Table II. Ratios (trans/cis) of 2-Butenes for *cis*-2-Pentene Metathesis with Supported Complexes at 0% Conversion[a]

Catalyst	Carrier	Trans/cis C_4
$W(CO)_6$	$Al_2O_3\eta$	0.37 ± 0.05
$W(CO)_5P(n\text{-}C_4H_9)_3$		0.38
$W(CO)_5P(C_6H_5)_3$		0.38
$W(CO)_5P(OC_6H_5)_3$		0.40

[a] No reliable data were obtained with hexenes, due to a capillary condensation of C_6 on the catalyst.

complexes $W(CO)_5L$ (L = CO, P $(n\text{-}C_4H_9)_3$, P $(C_6H_5)_3$, P $(OC_6H_5)_3$, $NH_2C_6H_{11}$), (2) on the number of coordination sites (1–3) occupied by the ligands (L) in $W(CO)_5L$, $W(CO)_3L_3$, or on the steric hindrance of these ligands, (3) on the oxidation state of the precursor complexes (W^{6+}, W^0).

Some of the zerovalent precursor complexes have been deposited on an η alumina carrier. Metathesis of *cis*-2-pentene was carried out in the gaseous phase at 25°C. Results concerning stereoselectivity are given in Table II.

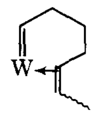
It is necessary to interpret these results by comparing homogeneous systems with heterogeneous ones. The fact that the stereoselectivity is modified upon interaction of the precursor complex with the surface of a solid indicates that this stereoselectivity depends on the steric environment of the transition metal.

Consequently steric results obtained in the pure homogeneous phase can supply valuable information on the steric effect of the ligand remaining coordinated to the active catalyst. It seems therefore that we have the same steric environment, whatever the precursor complex and the cocatalyst. That is, we have the same coordination sphere during the catalytic steps which govern stereochemistry of metathesis in all these cases. Tungsten has lost at least three ligands L; the complex $W(CO)_3$(arene) gives the same stereoselectivity as $W(CO)_6$. In fact tungsten has probably lost all its ligands L; $W(CO)_6$ and WCl_6 also exhibit the same stereoselectivity. Nevertheless this does not rule out the possibility of having one-electron ligands such as Cl, bonded to the active tungsten. It seems also that Al halide is not present on the active center since one obtains the same stereoselectivity with the catalytic systems WCl_6-$C_2H_5AlCl_2$-C_2H_5OH or WCl_6-$Sn(CH_3)_4$. This is corroborated by recent results of Dubois et al. concerning the photochemical activation of $W(CO)_6$ in a chlorine containing solvent.[13]

The results also seem to give an answer concerning the recent controversy about the homogeneous character of metathesis catalysts.[14] It now seems possible to make a clear distinction from a stereochemical point of view between homogeneous and heterogeneous systems. The two systems behave differently, and it seems that the homogeneous systems remain homogeneous in their active form at least with the precursor complexes used in the present work.

The rather weak stereoselectivity observed in the metathesis of acyclic olefins[15] neither supports nor refutes the mechanism of one carbene exchange proposed by Chauvin et al.[16,17] and verified later by others.[18-21]

This work does not seem to clarify the stereoselectivity aspect of metathesis of cyclic olefins. In the latter case about 90% cis or 90% trans polypentenamer can be observed[22-25] with cyclopentene depending on the experimental conditions. Although one could object than no precise stereochemical studies were performed with these systems at 0% conversion, the difference observed between metathesis of cyclic and acyclic olefins could be explained by the coordination to the catalyst of the first double bond after the carbene in the polymeric chain linked to the tungsten; evidently this cannot occur in the case of acyclic olefins



Finally it is worth mentioning that supported homogeneous catalysts exhibit a stereoselectivity which is quite different from that observed with pure homogeneous systems. Here we have evidence for the effect of the surface on the steric course of a catalytic reaction. This could represent one of the differences between homogeneous catalysis and catalysis by supported complexes.

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Steric Acceleration in Alkyldiazene (Azoalkane) Decompositions. Evidence for a Concerted Mechanism

Sir:

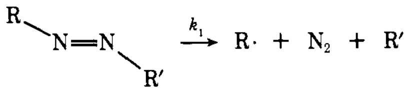
A number of techniques have been used to support either a concerted (two-bond, eq 1) or nonconcerted (one-bond, eq 2) mechanism for the thermal decomposition of dialkyl- and alkylaryldiazenes. These studies, which include CIDNP observations of diazenyl radicals;[1] effect of pressure,[2] solvent viscosity,[3] and structure[4] on decomposition rate; racemization of chiral diazenes;[5] intramolecular trapping of diazenyl radicals;[6] kinetic isotope effects;[7] and thermochemical considerations,[8] do not show total unanimity of thought.[1-8] However, most of the data can be accommodated by eq 1

Table I. Comparison of Activation Parameters and Strain Energies for Branched Alkyldiazenes (RN=NR')

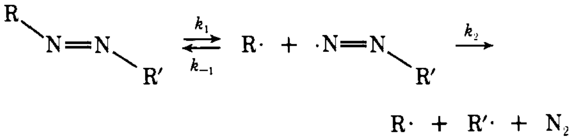
Compound	R	R'	$\Delta H^\ddagger$, kcal mol^{-1} ($\Delta S^\ddagger$ eu)	Strain energy,[d] kcal mol^{-1}
TBTB	$(CH_3)_3C-$	$(CH_3)_3C-$	42.2 ± 0.3[a] (16.1 ± 0.6)	(0)
TBTO	$(CH_3)_3C-$	$(CH_3)_3CCH_2(CH_3)_2C-$	38.1 ± 0.6[b] (12.3 ± 1.3)	4.6
TOTO	$(CH_3)_3CCH_2(CH_3)_2C-$	$(CH_3)_3CCH_2(CH_3)_2C-$	31.7 ± 0.6[c] (2.4 ± 1.4)	10.7

[a] Reference 14. [b] In diphenyl ether. [c] Reference 12. [d] Standard deviation ±1 kcal mol^{-1}.

when R· and R'· are of equal or similar stability and by eq 2 when R· and R'· are of greatly different stability. Since these mechanisms represent extremes, it is not surprising that intermediate situations are also known;[4d,7c,9,10] that is, both R–N bonds stretched in the transition state, but not to the same extent.



$$\mathrm{R{-}N{=}N{-}R'} \xrightarrow{k_1} \mathrm{R\cdot} + \mathrm{N_2} + \mathrm{R'\cdot} \tag{1}$$



$$\mathrm{R{-}N{=}N{-}R'} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{R\cdot} + \mathrm{\cdot N{=}N{-}R'} \xrightarrow{k_2} \mathrm{R\cdot} + \mathrm{R'\cdot} + \mathrm{N_2} \tag{2}$$

A fruitful approach to the question of one-bond vs. two-bond homolysis in alkyldiazenes[11] is found in comparison of steric effects on both sides of the diazene linkage. If appropriate models are selected such that the radicals produced do not differ in stability, then any rate variations observed should be attributable solely to differences in ground state energy. We have chosen three related compounds to test this postulate: di-*tert*-butyldiazene (hereafter TBTB for *tert*-butyl, *tert*-butyl), *tert*-butyl(1,1,3,3-tetramethylbutyl)diazene (hereafter TBTO for *tert*-butyl, *tert*-octyl), and bis (1,1,3,3-tetramethylbutyl)diazene (hereafter TOTO for *tert*-octyl, *tert*-octyl). Molecular models indicate that TBTB is essentially unstrained, but that TOTO has relatively severe steric interactions. On the basis of structure, the steric strain in TBTO should be approximately half that of TOTO. These suppositions find support in the relative thermolysis rates at 100° of TBTB, TBTO, and TOTO, which are 1.0:35:1320 (an essentially additive free energy effect; $\Delta\Delta G^\ddagger_{100} = 2.7$ kcal mol^{-1} for TBTB and TBTO and for TBTO and TOTO). Furthermore, a remarkably good correlation exists between the enthalpies of activation and strain energies. The latter are equal to the measured[13] heat of formation minus the heat of formation calculated using group contributions,[8] with TBTB as a strain-free model. As seen in Table I, the activation enthalpy of TBTO and TOTO is less than that of TBTB by 4.1 and 10.5 kcal mol^{-1}, respectively. Since these differences nearly equal the ground state strain energies (4.6 and 10.7 kcal mol^{-1}), we conclude that the more facile decomposition of TBTO and TOTO is purely a ground state effect.[14]

These results are best interpreted in terms of the concerted mechanism for alkyldiazene decomposition. Figures 1 and 2 show the energy diagrams expected for nonconcerted and concerted cleavage, respectively. The ground states are placed in experimentally determined order, and all steric strain is assumed to be relieved upon cleavage of *both* C–N bonds.[15] However, if the nonconcerted mechanism were operative, the transition state c for TOTO would be approximately 5 kcal mol^{-1} higher in energy than the transition state a for TBTB because at least half of the strain remains in c.[16] Thus, $\Delta H^\ddagger$ for TOTO should be roughly 5 kcal mol^{-1} lower than $\Delta H^\ddagger$ for TBTB (~37.7), in sharp disagreement with the experimental value (31.7). The nonconcerted mechanism leads to equally serious discrepancies in TBTO. For this compound it would seem likely that the more strained *tert*-octyl fragment would break off, giving a transition state b' equivalent to that for TBTB (a in Figure 1) and an expected rate for TBTO the same as that for TOTO. This is clearly not the case. If it is argued that the *tert*-butyl fragment breaks from TBTO, then transition state b would be the same energy as transition state c and the expected rate for TBTO would equal that of TBTB. This is also not the case.

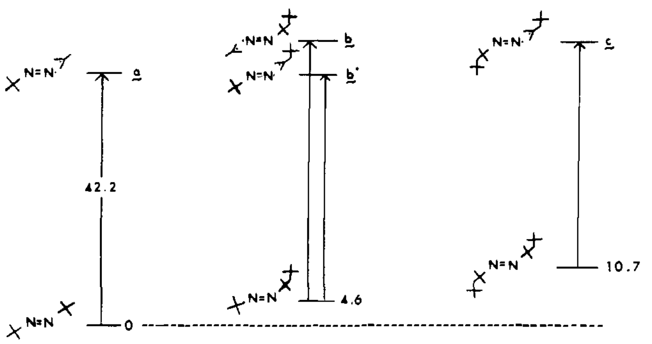


Figure 1. Energy diagram for the nonconcerted mechanism.

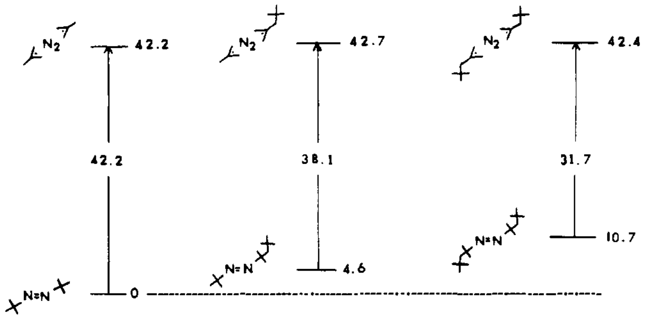


Figure 2. Energy diagram for the concerted mechanism.

These discrepancies vanish when the results are explained in terms of Figure 2. With concerted cleavage, no strain remains in any of the transition states.[15] Since they all have the same energy, the ground state energy difference should equal the $\Delta H^\ddagger$ differences, in accord with experiment.

These results offer strong support for the concerted mechanism for solution-phase decomposition of dialkyldiazenes with R and R' groups of similar radical stabilities.

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(16) Since 2,2,4-trimethylphentane (*tert*-octyl-H) possess 3.7 kcal mol^{-1} of strain, it is reasonable that the *tert*-octyldiazenyl radical would be strained by at least this amount.

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The Structure of the [Platinum(ethylenediamine)(guanosine)$_2$]$^{2+}$ Cation

Sir:

The surprisingly potent antitumor properties of *cis*-$Pt(NH_3)_2Cl_2$, $Pt(en)Cl_2$, and related compounds have been the subject of intensive investigation for the past few years.[1-3] Clinical trials using *cis*-$Pt(NH_3)_2Cl_2$ as a chemotherapeutic agent have been in progress in several hospitals since 1971.[3,4] It is suspected that the activity of these compounds is related to their ability to interact with DNA,[5-7] and several models involving the formation of platinum-bridged covalent cross-links have been proposed.[6-10] These models generally involve a *cis*-Pt(amine)$_2$ fragment chelated by certain atoms from DNA, usually nitrogen or oxygen atoms from the purine or pyrimidine bases.[7-10] Guanine in particular is thought to be especially vulnerable to attack,[9-12] since guanine derivatives are known to react more rapidly with platinum complexes than derivatives of the other nucleotide bases.[12] In this communication we wish to report the crystal structure of the [platinum(ethylenediamine)(guanosine)$_2$]$^{2+}$ cation and suggest a possible model for Pt-DNA interaction.

$[Pt(en)(Guo)_2]^{2+}$, prepared by treating $Pt(en)Cl_2$ with guanosine,[13] was isolated as crystals of a mixed chloride-iodide salt[14] by vapor diffusing[16] the reaction mixture against 1-propanol. Crystals of $[Pt(en)(Guo)_2]Cl_{1.5}I_{0.5}\cdot 2H_2O$ are tetragonal (space group $I4_122$), with $a = 17.557$ (4) Å, $c = 23.883$ (6) Å, and $Z = 8$. Two asymmetric sets of data were collected on a Nonius CAD-3 automated diffractometer using a $\theta/2\theta$ scan mode with Mo Kα radiation up to a 2θ limit of 50°. The data were corrected for absorption effects and merged to give 1146 nonzero reflections. The structure was solved by heavy atom methods and refined anisotropically to a final R factor of 5.9%.[17]

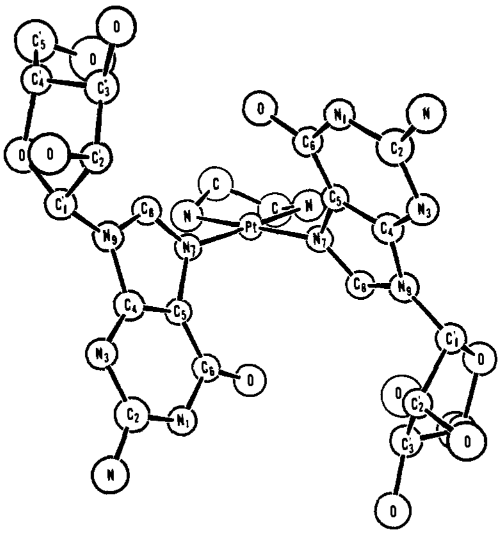

Figure 1. The geometry of the $[Pt(en)(Guo)_2]^{2+}$ cation. A crystallographic twofold rotation axis bisects the N_7-Pt-N_7 angle.

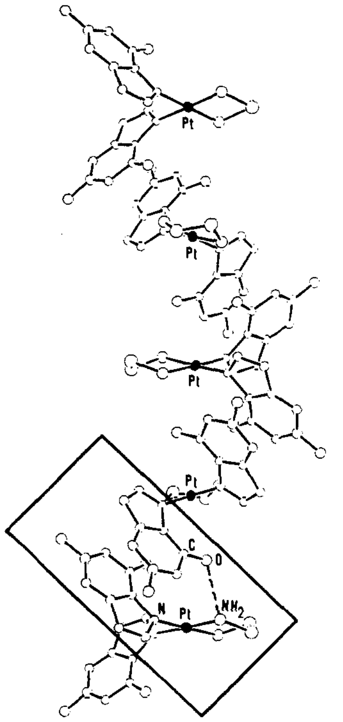

Figure 2. Part of the infinite spiral consisting of stacked $[Pt(en)(Guo)_2]^{2+}$ units, showing the pairing of the guanine bases. The ribose groups have been omitted for clarity. A crystallographic 4_1 screw axis is approximately defined by the row of platinum atoms. The boxed area shows a Pt(en) fragment forming a bridge between two parallel guanine rings. Hydrogen bonds connect the NH_2 groups of the ethylenediamine ligands to the carbonyl groups of the guanines. One of these is indicated (dotted line).

The square-planar geometry of the $[Pt(en)(Guo)_2]^{2+}$ cation is shown in Figure 1. A crystallographic twofold rotation axis passes through the platinum atom and the mid-point of the C-C bond of the ethylenediamine ligand. Each guanosine molecule coordinates in a monodentate fashion through the N_7 position of the guanine base, making a Pt-N_7 bond of 1.967 (15) Å and a N_7-Pt-N_7 angle of 87.0 (7)°. The planes of the guanine rings are tilted in such