

RELATION BETWEEN THE ELECTRONIC SPECTRA
OF FREE METHYLETHENES AND VIBRATIONAL SPECTRA
OF THE METHYLETHENES COORDINATED TO PLATINUM* **

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It is shown that the π -electron forward-donation from a coordinated methylene to Pt is equivalent to promotions of this π -electron into higher orbitals of the free methylene due to absorptions of UV light. The local electronic state of the coordinated methylene is then comparable to electronic excited states of the free molecule. In free species, a lowering of the C=C bond order markedly influences two vibrations of the molecule, namely the C=C stretching and torsion vibrations. The latter is excited by two quanta amounting in all the methylenes to $500 \pm 100 \text{ cm}^{-1}$. The corresponding frequency found in vibrational spectra of the coordinated species at about 500 cm^{-1} should therefore be assigned to the $(\text{C}=\text{C})_{\text{coord.}}^*$ torsion and not to a second Pt—C bond, *i.e.* the assumption of PtC_2 ring formation in the complexes is rejected. The position of $\nu(\text{C}=\text{C})^*$ of a coordinated alkene can be predicted from the first ionization potential of the free alkene (and *vice versa*). This empirical finding also substantiates why the percentual downshift of $\Delta\nu(\text{C}=\text{C}) = (\text{coordinated-free})$ cannot be constant for different alkenes bound to Pt.

In previous papers^{1,2} we pointed out that 1-alkenes¹ and ethene², when coordinated to platinum in Zeise's salt, $\text{K}[\text{PtCl}_3(\text{C}_n\text{H}_{2n})]$, are in a local excited electronic state (a near-radical-cation¹). Moreover with ethene², it is anticipated that this local electronic state is comparable to a Rydberg state of the free molecule.

It has been proved^{1,2} that the main change in the vibrational spectra of these coordinated alkenes is a remarkable downshift of the C=C torsion frequency from about 1000 to near 500 cm^{-1} . This corresponds to the C=C bond order lowered³ to about 1.5 by forward-donation of a π -electron from alkene to platinum. Both forward and back donated electrons between Pt and alkene form one bonding electron pair, the bond being characterized by single IR band near 400 cm^{-1} (*cf.*⁴). As a consequence, the assumed⁵ existence of the platinirane ring PtC_2 was rejected because any back-donation of electron from Pt to the alkene cannot form another, two-electron Pt—C bond. Our concept originates from the idea⁶⁻⁸ that the ground state of the " π -complex" (*cf.*^{9,10}) must include a large contribution of local excited electronic states of both the metal and the ligand.

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The aim of this work is to comment upon relations between the high resolution electronic spectra of free methylenes and the IR spectra of these species coordinated to platinum in Zeise's salt (ZS) or Zeise's dimer (ZD).

RESULTS

First of all, it is necessary to summarise some vibrational characteristics of the free methylenes in the electronic ground state. These are the fundamental frequencies of the stretching and torsion vibrations of the C=C bond, which will be mainly affected by a promotion of one π -bonding electron from the bond, and further those of the vibrations which are coupled with these modes in free species or which will become coupled after coordination due to changes in ligand geometry. Relevant data for the CH₃ and C=C torsions are presented in Fig. 1. From inspection of the figure it becomes clear that the fundamental frequency of the C=C torsion in the free methylenes decreases with increasing number of methyl groups appended to the C=C bond and, in the case of butenes, it strongly depends upon their configuration. Moreover, it is noteworthy that the value of the C=C torsion "converges" to about 200 cm⁻¹ which is roughly the highest possible fundamental for the CH₃ torsions¹¹.

In Fig. 2 are shown reported¹² electronic data for the free methylenes: the first ionization potentials, the Franck-Condon absorption maxima of the $V \leftarrow N$ (singlet $\pi^* \leftarrow \pi$) transition, and the origins of the (ns) Rydberg series ($3sR_{00} \leftarrow N$). For comparative purposes the dependence of the C=C torsion fundamental on the number of methyls from Fig. 1 is also presented (curve 1). It is seen that this dependence follows general trends observable for the three characteristics of the electronic excited states. From this it follows that the C=C torsion vibration in the electronic ground state is also closely related to the energy and geometry of the valence shell, especially of the highest occupied molecular orbital π . It is interesting that the sequence of dimethylenes on the ordinate is not the same for all the quantities being compared in decreasing eV-values¹²: *gem, trans, cis* (I.P.); *cis, trans, gem* ($V \leftarrow N$); *gem, trans, cis* ($3sR_{00} \leftarrow N$); *trans, gem, cis* (torsion C=C ($1'' \leftarrow 0''$))* . Up to now, there is no explanation for this interchange on going from one dimethylene to another. Experimental errors in I.P.'s determination, however, play a role here (cf. the sequence *gem, cis, trans* in refs^{13,14}).

Table I presents reported data for the (C=C)* stretching and torsion vibrations in electronic excited states V and R of the free methylenes. These data are laden with a relatively large experimental error, of several tens of cm⁻¹. Notwithstanding, it is evident that the main change of vibrational frequency is connected with the (C=C)* torsion (around 500 cm⁻¹). However, the torsion frequency does not show

* The doubly primed symbols denote the ground state quantities, those singly primed or with an asterisk are related to electronic excited states.

any such dependence on the number of appended methyl groups as was described for the ground state (Fig. 1).

The data for the free species being summarised, it is possible to assign or re-interpret published vibrational data for methylenes coordinated to platinum in Zeise's salt and/or dimer, under the assumption^{1,2} that the net yield of forward- and back-donation bonding with Pt is a local excited electronic state of the ligand which is comparable to excited states of the free molecules. For solid $K[PtCl_3(C_2H_4)]$, the carbon-carbon stretching⁵ and torsion² IR frequencies are 1241 and 491 cm^{-1} , respectively, for the propene analogue 1363 and 495 cm^{-1} , respectively¹. The increase in both quantities is obvious. Further undoubtful results are those for tetramethylethene in Zeise's dimer¹⁵, $[PtCl_2(C_6H_{12})]_2$: 1500 and 520 cm^{-1} , the assignment of the second band to the $(C=C)^*$ torsion being performed in this work. The in-

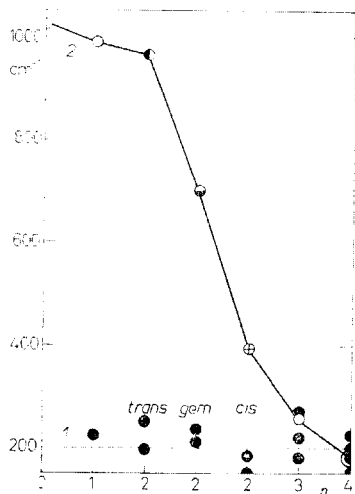


FIG. 1

Dependence of the $1'' \leftarrow 0''$ Torsion Frequencies on the Number n of Methyl Groups and their Configuration in Free Methylenes in the Electronic Ground State

1 The CH_3 torsions (IR data for frozen solids¹¹, cf. also^{38,67}). The dashed line through 200 cm^{-1} represents a rough convergency limit for curve 2; 2 the $C=C$ torsion or twisting (Raman and IR experimental or calculated data²¹, for the individual compounds cf. Table II).

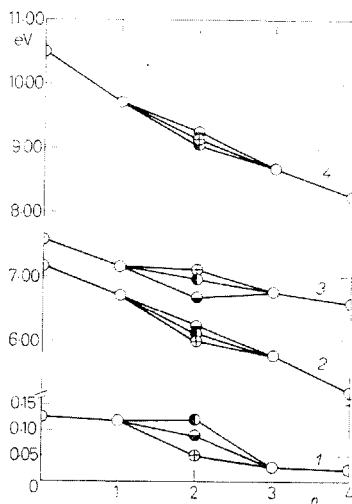


FIG. 2

Trends of Electronic Data in Free Methylenes¹²

1 The $C=C$ torsion or twisting $1'' \leftarrow 0''$ from Fig. 1; 2 the $3sR_{00} \leftarrow N$ transition¹² (for butenes cf. also^{39,40}); 3 the maxima of $V \leftarrow N$ transition¹²; 4 the first ionization potential¹² (for all cf. the most recent UPES data¹³).

● *trans*-2-Butene, ● 2-methylpropene,
○ *cis*-2-Butene.

TABLE I

The Vibrational Frequencies (cm^{-1}) in High Resolution Electronic Spectra of the Gaseous Methylenes (150–250 nm)

Alkene	(C=C)* stretch.	(C=C)* torsion	Electronic state (refs)
Ethene (I)	$1\,000 \pm 60$?	$T(41, 42)$
	800 ± 50^a	800 ± 50^b	$V(44, 45)$
	1 370	± 2	3 sR (45–48)
	1 349		
	1 324		
	1 310		
	$1\,290 \pm 30$	405 ± 30^c	${}^2B_{3u}, 1^{st}$ ionic (8, 39)
1 230			
Propene (II)	1 360	527^c	?R + V(50)
		390^c	3 sR (20)
	1 340	$\sim 600^c$	1^{st} ionic
	1 370	?	(51 resp. 49, 52)
2-Methylpropene ^d	$1\,392^e$	520^f	mystery band ^g (40)
	1 240	?	V(20)
<i>trans</i> -2-Butene (III)	1 585	? ^h	3 sR
	1 553		3 dR
	1 473		4 sR
	1 414		5 sR
	$\sim 1\,350^i$?	1^{st} ionic (39)
<i>cis</i> -2-Butene (IV)	$1\,580 - 1\,480^j$? ^h	3 to 6 sR ₁₀ (39)
	$\sim 1\,460^{i,k}$?	1^{st} ionic (39, 53)
2-Methyl-2-butene	?	590	3 sR (20)
	1 300	?	V(20)
	$1\,490 \pm 40^l$?	1^{st} ionic (64)
2,3-Dimethyl-2-butene (V)	1 500	?	3 sR (20)
	1 520	?	V(20)
	$1\,480 \pm 40^l$?	1^{st} ionic (54)

^a A coupling with excited (C=C)* torsion is assumed^{12,43}. ^b McDiarmid⁴⁴ assumes the excited (C=C)* torsion only, cf. also⁴⁵; ^c only the first overtone observed, $2\nu_4'$ ($2' \leftarrow 0'$); ^d the only case when the vibronically excited CH₃ torsion was identified⁴⁰ as being 94 cm^{-1} ; ^e coupled with =CH₂ twisting⁴⁰ (i.e. with the (C=C)* torsion); ^f coupled with the CH₃ torsions⁴⁰; ^g either A_2 , $3p_y$ (σ_{C-C}^* , b_2) or Rydberg B_1 , $3p_z$ (σ_{C-C}^* , a_1): vibronic considerations favor⁴⁰ the Rydberg state assignment; ^h not considered; ⁱ unpublished results of W. C. Price, King's College, London, quoted in Fig. 11 of ref.³⁹; ^j values estimated by us from Fig. 11 of ref.³⁹; ^k two separations, 1465 and 1510 cm^{-1} , can be read directly from Fig. 8 of ref.⁵³; ^l Penning ionization electron spectrum.

crease in both frequencies on going from propene to tetramethylethene is evident again. From this it follows that in intermediate cases, *viz.* coordinated butenes, these frequencies must lie near 500 cm^{-1} for the $(\text{C}=\text{C})^*$ torsion. The validity of this prediction is evident from Table I. As to the $(\text{C}=\text{C})_{\text{coord.}}^*$ stretching frequency, the restricting values are 1500 (tetramethylethene analogue¹⁵) and 1363 cm^{-1} (propene analogue¹), again in accordance with the UV data presented in Table I. Unfortunately, the $1450\text{--}1370\text{ cm}^{-1}$ region in the IR spectra of the free butenes (*e.g.* solids in argon matrices¹⁶) contains absorption bands due to the deformation vibrations of methyl groups, so that some ambiguities may arise as to the assignment of the $\nu(\text{C}=\text{C}_{\text{coord.}}^*)$. It is the case of free¹⁶ and coordinated¹⁷ 2-methylpropene. An exception is free *trans*-2-butene¹⁶, which is transparent in the $1440\text{--}1380\text{ cm}^{-1}$ region. The spectrum of the coordinated species shows¹⁸ two bands at 1429 (w) and 1437 (m) cm^{-1} in this region, one of which could be re-assigned to the $(\text{C}=\text{C})_{\text{coord.}}^*$ stretching vibration in the complex salt, since bands due to methyl groups could not be expected to be so much shifted.

The case of coordinated *cis*-2-butene can be well demonstrated with the aid of coordinated *cis*-cycloalkenes, since here any interference of methyl groups does not exist. In fact, the IR spectrum of cyclopentene analogue of anhydrous ZS does

TABLE II

The Observed IR Bands of the Coordinated $(\text{C}=\text{C})^*$ Stretching and Torsion, and of the Pt-alkene Stretching Vibrations (cm^{-1})

For roman numerals see Table I.

Quantity	I ^a	II ^a	III ^a	IV ^a	VI ^{a,b}	V ^c
$\nu(\text{C}=\text{C})_{\text{coord.}}^*$	1 241	1 363	{ 1 429 1 437	? ^d	1 430	1 500
$\nu(\text{C}=\text{C})_{\text{free}}$	1 623 ^e	1 562	1 682 ^e	1 660	1 614	1 683
$\Delta\nu(\text{c.-f.})^f$	-382	-289	-249 ^g	? ^d	-184	-183
$\Delta\nu$ (in %)	-23.6	-17.5	-14.8 ^g	? ^d	-11.4	-10.9
1 st I.P. (eV) ^h	10.515	9.744	9.122	9.124	9.0-9.2 ⁱ	8.271
$\tau(\text{C}=\text{C})_{\text{coord.}}^*$	491	495	491	493	462	520
$\tau(\text{C}=\text{C})_{\text{free}}^j$	1 023 ^k	990 ^l	975 ^m	394 ⁿ	387 ^o	183 ^p
$\Delta\tau$ (c.-f.) ^f	-532	-495	-482	+ 99	+ 75	+337
ν (Pt-alkene)	403	396	386	406	381	410

^a In Zeise's salt; ^b cyclopentene; ^c in Zeise's dimer¹⁵; ^d the value predicted from the 1st ionization potential is 1430 cm^{-1} , then $\Delta\nu = -230\text{ cm}^{-1}$ (-13.9%); ^e Raman frequencies of gases, the others for liquids; ^f coordinated minus free; ^g mean value; ^h ref.¹³; ⁱ see refs in Table IV; ^j for all see²¹, for 2-methyl-2-butene 250 cm^{-1} (IR, gas)⁵⁵; ^k calculated^{56,57}; ^l IR, gas⁵⁸; ^m IR, solid in Ar matrix¹⁶; ⁿ Raman, solid²⁷; ^o Raman, liquid⁵⁹; ^p calculated⁶⁰.

exhibit¹⁹ only one band at 1430 cm^{-1} , which was undoubtedly assigned¹⁹ to the coordinated $(\text{C}=\text{C})^*$ bond. This value is close to the 1457 cm^{-1} separation of the vibronic bands in the $3sR \leftarrow N$ transition of gaseous cyclopentene in its UV spectrum (200–212 nm) (ref.²⁰). The results are summarised in Table II.

DISCUSSION

As to the $\text{C}=\text{C}$ torsion in the methylenes in their electronic ground state (Fig. 1), the calculations of the fundamental frequencies for individual compounds by Sverdlov and coworkers²¹ were confirmed experimentally or by detailed calculations (*cf.* notes to Table II). The dimethylenes had become a subject of some controversy. A proposal of the calculated value 981 cm^{-1} for 2-methylpropene (“isobutene should have a frequency close to that of ethylene and 1-butene”²²) had been disproved in three papers^{16,23,24} (all: near 700 cm^{-1}), similarly for *cis*-2-butene (earlier²⁵ 965 , later^{26,27} near 400 cm^{-1}). Recently, the largest discrepancy has arisen with *trans*-2-butene: either 975 or 300 cm^{-1} . The value of 975 cm^{-1} is confirmed empirically by appearance of a strong IR band in the $1000\text{--}930\text{ cm}^{-1}$ interval which is generally characteristic for both isolated and conjugated *trans*- $\text{HC}=\text{CH}$ grouping^{28–30}. Assignments of an IR band near 300 cm^{-1} to the $\text{C}=\text{C}$ torsion fundamental^{26,31} of *trans*-2-butene have been carried out on the basis of a normal coordinate analysis; however, the description of the $\text{C}=\text{C}$ torsion as a B_u mode²⁶ is incorrect. It has to be A_u , regardless of the orientation of Cartesian (x, y, z) axes. The other work³¹ (band at 294 cm^{-1}) unfortunately differentiates between the symmetric (*i.e.* in-phase) $=\text{C}-\text{H}$ wagging and $\text{C}=\text{C}$ torsion, although these two motions compose one identical A_u mode. This is clear from Fig. 3a in which both single $\text{C}-\text{C}$ bonds wag in the opposite direction than do the $=\text{C}-\text{H}$ bonds. For these reasons, we consider the two assignments^{26,31} dubious. We adopt the assignment of the 975 cm^{-1} band to the $\text{C}=\text{C}$ torsion fundamental. Presumably, an approximate separation of high and low frequency modes of molecular vibrations³² is not feasible in this particular case³¹.

On the basis of curve 2 shown in Fig. 1, it is possible to assume a vibrational coupling between the $\text{C}=\text{C}$ torsion and torsions of methyl groups. The increasing number of methyls (and their configuration for $n = 2$) strengthens their coupling and reduces the value of the $\text{C}=\text{C}$ torsion fundamental. The value of 200 cm^{-1} common to the CH_3 and $\text{C}=\text{C}$ torsions for $n = 4$ can be regarded as a case of accidental degeneracy of these two vibrations.

With methylenes in electronic excited states (V and $(3s)$ Rydberg, *cf.* Table I), the $(\text{C}=\text{C})^*$ torsion is uniform and its excitation energy amounts to about 500 cm^{-1} . In other words, a lowering of the $\text{C}=\text{C}$ bond order (3 instead of 4 bonding electrons) has the consequence that the $(\text{C}=\text{C})^*$ torsion becomes practically independent of the number of methyl substituents. The value of 500 cm^{-1} represents two vibrational

quanta and, therefore, it can be interpreted as the first overtone of the $(C=C)^*$ torsion, $2\tau_{C=C}$ ($2' \leftarrow 0'$), *i.e.* a totally symmetrical species. The estimated value of the corresponding fundamental $1' \leftarrow 0'$ is about 200 cm^{-1} . On this ground, the $(C=C)^*$ torsion in the electronic excited states is comparable by its energy to the CH_3 torsions in the electronic ground state of the free methylenes. The preceding assumption is also applicable to the $C=C$ bond without methyl substituents ($n = 0$), *i.e.* for $\text{H}_2\text{C}=\text{CH}_2$. In the excited states (V and $3sR$) and in the first ionic state (C_2H_4^+) the estimated^{8,33} $(C=C)^*$ torsion fundamental of ethene is about 200 cm^{-1} , in other words, the CH_2 groups of the excited ethene behave, as to the torsion, like methyls in methylenes in the ground state. Thus, another possible interpretation of the observed 500 cm^{-1} frequency can be formulated as follows: it is the sum of one quantum of the $(C=C)^*$ torsion and of one quantum of the CH_3 torsion of appropriate symmetry (giving again a totally symmetrical species).

Let us turn attention to the stretching frequencies of the sp^2 -hybridized carbon atoms in the ground (Table II) and excited states of methylenes (Table I). It is clear that the trend is common to both cases because the fundamental frequencies increase with increasing number of appended methyl groups. In the case of the ground state, however, a range of the $\nu(C=C)$ is narrower ($n = 0$, $1623\text{ cm}^{-1} \rightarrow$

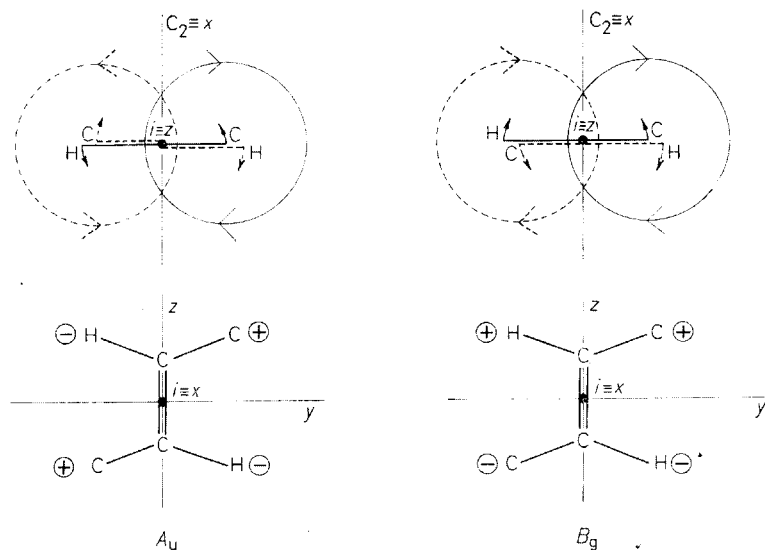


FIG. 3

The Schematic Representation of the Counter-Phase (A_u) and In-Phase (B_g) CH_3 Torsions (upper part) Coupled with the $C=C$ Torsion (A_u) and Out-of-Plane $=C-H$ Wagging (B_g), (respectively in lower part) in *trans*-2-Butene

The full circles represent rotations of the three hydrogens in the front CH_3 group, the dashed ones in the rear methyl. The signs (+, -) denote the motions above and below the molecular (yz) plane, the black dot is the centre of inversion i .

→ 1683 cm^{-1} , $n = 4$) than for $\nu(\text{C}=\text{C})^*$ in electronic excited states (from about 1250 to 1580 cm^{-1}). From this it follows that the stretching vibration is presumably coupled with other totally symmetrical modes, their number being increased by increasing number of methyl substituents. It was noted above that the coupled CH_3 and $(\text{C}=\text{C})^*$ torsions in vibronic transitions are excited by even number of quanta, giving a totally symmetrical species. These are the species which can couple with $\nu(\text{C}=\text{C})^*$. Another possibilities are the C—C stretching and CH_3 symmetrical deformation vibrations which, with a greater probability, could be coupled to $\nu(\text{C}=\text{C})$ in the electronic ground state of a methylethene.

In any case, an important conclusion can be drawn: promotions or the removal of a π -electron from the C=C bond in the series of free methylenes lead to a non-uniform lowering of $\nu(\text{C}=\text{C})^*$ which is small for $n = 2, 3, 4$ ($\Delta\nu$ is between 150 and 250 cm^{-1}), larger for propene (about 300 cm^{-1}), and maximum for ethene ($350\text{--}400\text{ cm}^{-1}$), depending on the respective excited state (Table I).

As follows from the results presented in Table II, coordination of the methylenes to Pt also leads to a non-uniform change of $\Delta\nu = (\text{coordinated-free})$ which is comparable to the free species in electronic excited states. Moreover, an analogous trend of $\Delta\nu$ is observable even in the homologous series of n-alkenes, which constitute a subclass of 1-alkenes (Table III). This variable change of $\Delta\nu$ correlates with the trend of the first ionization potentials of all the alkenes mentioned above (Tables II and III). This empirical finding allows us to predict the first ionization potential of the free alkene if the $\nu(\text{C}=\text{C})_{\text{coord}}^*$ is known or to predict the position of a $\nu(\text{C}=\text{C})_{\text{coord}}^*$ band in infrared spectrum of the complex if the known quantity is the first I. P. of the free alkene. Using the data for ethene, propene, *trans*-2-butene, and tetramethylethene, a simple non-linear plot can be constructed from $\nu(\text{C}=\text{C})_{\text{coord}}^*$ vs 1st I.P. On this ground, we predict the first I.P. for 1-decene and cyclopentene and the value of $\nu(\text{C}=\text{C})_{\text{coord}}^*$ for trimethylethene. Our predictions are summarised in Table IV. For trimethylethene, the $\nu(\text{C}=\text{C})_{\text{coord}}^*$ should be $1465 \pm 5\text{ cm}^{-1}$ and this value should be also close to the separation of vibrational structure on the first photoelectron (PE) band of the free trimethylethene. The PE spectrum was already measured several times, however, the exact positions of these vibronic bands had not been published. For 1-decene, the first I.P. should be about 9.40 eV . This value is in agreement with 9.405 eV obtained by extrapolation of the data¹³ for propene, 1-butene, 1-pentene, 1-hexene, and 1-heptene. The prediction of the first I.P. of cyclopentene can be most easily verified (Table IV), our estimate being within the range of the experimental data.

Summarising, our finding relates closely to the rules established for the first I.P. of free alkenes. Masclet and coworkers¹³ found that the first I.P. decreases with increasing number of substituents on the double bond and, further, with increasing number of carbon atoms in one substituent. In case of the alkenic Pt complexes, the downshift of $\nu(\text{C}=\text{C})_{\text{coord}}^*$ is smaller the larger number of substituents is on the C=C

bond (1500 cm^{-1} , $n = 4$ and 1240 cm^{-1} , $n = 0$, Table II) and, further, the higher is the number of carbon atoms in the alkyl group (propene 1363 cm^{-1} , 1-decene 1397 cm^{-1} , Table III).

In literature¹⁵, there exists a guide rule for interpretations of vibrational spectra of alkenic complexes assuming a constant downshift of $\nu(\text{C}=\text{C})_{\text{coord.}}^*$ with a particular metal, e.g. $12 \pm 2\%$ with Pt and about 4% with Ag^+ (in per cent of the $\nu(\text{C}=\text{C})_{\text{free}}$

TABLE III

Trends in Ionization Potentials of n-Alkenes and in $\Delta\nu_{\text{C}=\text{C}}(\text{cm}^{-1})$ after their Coordination to Pt in Zeise's Salt (ZS) or Dimer (ZD)

n-Alkene	Free $\nu(\text{C}=\text{C})$	Coord. $\nu(\text{C}=\text{C})^*$	$\Delta\nu_{\text{C}=\text{C}}$	First I.P. (eV) ^a
Ethene	1 623 ^b	1 240 ^c	383	10.515 (3)
Propene	1 650 ^d	1 363 ^e	289	9.744 (3)
1-Butene	1 641 ^d	1 376 ^f	265	9.625 (3)
1-Decene	1 642 ^g	1 397 ^h	245	9.405 (5) ⁱ

^a From UV photoelectron spectra of free gases (uncertainty in the last digit), ref.¹³; ^b Raman, gas⁶¹; ^c IR, solid ZS, ref.⁵; ^d IR, solid in Ar matrix¹⁶; ^e IR, solid ZS, ref.¹; ^f IR, solid ZD, ref.⁶², the interpretation is ours: overlapped with the CH_3 sym. deformation; ^g IR, liquid⁶³; ^h IR, solid ZS, ref.¹; ⁱ our extrapolation from the data of ref.¹³.

TABLE IV

Predictions of $\nu(\text{C}=\text{C})_{\text{coord.}}^*$ (cm^{-1}) from the First Ionization Potential (eV) and *vice versa*

Prediction for	From	Predicted	Note
Trimethylethene	8.682 eV	$1\,465 \pm 5\text{ cm}^{-1}$	$1\,490 \pm 40^a$, $1\,506\text{ strong}^b$
2-Methylpropene	9.239 eV	$1\,415 \pm 5\text{ cm}^{-1}$	$1\,416\text{ strong (IR)}^{17}$
<i>cis</i> -2-Butene	9.124 eV	$1\,430 \pm 5\text{ cm}^{-1}$	$1\,435\text{ medium}$ } (IR) ¹⁸ $1\,428\text{ shoulder}$ }
1-Butene	9.625 eV	$1\,375 \pm 5\text{ cm}^{-1}$	$1\,376\text{ strong}^c$ (IR) ¹⁷
1-Decene	$1\,396\text{ cm}^{-1}$	9.40–9.41 eV	9.405 ± 0.005^d
Cyclopentene	$1\,430\text{ cm}^{-1}$	9.05–9.15 eV	9.06 and $9.23^{a,e}$ 9.01^f 9.18^g

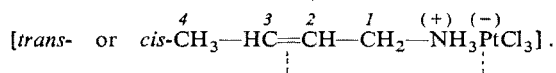
^a Penning ionization electron spectrum of gas⁶⁴; ^b ref.⁶², according to our interpretation this band is due to a def. vibration of the lone $=\text{C}-\text{H}$ bond, *cf*¹⁸; ^c overlapped with the CH_3 sym. deformation; ^d extrapolated from the data of ref.¹³; ^e adiabatic and vertical, resp.⁶⁴; ^f photoionization⁶⁵; ^g UV photoelectron spectrum⁶⁶.

fundamental frequency). For the reasons mentioned, this assumption¹⁵ does not seem to be justified (*cf.* $\Delta\nu$ (in %) in Table II).

On the basis of semiquantitative data presented above, it is possible to make intuitively the prediction for alkenic complexes of other transition metals. The trend of $\nu(\text{C}=\text{C})_{\text{coord.}}^*$ in the methylethene series would be preserved, since it is generally governed by the value of their first ionization potentials. However, the individual values would be shifted systematically to higher or lower wavenumbers. This shift with respect to Pt complexes would reflect the different back-donation ability of *d* electrons of the particular metal.

Another consequence of coordination could be the change in equilibrium geometry, compared to that of free ligand⁶, which can provide more information about the local excited electronic state of the ligand. In the case of free ethene in the *V* state (singlet π^*), it is assumed¹² that geometry of the excited molecule is twisted by 90° around the original C=C bond (point group of symmetry D_{2d}). This geometry allows photochemical *cis-trans* isomerization to occur (*e.g.* 1,2-dideuterioethenes). The same reasoning holds for other alkenes^{1,2}. The Chatt-Duncanson model¹⁰ of π -complexes between Pt and alkenes assumes that a *d* electron, which is back-donated from Pt to an alkene, terminates on its antibonding π^* -orbital. However, the local symmetry of ethene coordinated in ZS is neither D_{2d} nor D_2 but C_{2v} . Moreover, $\nu(\text{C}=\text{C})_{\text{coord.}}^* = 1241 \text{ cm}^{-1}$ is far from values for the $\nu(\text{C}=\text{C})^*$ in "free" π^* -states (800 cm^{-1} for *V* and 1000 cm^{-1} for *T*, *cf.*¹². The spin-orbit coupling constant³⁴ of Pt is 4052 cm^{-1} and therefore any spin labeling of the local excited state of ethene is questionable). Accordingly, no isomerization of the ligands had been observed¹ with the series of 1-decenes-1,2-*d*_x (*x* = 1–3) coordinated in ZS. From these facts it has been concluded that an electron back-donated to ethene and 1-alkenes terminates on a Rydberg MO and not on their π^* -orbitals². If the assumption of Chatt and Duncanson¹⁰ were valid for other alkenes, the Pt complex with a pure *trans*- or *cis*-alkene would yield an equilibrium mixture of the *cis*- and *trans*-species after displacement of this alkene from the complex. It is the empirical fact that Pt (in the complexes of the type of Zeise's salt or dimer) does not isomerize either *trans*- or *cis*-2-butene at ambient temperature³⁵.

Unfortunately, none of the methylethene analogues of Zeise's salt was studied crystallographically. However, some information could be supplied by the X-ray diffraction data on the zwitter-ionic alkenylammonium compounds³⁶



In the first approximation, these internal salts can be considered as models for $\text{K}[\text{PtCl}_3(\textit{trans,cis-C}_4\text{H}_8)]$, the complexes which were presented in Table II. As usual with platinum metal complexes containing organic ligands, no attempt had been

made³⁶ to locate light H atoms having small X-ray scattering amplitudes. However, regardless of the positions of H(2) and H(3) in *trans*-species, the bonds C(1)–C(2) and C(3)–C(4) make³⁶ a dihedral angle of 143.2°, being thus far from the perpendicular orientation needed for *trans-cis* isomerization (*cf.* also³⁷ $150 \pm 5^\circ$ in (–)-*cis*-dichloro[(*R,R*)-*trans*-2-butene]-[(*S*)- α -phenylethylamine]platinum(II)). With the *cis*-species, the dihedral angle of 0° remained unchanged by coordination³⁶. Combining information about geometry of these complexes and free alkenes in the π^* -states¹², the Chatt–Duncanson¹⁰ model may be disputed. In other words, the electron back-donated from Pt does not seem to terminate on the π^* -orbital of these alkenes but presumably, and similarly to coordinated ethene², it occupies an analogue of the Rydberg MO's for the free species.

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Note: Recent calculations⁶⁷ support the vibrational assignments adopted here for free *trans*-, *gem*-, *cis*-dimethylenes: the C=C torsions are 964, 697, and 402 cm⁻¹, resp., the CH₃ torsions are 252 and 195 cm⁻¹ (*trans*), 179 and 132 cm⁻¹ (*cis*).