A Model for Catalysis by Nickel(II) Complexes

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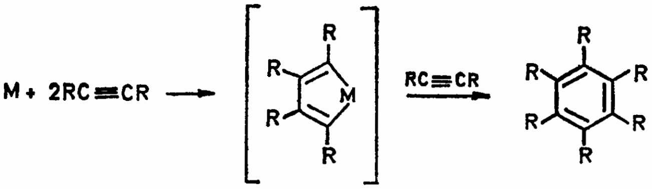
The tetrahedral-planar isomerisation of four-co-ordinate complexes of the nickel(II) ion of the type $[L_2NiX_2]$ (L is a neutral ligand and X an anionic ligand) is discussed in terms of the second-order Jahn–Teller effect. It is shown that when the ligands L possess π-acceptor orbitals the isomerisation may be facilitated and it is suggested that a ready isomerisation may account for the catalytic activity of these, and possibly other, transition-metal complexes with π-bonding ligands.

THE recognition that homogeneous catalysis often proceeds by a series of steps involving formation of a co-ordinatively unsaturated metal ion, followed by a series of oxidative additions or reductive eliminations and rearrangements, has increased our understanding of these reactions.[1] A central problem remains, however, namely why certain compounds behave as catalysts while others do not. In this paper we examine a model for the cyclotrimerisation of acetylenes to benzene derivatives catalysed by certain nickel(II) complexes.[2] We show that a vibrational path leading to the intermediate may be facilitated by the second-order Jahn–Teller effect, provided that π bonding is included in the molecular bonding scheme. The model is concerned only with the electronic factors involved and is based on the planar–tetrahedral isomerisation that occurs in many four-co-ordinate Ni^{II} complexes.

RESULTS AND DISCUSSION

Mechanism and Model.—The elegant work of Whitesides and Ehmann showed [3] that cyclobutadiene intermediates play little or no part in the formation of arenes from acetylenes and that the reaction probably proceeds *via* a five-membered metallocycle intermediate as shown in Scheme 1. These workers emphasised that no one mechanism is capable of rationalising all the experimental results from metal-catalysed cyclotrimerisation reactions, and a common problem of all mechanisms is the role played by the metal in formation of carbon–carbon bonds.



SCHEME 1

Previous discussions [4,5] concerning the involvement of metal ions in the catalysed cycloaddition of olefins have been based on the Woodward–Hoffmann rules or by considering a tetrahedral–planar isomerisation of an unspecified metal complex. Caldow and MacGregor [5] thus concluded that catalysis would occur if there was a ground-state correlation for the tetrahedral–planar isomerisation or, possibly, if a low-lying excited state of one stereoisomer correlated with the ground state of the alternative isomer. Only d^1 and d^{10} metal ions possess ground-state correlations whereas ground- to excited-state correlations exist for d^2, d^8, and d^9 ions. Examples of Ni^{II} complexes which have been used as catalysts for cyclotrimerisation of acetylenes are $[(R_3P)_2NiX_2]$ and several bis(*N*-alkylsalicylaldiminato) species.[6] Members of both these series have been found to undergo tetrahedral–planar isomerisation, and we believe this to be an important property which imparts catalytic activity. In some cases both isomeric forms of the complexes have been isolated [7-9] and it is found that the stereoisomerisation is accompanied by a magnetic isomerisation with the tetrahedral forms being paramagnetic and the planar forms diamagnetic. However, catalysis is not restricted to diamagnetic or paramagnetic complexes but occurs in both types. Following the conclusions of Caldow and MacGregor it seems likely that the tetrahedral–planar isomerisation is of importance since neither tetrahedral complexes such as $[NiCl_4]^{2-}$ and $[NiBr_4]^{2-}$ nor planar complexes such as $[Ni(dimethylglyoxime)_2]$ have been reported as being catalysts. We consider first how the tetrahedral–planar isomerisation may occur in $[L_2NiX_2]$ complexes and then discuss this phenomenon in relation to catalytic activity.

(a) *Vibronic-coupling effects*. Following Bader,[10] Pearson showed [11] that the relative stability of stereoisomers may be predicted from a consideration of the second-order Jahn–Teller effect. The effect arises by vibronic coupling of the ground and excited states of a molecule resulting in a decrease in the force constants of the ground potential surface. If the force constants are reduced to near zero for a particular mode of displacement there will be a wide amplitude of vibration for this mode and the molecule will easily adopt an

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[1] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York, 1972, p. 770.

[2] C. W. Bird, 'Transition Metal Intermediates in Organic Synthesis,' Lagos Press, London, 1966, p. 1.

[3] G. M. Whitesides and W. J. Ehmann, *J. Amer. Chem. Soc.*, 1969, **91**, 3800.

[4] F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, 1967, **89**, 2484.

[5] G. L. Caldow and R. A. MacGregor, *J. Chem. Soc.* (*A*), 1971, 1654.

[6] G. N. Schrauzer, P. Glockner, and S. Eichler, *Angew. Chem. Internat. Edn.*, 1964, **3**, 185.

[7] L. H. Pignolet, W. De W. Horrockes, jun., and R. H. Holm, *J. Amer. Chem. Soc.*, 1970, **92**, 1855.

[8] G. N. La Mar and E. O. Sherman, *J. Amer. Chem. Soc.*, 1970, **92**, 2691.

[9] R. H. Holm, G. W. Everett, jun., and A. Chakavorty, *Progr. Inorg. Chem.*, 1966, **7**, 83.

[10] R. F. W. Bader, *Canad. J. Chem.*, 1962, **40**, 1164.

[11] R. G. Pearson, *J. Amer. Chem. Soc.*, 1969, **91**, 1252.

alternative structure which differs little in energy from the first. If the vibrational amplitude is sufficiently large the two structures will interconvert in a typical dynamic fashion. However, if the force constants are reduced below zero the molecule will distort to another structure spontaneously and a static situation is found. Pearson [11] and also Caldow and MacGregor [5] were concerned with the latter situation (the prediction of one stereoisomer in preference to another) and then only for the tetrahedral T_d-planar D_{4h} isomerisation. The precise symmetry chosen for the molecule is important since it determines which particular mode of vibration may be facilitated because the direct product of the representations of the filled and unoccupied molecular orbitals (m.o.s) must contain the representation of the vibration.

The Ni^{II} complexes with which we are concerned have C_{2v} symmetry and they may be either pseudo-tetrahedral with bond angles close to 120° (θ in Figure 1) or pseudo-planar with bond angles close to 180°. Provided that exact planarity is not achieved the C_{2v} molecular symmetry prevails for any value of θ between the two extreme structures. In the case of complexes of the type $[L_2NiX_2]$ (L is a neutral ligand and X an anion) the pseudo-tetrahedral structure is shown in Figure 1, L and X representing the appropriate ligand positions with the choice of co-ordinate axes as shown. The pseudo-planar form can adopt either a *trans* or a *cis* form, the ligand positions being given by L′ and X′ for the former and L″ and X″ for the latter. The normal mode of vibration that will convert pseudo-tetrahedral $[L_2NiX_2]$ to *trans*-$[L'_2NiX'_2]$ is of a_1 symmetry (the LNiL and XNiX bending vibrations) whereas $[L_2NiX_2]$ is converted to $[L''_2NiX''_2]$ by the a_2 vibration (the torsional oscillation about the z axis). Bending vibrations would be expected to be more susceptible to the second-order Jahn–Teller effect because they have low frequencies. In order to establish which vibration is more likely to be facilitated we need to consider the m.o. schemes for the various stereochemistries.

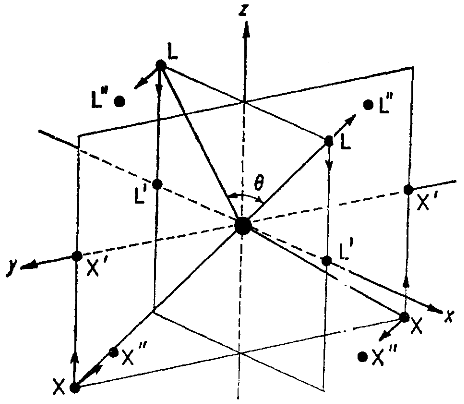

FIGURE 1 Cartesian axes and relative ligand positions for the pseudo-tetrahedral $[L_2NiX_2]$, *trans*-$[L'_2NiX'_2]$, and *cis*-pseudo-planar $[L''_2NiX''_2]$ complexes

(b) *Interconversions of the pseudo-tetrahedral and pseudo-planar forms.* In the diamagnetic pseudo-planar *trans* form the likely m.o. sequence for C_{2v} symmetry can be deduced from results obtained for planar D_{4h} molecules [12] and by use of correlation tables for the $D_{4h}\rightarrow D_{2h}\rightarrow C_{2v}$ sequence. The order of the mainly d-orbital m.o.s will probably be $z^2(a_1) < xz(b_1) < yz(b_2) < xy(a_2) \ll x^2 - y^2(a_1)$, with the lowest four orbitals containing the eight d electrons. The $x^2 - y^2$ orbital is strongly σ antibonding and is at a higher energy than the other four orbitals for ligands of moderate π-bonding strengths; the order of the remaining orbitals is taken to be the same as in D_{4h} complexes except that the xz orbital will be lowered in energy compared with the yz because it interacts with the L ligand vacant π^* orbitals whereas yz is raised by interaction with low-lying filled X π-donor orbitals. The remaining vacant antibonding m.o.s comprise the nickel σ^* orbitals, $4s(a_1)$, $4p_x(b_1)$, and $4p_y(b_2)$, the nickel π^*, $4p_z(a_1)$, orbital together with the linear combinations of L (phosphorus atom) orbitals $1/2^{\frac{1}{2}}(\pi_v - \pi_v)$ of symmetry b_1, being vertical to the xy plane, and $1/2^{\frac{1}{2}}(\pi_h - \pi_h)$ of symmetry a_2, lying in the xy plane.

Estimation of the likely sequence of the vacant orbitals is difficult. Intense bands in the electronic spectra of Ni^{II} phosphine complexes at *ca.* 25 000 cm^{-1} have been variously assigned to $3d \longrightarrow 4p$ transitions [13] and to electron transfer from filled σ orbitals located mainly on phosphorus to the vacant $x^2 - y^2$ orbital.[14] It seems likely that [12] the energy separation between the mainly $3d$ and mainly $4s$ or $4p$ m.o.s will be appreciably greater than the 4 eV † which has been arbitrarily taken as the energy gap below which the vibronic coupling of the ground and excited states is important.[11] On the other hand it seems reasonable that the a_2 and b_1 π^* m.o.s of the ligands L (phosphorus) lie below the $4s$ and $4p$ orbitals since they are only weakly π bonding. We assume, therefore, that these vacant m.o.s are sufficiently close to the highest-filled m.o.s to at least lead to substantially reduced force constants by vibronic coupling. The direct product of the representations of the highest-filled m.o. of symmetry a_2 with the π^* combination of phosphorus $3d$ orbitals also of symmetry a_2 contains the representation a_1 so that the normal mode of vibration of a_1 symmetry will be facilitated, and under favourable circumstances this vibration will convert the pseudo-planar *trans* form $[L'_2NiX'_2]$ to the pseudo-tetrahedral $[L_2NiX_2]$. Normally the totally symmetric vibrations of a molecule would not be considered in applications of the second-order Jahn–Teller effect since clearly such a vibration cannot interconvert two alternative structures of differing molecular symmetry. However, we here assume that C_{2v} molecular symmetry is retained throughout and that only the amplitude of the vibration is affected.

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† 1 eV ≈ 1.60×10^{-19} J.

[12] W. R. Mason and H. B. Gray, *J. Amer. Chem. Soc.*, **1968**, **90**, 5721.

[13] L. E. Orgel, *J. Chem. Phys.*, **1955**, **23**, 1004.

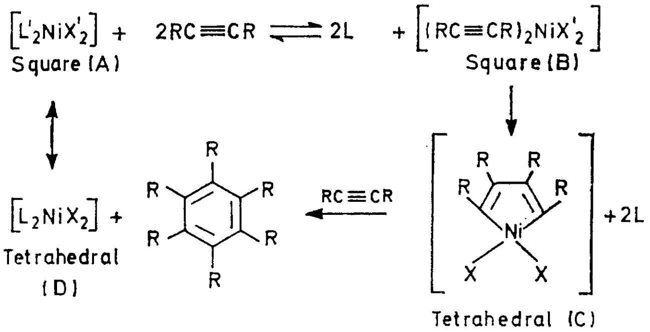
[14] C. K. Jørgensen, 'Inorganic Complexes,' Academic Press, New York, 1963, p. 157.

In the C_{2v} pseudo-tetrahedral paramagnetic complexes the mainly metal *d* m.o. sequence has been shown to be [15,16] $z^2(a_1) < xy(a_2) < yz(b_2) < xz(b_1) < x^2 - y^2(a_1)$ for LNiL bond angles of *ca.* 120° and the cartesian axes as shown in Figure 1. Both the *xz* and *yz* orbitals become σ antibonding with the L and X ligands respectively and are raised in energy in the $[L_2NiX_2]$ complex compared with $[L'_2NiX'_2]$; also the π bonding in the *xy* plane decreases, stabilising the *xy* orbital, although the $x^2 - y^2$ orbital is sufficiently σ and π antibonding to remain as the highest of the mainly *d*-orbital m.o.s, but its energy is much closer to the remaining *d* orbitals than in the pseudo-planar form. The linear combinations of vacant L π* orbitals will probably become less involved in π bonding with the *xz* and *yz* orbitals as these latter become σ bonding so that the π* orbitals may become essentially non-bonding in the $[L_2NiX_2]$ complexes. For a pseudo-tetrahedral complex the a_1 vibration may thus be enhanced by vibronic coupling between the partially filled $xz(b_1)$ mainly *d* m.o. and the vacant b_1 π* ligand combination. Therefore we postulate that the catalytically active Ni^{II} complexes of the type $[L_2NiX_2]$ may undergo dynamic interconversion between a pseudo-tetrahedral and a pseudo-planar form by virtue of the increased amplitude of the a_1 vibration arising from the second-order Jahn–Teller effect. Furthermore, the interconversion will only be facilitated if L (or X) contains π-acceptor orbitals.

By similar arguments it can be seen that the amplitude of the a_2 vibration of the pseudo-tetrahedral $[L_2NiX_2]$ complex may also be enhanced by the vibronic coupling of the highest partially filled $x^2 - y^2(a_1)$ mainly *d* m.o. with the π* combination of L orbitals of a_2 symmetry. The increased amplitude of the a_2 vibration could lead to a dynamic interconversion of the pseudo-tetrahedral $[L_2NiX_2]$ and the pseudo-planar *cis*-$[L''_2NiX''_2]$ complex. Whether both or only one of the a_1 and a_2 vibrations are enhanced will depend on several factors including the relative values of the reduced force constants and the energy separations between the various filled and vacant orbitals.

In the above discussion we have implicitly assumed that the m.o. sequences will be those suggested by semi-empirical m.o. calculations and that Koopmans' theorem is valid. Thus, we equate the highest-filled m.o.s with the mainly metal 3*d* orbitals. Recent calculations by Demuynck and Veillard [17] have suggested that Koopmans' theorem may not be generally valid although it has been shown to hold for complexes containing neutral ligands with limited π systems (olefins, acetylenes, and phosphines). Although an SCF MO calculation on the $[L_2NiX_2]$ complexes might lead to different m.o. sequences, the facilitation of the a_1 and a_2 vibrations could still be energetically feasible.

Application to Catalysis.—We consider the initial step in the catalysis reaction to be replacement of the two neutral ligands L by two acetylene molecules (Scheme 2). Four-co-ordinate complexes of Ni^{II} are fairly labile so that this replacement may be achieved readily, probably *via* an S_N2 mechanism. We replace the ligands L rather than X because it has been shown that $[(Ph_3P)_2NiX_2]$ complexes dissociate thermally or in methanol to yield triphenylphosphine [18] and that heating $[(Ph_3P)_2Ni(CN)_2]$ under reflux in benzene eliminates the phosphine.[19] Two molecules of acetylene may thus be bound to the nickel ion and in the pseudo-planar form either a *cis* or *trans* arrangement is possible. We now consider how the square-planar complex, (B) in Scheme 2, can convert into the metallocycle intermediate in which the metal is formally tetrahedral, (C). In the *trans* form the acetylenes will probably be oriented perpendicular to the *xy* plane so that the filled π orbitals of the acetylenes overlap with the vacant $x^2 - y^2$ and the vacant π* acetylene orbitals overlap with the filled *xz*. Group theoretically this is an entirely analogous situation to that discussed above for the $[L_2NiX_2]$ complexes. The linear combination of acetylene π* orbitals $1/2^{\frac{1}{2}}(\pi_v - \pi_v)$ has symmetry b_1 and vibronic coupling of this orbital with the filled b_1 mainly metal orbital may enhance the amplitude of the a_1 vibration. Motion of the two acetylenes in the *xz* plane by this vibration will bring them into much closer proximity to each other than is possible in the pseudo-planar form [Figures 2(*a*) and 2(*b*)].



Scheme 2

In the pseudo-tetrahedral form [Figure 2(*b*)] the overlap between the vacant π* orbitals of the acetylenes and the filled *xz* metal orbitals will be reduced so that there will be a decrease in the metal to ligand π donation. Also the filled acetylene π orbitals will overlap simultaneously with the metal $x^2 - y^2$ and z^2 orbitals, all being of a_1 symmetry, and since the $x^2 - y^2$ orbital contains one electron rather than none [as in square (B)] the σ donation from the acetylene to the metal will be reduced. Thus the acetylene molecules will probably be less tightly bound to the metal in the pseudo-tetrahedral complex compared with the pseudo-planar one.

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[15] J. Demuynck and A. Veillard, *Theor. Chim. Acta*, 1973, **28**, 241.

[16] K. D. Huddersman and R. C. Slade, unpublished work.

[17] A. A. G. Tomlinson, C. Bellitto, O. Poivesana, and C. Furlani, *J.C.S. Dalton*, 1972, 350.

[18] K. Yamamoto and M. Oku, *Bull. Chem. Soc. Japan*, 1954, **27**, 509.

[19] G. N. Schrauzer and P. Glockner, *Chem. Ber.*, 1964, **97**, 2451.

However, the σ donation, while no longer synergistically favoured by the metal to ligand π donation, may be enhanced by electron drift from the z^2 orbital into the acetylene π orbitals in the direction shown in Figure 2(*b*). This cyclic drift of σ electrons appears to provide a plausible route to formation of the five-membered metallocycle intermediate shown in Schemes 1 and 2. The metallocycle intermediate is formally a complex of nickel(IV); while such an oxidation state, which is not unknown for nickel, may not be energetically favoured in stable compounds, its occurrence in an intermediate or transition state cannot be ruled out [see the oxidative addition of C–H bonds to chromium(III) to give formally a compound of chromium(V) [20]]. Subsequent reaction of this metallocycle intermediate with a molecule of acetylene in a Diels–Alder type reaction will yield benzene derivatives and regenerates the catalyst as a co-ordinatively unsaturated Ni^{II} compound. This can react with two further molecules of acetylene or take up the neutral ligands L, allowing $[L_2NiX_2]$ to be recovered from the reaction, apparently unchanged, in either the pseudo-tetrahedral form (D) or the pseudo-planar form (A) depending on which isomer is stable in the solid state.

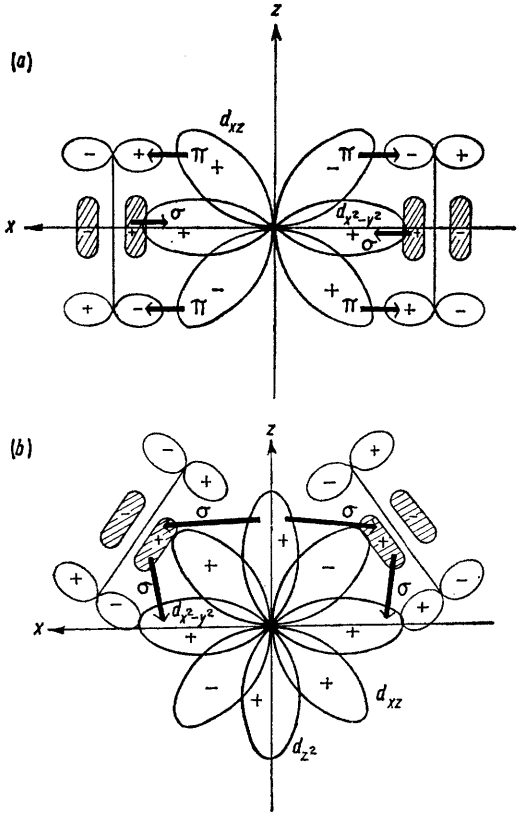

FIGURE 2 (*a*) Schematic representation of the bonding of the acetylene molecules in the *trans*-pseudo-planar $[(RC{\equiv}CR)_2NiX_2]$ intermediate. The σ-bond electron donation is shown from the filled π orbitals of the acetylene to the vacant $d_{x^2-y^2}$ orbital and the π-bond electron donation is shown from the filled metal d_{xz} to the vacant π^* orbitals of acetylene. (*b*) Acetylene molecules bonded to the nickel ion in the pseudo-tetrahedral $[(RC{\equiv}CR)_2NiX_2]$ intermediate. Electron donation through the σ-bonding orbitals is shown from the filled d_{z^2} and π orbitals to the partially filled $d_{x^2-y^2}$ orbital

In the *cis*-planar form cyclisation may occur directly by some other mechanism without distorting the tetrahedron as the acetylenes can rotate about the metal–acetylene axis. Alternatively, the *cis*-pseudo-planar form of (B) may dynamically interconvert to the pseudo-tetrahedral intermediate by facilitation of the a_2 vibration. However, such an interconversion will have little effect on the separation of the two acetylene molecules and so will probably not facilitate reaction between them. If both the a_1 and a_2 vibrations are enhanced then both $[L'_2NiX'_2]$–$[L_2NiX_2]$ and $[L''_2NiX''_2]$–$[L_2NiX_2]$ interconversions are possible so that the *cis* and *trans* forms may isomerise *via* a pseudo-tetrahedral intermediate. Thus this model may be applied to catalysis by *cis* and *trans* isomers of planar Ni^{II} complexes, although it appears that the *trans* isomer will be the more common, presumably because of the steric interactions between the bulky phosphine ligands.

The Effect of Ligand X.—There has been no comparison of the catalytic efficiencies of $[L_2NiX_2]$ complexes for various anions X, although $[(Ph_3P)_2Ni(CN)_2]$ is reported as giving a high yield of benzene from acetylene.[6] However, we can assess the likely effect of the ligand X by reference to the work of Wittig [21] on reactions of cyclo-octyne with NiX_2 salts. In principle, since we consider catalysis to be associated with dynamic interconversions of the $[(RC{\equiv}CR)_2NiX_2]$ intermediate, there is little difference between the formation of this intermediate by replacement of ligands L as in Scheme 2 and its formation by direct reaction of acetylenes and NiX_2 salts. The subsequent reaction of the intermediate with an unco-ordinated acetylene requires a reactive co-ordinated organic entity which is not too strongly bound to the metal. In the pseudo-planar to pseudo-tetrahedral interconversion there is a decrease in the metal to ligand π donation so that the metal–acetylene bonding is weakened, presumably at the same time as the new carbon–carbon bond is formed. Depending on the ligand X, the π donation from the metal to the acetylenes, *xz* to π*, may be enhanced or reduced. Ligands which act as π donors will tend to push electron density onto the metal whereas π-acceptor ligands will tend to draw electron density away from the metal in competition with the co-ordinated acetylene groups. Thus π-acceptor ligands may increase the catalytic efficiency by weakening the metal–carbon bonds whereas π-donor ligands could lead to a strengthening of the metal–carbon bonds giving a more stable, *i.e.* less reactive, intermediate. Experimental results where available support such a notion. Cyclo-octyne reacts with $Ni(CN)_2$ to give an arene whereas reaction with $NiBr_2$ occurs to give a stable dibromo(cyclobutadiene)-nickel complex and some arene.[21]

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[20] G. M. Whitesides and W. J. Ehmann, *J. Amer.* ***Chem. Soc.***, 1970, **92**, 5625.

[21] G. Wittig and P. Fritze, *Annalen*, 1968, **712**, 79.

Comparison with Palladium and Platinum.—Although the second-order Jahn–Teller effect can increase the amplitude of a particular mode of vibration to give a dynamic interconversion between the pseudo-planar and tetrahedral forms of the four-co-ordinate metal complexes, the interconversion will also be affected by the relative energy separations of the m.o.s involved. The ready interconversions of numerous Ni^{II} complexes suggest that these energy separations are sufficiently small to make the effect of importance. Also the energies of the two isomers are probably comparable for four-co-ordinate Ni^{II} complexes. In comparing nickel with palladium(II) and platinum(II), the one-electron orbital splittings arising from ligand-field effects increase whilst the interelectron repulsions decrease, so that there is an increasing tendency towards diamagnetism in the order nickel < palladium < platinum and the predominant four-co-ordinate structure for the $4d^8$ and $5d^8$ ions is the planar one.[22] Accordingly we expect the catalytic activity of complexes of the later members of the d^8 triad to be less pronounced. Complexes $[L_2PtX_2]$ have not been reported as catalysts and in fact Pt^{II} acetylene complexes are known to be stable and rather inert.[23] The situation with Pd^{II} is intermediate and complicated.[24] Cyclotrimerisation of acetylenes certainly occurs, although possibly by a cyclobutadiene intermediate[3] rather than a five-membered metallocycle. We conclude that favourable conditions for the stereoisomerisation are more important than the number and arrangement of the d electrons.

Summary.—The catalysis model which we propose involves formation of a reactive intermediate, $[(RC{\equiv}CR)_2\text{-}NiX_2]$, which is a non-rigid molecule. The second-order Jahn–Teller effect is applied to show how the amplitude of the a_1 vibration can be increased leading to interconversion of the pseudo-planar and -tetrahedral forms so bringing the acetylenes close together. Formation of the metallocycle intermediate is then promoted by a drift of σ-bonding electrons from the metal z^2 to $x^2 - y^2$ orbitals *via* the filled π orbitals of acetylene while at the same time the metal to acetylene π bonding is reduced. The subsequent Diels–Alder reaction of the metallocycle is shown to be dependent on the nature of the anion X. However, we stress that the model is concerned only with one particular metal-catalysed reaction and with the electronic factors involved in the various steps shown in Scheme 2. There are many assumptions in the model that cannot be tested directly, their validity only being justified in retrospect.

The preparation of cyclo-octatetraene by the catalysed tetramerisation of acetylene itself appears to be an atypical reaction and so does not necessarily occur by a mechanism similar to that discussed above. However, it is found that even in this case $Ni(CN)_2$ is a much better catalyst than $NiBr_2$[25] so that the availability of π-acceptor orbitals on the ligand may also be of importance here. Other intermediates and mechanisms have been proposed[6,26,27] for these and related reactions, but they do not readily yield general conclusions about catalysis. The mechanism which we have suggested rationalises catalytic activity in terms of the availability of π orbitals on the ligands co-ordinated to the metal ion in a non-rigid intermediate. Finally, it seems reasonable to suppose that many other metal-catalysed reactions involve dynamic interconversion of some labile intermediate facilitated by vibronic coupling, although the overall driving force for these reactions is undoubtedly the very favourable free-energy changes accompanying the organic reactions.

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[26] O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 1964, 187.

[27] E. M. Arnett and J. M. Bollinger, *J. Amer. Chem. Soc.*, 1964, **86**, 4729.