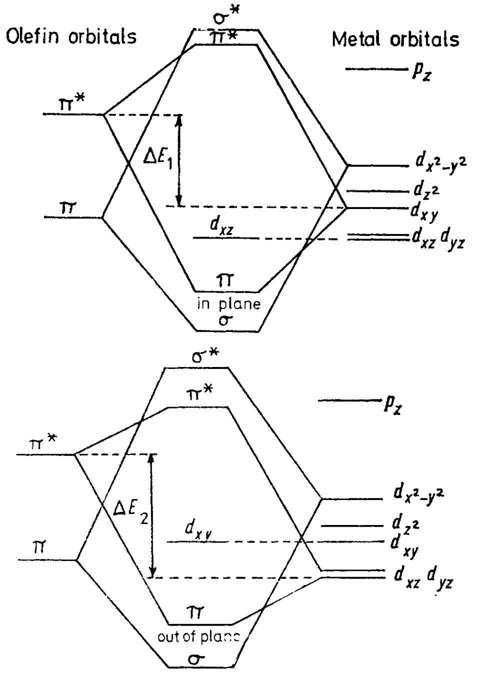


FIGURE 1 Qualitative molecular orbital description for a platinum(II)–olefin system

If we consider variation in the parameters then for a given set of ligands, on varying the metal the d_{xy}-d_{xz} orbital separation would be expected to increase on descending a transition-metal triad and this may account for the energy-barrier differences between the $\mathrm{Rh^I}$ and $\mathrm{Ir^I}$ systems observed by Maitlis.[7] Substitution of ethylenic hydrogen atoms by more electronegative groups would lower the metal–ligand energy separation and thus raise the energy difference between the in- and out-of-plane π-bonds, resulting in an increased barrier to rotation, whilst substitution by an electron releasing group would increase the energy separation ΔE_1 and ΔE_2 and lead to a lower energy barrier. Variation in the ligands around the metal will affect changes in the separation of the bonding energies by either a ligand-field effect (*i.e.* variation in d_{xy}-d_{xz} energy separation), or by being directly in competition for the π-bonding orbitals of the metal (*i.e.* influence the overlap integral S). In the latter case substitution in the *cis*-position will lead to competition for the d_{xy} orbital and affect the in-plane bond energy, whilst substitution in the *trans* position will affect the out-of-plane conformation *via* the d_{xz} orbital.

Since $\Delta E_1 < \Delta E_2$, the most stable conformation for a square planar platinum(II)–olefin complex predicted by this simple model would be with the olefin in the plane of the platinum–ligand system, in contrast with the experimentally observed conformation perpendicular to the plane. If we invoke hybridization of the p_z and d_{xz} orbitals as suggested by Chatt this would reduce the energy separation ΔE_2 and increase the overlap integral S, thus favouring the perpendicular orientation of the olefin, although it is important to emphasize that the stereochemistry observed may reflect steric rather than electronic stabilization.

The Steric Contribution.—The steric contribution to the barrier to rotation will be the difference between the maximum and minimum energy potentials induced by non-bonded interactions, which are encountered as the olefin rotates about the metal–olefin axis.

The steric energy minima will occur when the olefin is close to the out-of-plane configuration which, for olefins of C_{2v} and D_{2h} symmetry in complexes with an axis of symmetry along the metal–olefin bond, will coincide with the electronic minimum perpendicular to the plane. If olefins of these symmetry groups with bulky substituents are to attain as great an overlap with the metal orbitals as ethylene achieves, destabilizing non-bonded interactions will result. For mono-substituted and *trans*-1,2-disubstituted olefins the steric minimum would be achieved by a slight rotation about the metal–olefin axis away from the perpendicular electronic minimum. Crystallographic studies of but-1-ene[11] and *trans*-but-2-ene[12] platinum(II) complexes show that in the solid state the olefin is 13° from the perpendicular. The steric maxima will occur when the largest group on the olefin passes the largest ligand, which will not coincide with the in-plane electronic maximum. The value for the energy maximum will be exceptionally high for olefins with *trans*-substituents as the bulky groups must simultaneously pass the adjacent ligands on either side of the metal. Thus the difference between the maximum and minimum, non-bonded interactions, the steric contribution to the

[11] C. Pedone and E. Benedetti, *J. Organometallic Chem.*, 1971, **29**, 443.

[12] E. Benedetti, P. Coradini, and C. Pedone, *J. Organometallic Chem.*, 1969, **18**, 203.

activation energy, is dependent not merely on the size of the groups but may be related to the symmetry of the olefin.

Monosubstitution.—Co-ordination of a monosubstituted ethylene to a metal to form a square planar complex where the ligands *cis* to the olefin are dissimilar yields two ground state isomers (in fact two sets of mirror image pairs) (Figure 2). Rotation about the co-ordination axis interchanges these isomers (but not the mirror images). Usually the isomer populations are of the same order and the energy difference between them is slight. Two rates for isomer interchange exist, since the unique olefinic group can pass either ligand, and if the energy barriers for these routes are sufficiently dissimilar, oscillation rather than rotation may occur.

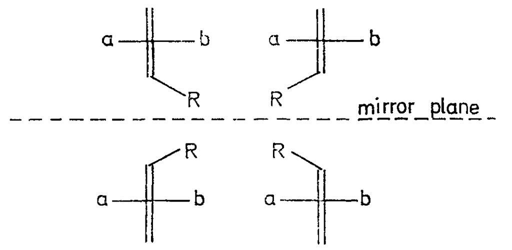
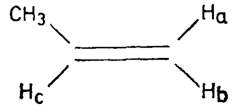


FIGURE 2 Ground state isomers for $PtCl_2(L)(RCH{=}CH_2)$

The number of compounds $PtCl_2(L)(RCHCH_2)$ with sufficient stability and solubility for n.m.r. study is limited. However, a number of propene complexes have been prepared and thermodynamic and spectroscopic data for these and the analogous ethylene complexes are given in Table 1.

TABLE 1

Thermodynamic and spectroscopic data for $PtCl_2L(C_3H_6)$ *



L	$\Delta G^{\ddagger}$ † kcal mol^{-1}	J(PtH)/Hz a	J(PtH)/Hz b	J(PtH)/Hz CH_3	Chemical shift a	Chemical shift b	Isomer ratio	$\Delta G^{\ddagger}$ for † $PtCl_2L(C_2H_4)$ kcal mol^{-1}
Et_3As	12·0	66	70	46	5·58	5·92	3 : 1	10·9
Et_3P	12·5	68	70	45	5·48	5·95	3 : 1	12·8
Me_2PhP	13·5				5·70	6·45	3 : 1	12·3
Ph_3As	16	60	64	42	5·70	6·25	4 : 1	11·9
Ph_3P	16	64	65	41	5·60	6·30	5 : 1	13·4
$(2MeOC_6H_4)_3P$	16			40	5·60		7 : 1	13·9

* J(PtH) could not be measured for H_c in the most favoured isomer or H_a, H_b, or H_c in the least favoured. † Errors are estimated to be *ca.* 0·2 kcal mol^{-1}.[15]

The presence of unequal concentrations of isomers and the multiplicity of the resonances make accurate measurement of the coalescence temperature more difficult than for the ethylene complexes, but despite this greater error, the rotation of propene is seen to be less ready than that of ethylene. In three cases the only spectra obtainable were those below coalescence. Raising the temperature decomposed the samples and thus only a minimum value of $\Delta G = 16$ kcal mol^{-1} is given. Since the difference between the energy values for ethylene and propene correlates with increased steric requirements of ligand, the cause of this increase is probably steric.

The n.m.r. data in Table 1 are those for the more abundant isomers. Phenyl groups attached to the Group V ligand atom shield the olefinic protons nearest to them.[1] The resonances assigned to the (b) protons are shifted to higher field than are the signals due to proton (a) on changing alkyl to aryl groups and moreover the methyl resonance for the more abundant isomer is at lower field than that for the less-stable isomer. Therefore, as expected on steric grounds the most stable configuration is obtained when the methyl is remote from the larger ligand.

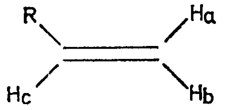
The coupling between olefinic protons and the ^{195}Pt nuclei to which the olefin is co-ordinated can be considered as the sum of Fermi contact and through-space contributions. Differences in $J(^{195}Pt\text{-}H)$ for geminal olefin protons most probably arise from differences in the through-space effect due to dissimilar Pt–H distances, since the *s*-character of the platinum–carbon bond affects both protons equally. However, differences in $J(^{195}Pt\text{-}H)$ between *cis*-vicinal protons must be interpreted with caution since these may arise both from differing interatomic distances and differences in the natures of the platinum–carbon bonds resulting from the electronic effect of the substituent group.

The observation that $J(Pt\text{-}H_a)$ is always smaller than $J(Pt\text{-}H_b)$ for the most favoured isomer suggests that the repulsive interaction between the methyl group and the chloride ion is greater than that between the proton and the Group V ligand and that the olefin is slightly rotated around the carbon–carbon axis away from the ideal orientation perpendicular to the metal–olefin bond. The difference of the geminal Pt–H coupling constants decreases on going from Et_3As to Ph_3P suggesting that the ligand–proton interaction increases and the olefin nearly achieves the ideal orientation. The through-space contribution to $J(^{195}Pt\text{-}CH_3)$ is of opposite sign to the contact contribution [4] and as the size of the ligand increases, the methyl group is forced nearer the metal and $J(Pt\text{-}CH_3)$ decreases. If the methyl group were adjacent to the bulkier ligand, severe twisting around the carbon–carbon axis would be required to minimize non-bonded interactions. The decrease in stability of the less-favoured isomer as ligand size increases is reflected in the isomer ratios.

In the complexes PtCl(acac)(RCH=CH$_2$) the barrier to rotation is seen to be somewhat dependent on the nature of R (Table 2). For a large electronegative group (R = CF$_3$) the barrier is high and for a small less electron-withdrawing group (R = H) the barrier is low. Thus the apparent insensitivity of the barrier to substituent on going through the series R = F, Cl, or Br can be seen to be the result of equal but opposing steric and electronic factors. The electron-releasing methoxide group (R = OMe) gives methyl vinyl ether the lowest ΔG value of the series. Unfortunately no value could be measured for R = Ph since the unstable isomer could not be detected by n.m.r. and is probably present in less than 10% concentration. Increasing a normal alkane chain length has little effect after the first two homologues as the destabilizing nonbonded interactions appear to occur only with the first few methylene groups, the rest of the chain being bent away from the complex. This steric evasion is not possible where the alkyl group is tertiary butyl, and despite the basic nature of the group the rotational barrier is somewhat higher.

TABLE 2

Thermodynamic and spectroscopic data for PtCl(acac)(olefin)



R	$\Delta G^{\ddagger}(\pm 0{\cdot}2)$ kcal mol^{-1}	J(HH)/H$_z$ [a] *cis*	J(HH)/H$_z$ [a] *trans*	$\Delta\nu$/H$_z$ [b] a	$\Delta\nu$/H$_z$ [b] b	$\Delta\nu$/H$_z$ [b] c	J(PtH)/H$_z$ a	J(PtH)/H$_z$ b	J(PtH)/H$_z$ c	Isomer ratio
H	12·5			132	137		64	66	66	
F	13·3	1·0	3·2	−7	−36	−98	68	72	81	7
Cl	13·2	1·1	3·2				68	72	76	6
Br	13·4	1·1	3·2	35	111	102	68	72	72	7
CF$_3$	15·0	2·0	3·0	110	106	30	62	68		4
Ph		2·6	4·4	83	63	33	60	68	70	
OMe	10·5	2·8	4·2	−16	−30	−47	64		72	3
Me	13·3	2·5	2·8	75	34	25	65	70	68	3
Et	13·6	2·6	3·0							3
Pr^n	13·9	2·8	3·2							4
n-C$_8$H$_{17}$	14·0	2·8	3·2							6
Bu^t	15·0	2·8	3·5	69	36	16	63	72	79	10

[a] Decrease in internal coupling constant on co-ordination. [b] Increase in chemical shift on co-ordination.

The internal coupling constants of the olefin decrease on co-ordination, and unfortunately the geminal coupling constant becomes so small compared with the line width that precise measurement is impossible and an accurate guide to olefin geometry is lost. However, the general decrease in coupling constants is usually associated with a bending back of the olefinic groups towards an eclipsed ethane-type structure interpreted as a tendency toward sp^3 character. The bending back of the olefinic groups may be viewed as mixing of the π- and σ-orbitals of the olefin. On co-ordination to the metal the π inequivalence in the free olefin is destroyed, and mixing of the appropriate orbitals may then occur to give a situation corresponding to enhancement of the p character in the hydrogen–carbon bonds and s character to the carbon–platinum bonds. The size of the change in coupling constants appears to be independent of the class of substituent.

The degree of bending back of substituents on co-ordinated olefins has been measured crystallographically by Guggenberger and Cramer [13] and an olefin with electronic-withdrawing substituents, tetrafluoroethylene, was found to be distorted fully to the ideal sp^3 geometry whereas the hydrogen atoms on ethylene were bent back to a lesser extent, suggesting partial transition from sp^2 to sp^3 hybridization.

The increase in proton chemical shift on co-ordination has also previously been taken as a sign of increased shielding on going from sp^2 towards sp^3 character. However, for R = F or OMe the chemical shifts decrease, the decrease for H$_c$ being most marked. This is apparently not the result of deshielding electronegative atoms in the adjacent group, as similar decreases have been observed for R = Me and Bu^t in complexes *trans*-PtCl$_2$(C$_5$H$_5$N)(RCHCH$_2$).[8] Since the chemical shifts are dependent on R as well as the proximity of the *cis*-ligands the configuration of the more stable isomer cannot be deduced. Nor can a consistent picture of olefin tilting be obtained from a study of the chemical-shift changes.

The value of J(PtH$_b$) is consistently larger than that of J(PtH$_a$) suggesting a rotation around the carbon–carbon axis to accommodate the bulk of R. The largest geminal differences are for R = Ph and Bu^t which supports this idea. The value of J(PtH$_c$) shows a steady increase with increased electronegativity of R through the series R = Me, Ph, MeO, Br, Cl, or F, consistent with the expected increase in s-character of the Pt–carbon bond. However, J(PtH$_c$) when R = Bu^t is anomalously high, considering the group's electropositive character. If then the large coupling constant is due to through-space effects and since a tilt of the olefin such that the bulky

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[13] L. J. Guggenberger and R. Cramer, *J. Amer. Chem. Soc.*, 1972, **94**, 3779.

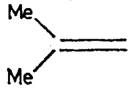
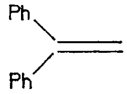
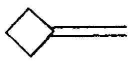
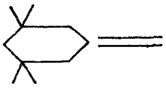
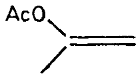
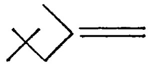
group is nearer to the metal is unlikely, the short platinum–proton distance may arise from a twisting of the two halves of the olefin relative to one another about the carbon–carbon axis. Thus, while the ethylenic fragment of the olefin is somewhat twisted from the ideal orientation, the substituted portion is further rotated to relieve steric strain and thus forces proton H_c nearest to the platinum atom. This type of deformation has previously been suggested [8] as a possible explanation of the platinum–proton coupling constants in *trans*-$PtCl_2(C_5H_5N)(Bu^tCHCH_2)$.

Whereas the isomer ratio is largest for the bulkiest ligands this trend is not strictly followed and the concentration of most-favoured isomer is high when R is relatively small but electronegative.

1,1-*Disubstitution*.—The value for the rotational barrier of isobutene (Table 3) is low compared with that of ethylene or propene. The use of molecular models suggests that the out-of-plane conformation is no more stabilized than the in-plane, which could account for this lower value. The interaction of atoms beyond the alkyl methylene groups in the puckered ring systems of methylene cyclobutane and the substituted methylene-cyclohexane with the *cis*-ligands will be greater in the in-plane configuration than is the out-of-plane. The barriers for these olefins are higher than for isobutene. (It is of interest that the methylene cyclobutane does not ring-open on co-ordination, as it does on reaction with certain transition-metal complexes.[14]) The proton–platinum coupling constants are noticeably higher than in the ethylene complex and while there are no data for protons on the other carbon atom for comparison, it is possible that this arises from a tilt of the olefin such that the two protons are forced closer to the platinum.

TABLE 3

Thermodynamic and spectroscopic data for PtCl(acac)olefin

Olefin	$\Delta G^{\ddagger}$ (±0·2) kcal mol^{-1}	J_{Pt-H} Hz	τ	$\Delta\nu$ * Hz
	10·6	70	5·52	13
	12·8	68	4·90	30
	13·5	72	5·60	24
	14·3	71	5·54	18
	13·7	72	5·38 5·46	3 −5
	10·2	75	5·34 5·40	22 3

* Increase in chemical shift on co-ordination.

When the two groups are different there is the possibility of geometrical isomerism (Figure 3); in the two cases observed the isomers were in equal concentration. This type of olefin did not form complexes $PtCl_2(L)$(olefin).

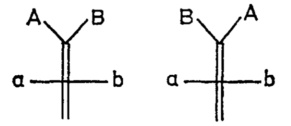


FIGURE 3 Geometrical isomers for $PtCl_2(L)\{C(A)(B)C{=}CH_2\}$

cis-1,2-*Disubstitution*.—The barrier to rotation of *cis*-butene in $PtCl(acac)(C_4H_8)$ has been determined as 13·3 kcal mol^{-1} and the isomer ratio as 6 : 1. In the spectra of the complexes studied (Table 4) only one isomer was detected and thus no value for the barrier to rotation could be calculated (Figure 4).

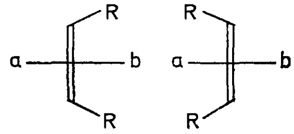


FIGURE 4 Geometrical isomers for $PtCl_2(L)(RCH{=}CHR)$

TABLE 4

Spectroscopic data for complexes $PtCl_2(L)(C_4H_8)$ and PtCl(acac)(dien)

Complex	J(PtH) Hz	J(PtMe) Hz	τ	$\Delta\nu$ * Hz
$PtCl_2(Et_3As)(C_4H_8)$	74	40		
$PtCl_2(Ph_3As)(C_4H_8)$	68	36		
$PtCl(acac)(C_4H_8)$	73	30	4·62	8
PtCl(acac)(cyclo-C_6H_{10})	81		4·43	13
PtCl(acac)(norbornene)	81		4·66	60

* Upfield shift on co-ordination.

For $PtCl_2L(C_4H_8)$ (where L = Ph_3As or Et_3As) chemical shift and coupling constant data suggest that the observed isomer is that with the methyl groups remote from the arsenic. The decrease in both J(PtH) and $J(PtCH_3)$ on increasing the size of the ligand indicates the greater rotation from ideal orientation. For the cyclic olefins cyclohexene and norbornene the platinum-coupling constants to the ethylenic protons are much higher than in the ethylene or even *cis*-butene complexes. Since the substituents are only alkyl fragments and unlikely to greatly change the mode of bonding it is thought that this is a through-space effect, the short platinum–hydrogen distance resulting from the steric requirements of the ring. The complexes of the cyclic olefins are very unstable in solution and could only be recrystallized in the presence of an excess of olefin; no complexes $PtCl_2L$-(cyclic olefin) could be prepared. Correlation of this instability with the high J(PtH) values suggests that a partial rotation of an olefin around the carbon–carbon axis seriously destabilizes the complex, involving bond-

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[14] R. Rossi, P. Diversi, and C. Pori, *J. Organometallic Chem.*, 1970, **31**, C40.

breaking as predicted by the conventional Dewar–Chatt–Duncanson model for olefin–metal bonds.

trans-1,2-*Disubstitution*.—The rotation barrier of *trans*-butene in PtCl(acac)(C_4H_8) has been determined as 15·8 kcal mol^{-1}. For *trans*-stilbene, although the large substituents may cause the steric ground state to differ greatly from the electronic minimum, the non-bonded interactions produced when the phenyl groups simultaneously pass the *cis*-ligands are sufficient to give a barrier of 19 kcal mol^{-1}. Although the spectra for rapid rotation on the n.m.r. time scale could not be reached, spectra at slow exchange (—60 °C) and coalescence (+80 °C) were obtained.

For $PtCl_2Et_3As(C_4H_8)$ only spectra below coalescence were observed, suggesting a high barrier to olefin rotation, certainly greater than 16 kcal mol^{-1}.

Trisubstitution.—The barrier to rotation of 2-methylbut-2-ene in PtCl(acac)(C_5H_{11}) is 11·5 kcal mol^{-1}. That the barrier is higher than for tetramethylethylene (10·9 kcal mol^{-1})[2] is somewhat surprising as the out-of-plane ground states might be predicted to be equally unstable and the steric maxima equally high since both contain *trans*-methyl groups. However, the use of molecular models shows that a slight stabilization of the ground state can occur by a rotation about the co-ordination axis such that the main interactions are with the unique proton and the methyl *trans* to it. This would cause a tilting of the olefin about an axis through the mutually *trans*-methyl groups. The high platinum coupling constant to the ethylenic proton (70 Hz) is consistent with this. The chemical shift of the olefinic proton decreases by 10 Hz on co-ordination. Similarly high values for ΔG, 12·5 kcal mol^{-1}, and J(PtH) 71 Hz were observed for 1-methylcyclohexene, however the chemical shift change on co-ordination was 90 Hz upfield.

EXPERIMENTAL

Solutions of the complexes were prepared, *ca.* 0·5M in $CDCl_3$ for PtCl(acac)(olefin), and *ca.* 0·1M in $CDCl_3$ or CD_2Cl_2 for $PtCl_2L$(olefin).

Tetramethylsilane was used as internal reference, τ 10. Variable-temperature n.m.r. studies were carried out on a Varian Associates HA-100 spectrometer. Probe temperatures were measured using the precalibrated internal chemical shift of a methanol sample. Values for the free energy activation were calculated using the expression

$$\Delta G^{\ddagger}_{T_c} = -RT \ln \frac{\pi \Delta \nu h}{\sqrt{2kT}}$$

where $\Delta\nu$ represents the chemical shift of the coalescing peaks in the absence of exchange, T represents the coalescence temperature, and R, k, and h have their normal thermodynamic significance. The values obtained using the approximate expression are subject to the limitations outlined by M. Raban and his co-workers.[15] However, in general, the coalescing resonances studied were not associated with second-order spin systems and the chemical shifts were large compared with the coupling constants (if any).

The complexes $PtCl_2L$(olefin) were obtained after the method of Chatt[16] by treatment of a solution of $Pt_2Cl_4L_2$ in methylene chloride with the olefin in excess. The complexes PtCl(acac)(olefin) were prepared by the method of Lewis[17] by treatment of PtCl(acac)(acacH) in benzene with an excess of the olefin. Satisfactory elemental analyses were obtained on all complexes and the mass spectra of the complexes PtCl(acac)olefin showed the expected parent ions. The purity of the complexes was demonstrated by n.m.r. spectroscopy.

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