The tribromomethyl group in $Mn(CO)_5CBr_3$ is subject to facile homolytic replacement of Br by H upon treatment with $HSn(n\text{-}Bu)_3$. Rapid exothermic reaction occurs when $Mn(CO)_5CBr_3$ is treated with 2 equiv of $HSn(n\text{-}Bu)_3$ to afford a mixture of $Mn(CO)_5CHBr_2$ and $Mn(CO)_5CH_2Br$. Complete replacement of all the bromine atoms by hydrogen to yield $Mn(CO)_5Me$ requires heating to 60 °C (eq 12). Some $Mn_2(CO)_{10}$ is detected in the reaction mixture

$$Mn(CO)_5CH_2Br + HSn(n\text{-}Bu)_3 \rightarrow Mn(CO)_5Me + BrSn(n\text{-}Bu)_3 \quad (12)$$

implying that Mn–C bond cleavage also takes place. No reaction is observed between $Mn(CO)_5CF_3$ and excess $HSn(n\text{-}Bu)_3$ under similar conditions. Homolytic halide replacement by $HSn(n\text{-}Bu)_3$ also has been observed in halomethylidyne cluster complexes.[39]

Conclusion

The reaction chemistry of transition-metal trihalomethyl complexes (X = Cl, Br) is much more diverse than that of their thermally stable trifluoromethyl precursors. The enhanced reactivity is particularly evident in reactions with nucleophiles or in homolytic processes. Cation dihalocarbene complexes are implicated as intermediates in heterolytic reactions, whereas transition-metal dihalocarbene radicals may be involved in the free radical reactions.

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Registry No. $[CpFe(CO)_2(CF_2)][BF_4]$, 88211-34-1; $[CpFe(CO)_3][BF_4]$, 12244-69-8; $[CpFe(CO)_2(CCl_2)][BCl_4]$, 88211-36-3; $[CpFe(CO)_2(CN\text{-}i\text{-}Pr)][PF_6]$, 69532-19-0; $CpFe(CO)_2CF_3$, 52409-72-0; $CpFe(CO)_2CCl_3$, 86392-66-7; $CpFe(CO)_2CN$, 12152-37-3; $CpFe(CO)(CN\text{-}i\text{-}Pr)(C(O)NH(i\text{-}Pr))$, 88211-37-4; $[CpFe(CO)_3]^+$, 32660-74-5; $Mn(CO)_5CF_3$, 13601-14-4; $[Mn(CO)_6][BF_4]$, 15557-71-8; $Mn(CO)_5CBR_3$, 86392-60-1; $Mn(CO)_5CH_2BR$, 86392-63-4; $Mn(CO)_5CHBr_2$, 86392-65-6; $Mn(CO)_5Me$, 13601-24-6; $CpMo(CO)_3CF_3$, 12152-60-2; $[CpMo(CO)_4]^+$, 48138-37-0; $CpMo(CO)_3C_2F_5$, 88180-66-9; BF_3, 7637-07-2; BCl_3, 10294-34-5; NH_3, 7664-41-7; $i\text{-}PrNH_2$, 75-31-0; $HSn(n\text{-}Bu)_3$, 688-73-3; HBF_4, 16872-11-0; cyclohexene, 110-83-8; 1-pentene, 109-67-1; *trans*-2-butene, 624-64-6; cumene, 98-82-8; toluene, 108-88-3.

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Olefin Oligomerization on Nickel. A Theoretical Study of the Barrier to Olefin Rotation and Insertion

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The mechanism of Ziegler–Natta catalysis has been investigated by using the atom superposition and electron delocalization moleculer orbital theory. Model nickel compounds of the form $Ni(C_2H_4)(CH_3)LX$ ($L = PH_3$, $X = Cl$) were studied. Polymerization was examined by assuming a Cossee mechanism. From MO symmetry considerations, a rearrangement involving rotation of the olefin around its bond to the metal is required before the reaction will occur. The barrier to this rotation is found to be a function of the ligand trans effect and steric interactions with the cis ligands. Calculated barriers for Pt(II) and Rh(I) compounds compare favorably with results obtained from NMR experiments.

Introduction

Typical Ziegler–Natta catalysts are formed from transition-metal salts and main-group (usually aluminum) metal alkyl, metal aryl, and alkyl metal halides.[1,2] These catalysts are used for polymerization of α-olefins such as ethylene, propylene, etc.[3-5] Only moderate pressures (8–30 atm) and slightly elevated temperatures (20–120 °C) are required for the reaction to proceed. The products of polymerization, in contrast to the polymers produced by free radical reactions, have a narrow molecular weight distribution and high stereospecificity.[3,6-8] The reaction offers the possibility of forming a well-controlled product through the choice of an appropriate metal center, with appropriate conditions of temperature and pressure. A polymer of a lower molecular weight usually is produced at elevated temperatures.[9]

A most interesting question about the polymerization mechanism is the origin of high stereoselectivity. This stereoselectivity can lead to a polymer with special characteristics such as crystallinity or (with dienes) high tacticity. A number of theories exist that attempt to explain the stereoregularity.[2,6,10,11] Most involve formation of a

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Table I. Parameters Used in the ASED Calculation

	orbital	adjusted ionizatn potential, eV	exponent $(QV)^{53}$	double-ζ d orbitals exp	double-ζ d orbitals coeff $c(1)$	double-ζ d orbitals coeff $c(2)$
Ni[21]	4s	7.64	1.8			
	4p	3.99	1.5			
	3d	10.00	5.75	2.00	0.5631	0.6293
Pt[50]	6s	10.00	2.55			
	6p	5.96	2.25			
	5d	10.60	6.01	2.40	0.6561	0.5711
C	2s	20.00	1.65			
	2p	11.26	1.61			
p	3s	16.15	1.88			
	3p	10.55	1.62			
Cl	3s	24.54	2.35			
	3p	13.01	2.03			
H	1s	13.60	1.2			

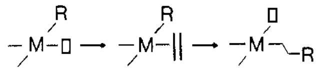

Figure 1. Important steps in the Cossee mechanism for polymerization of olefins. ◻ represents an open coordination site.

four-membered metallacycle that includes the metal atom, the last carbon of the polymer chain, and the two carbon atoms of the olefin. The ring can exist with the growing polymer chain in a configuration either cis or trans relative to other ligands on the metal atom and the substituents on the ring. Preference for one of those conformations dictates stereospecificity of the polymer. The asymmetry of the metal center appears to be the determining factor in this stereoregularity.[12]

The usual Ziegler–Natta catalysts are formed from compounds of metals in groups 4 or 5 in the transition series. Metals from group 8, particularly cobalt and nickel, also may act as catalysts under Ziegler–Natta conditions. These metals, however, generally promote dimerization or oligomerization of α-olefins rather than long-chain polymerization. Oligomerization with a nickel catalyst in the absence of cocatalyst is the basis of Shell's SHOP process.[13]

Although the precise mechanism and structure of d^8 metal catalysts are not known, many of the factors affecting such reactions have been studied. It is known that the stereochemistry of the product is more dependent on the asymmetry of the metal ion and the ligands surrounding it than the geometry of the olefin itself.[12,14] Polymerization reactions in the presence of cobalt or nickel can be accompanied by isomerization of the products. Because of the mild reaction conditions generally required and a tolerance to various functional groups, nickel complexes often can be used in organic synthesis when high stereospecificity is demanded.[15,16]

Polymerization reactions with d^8 metal ions require the presence of Lewis acids. Although Lewis acids can themselves cause oligomerization and isomerization of olefins, the transition metal is essential for the reaction to proceed at a significant rate.[14] With nickel the catalyst may be formed from either Ni(0) or Ni(II) complexes, depending on specific reaction conditions.[14,16]

Table II. Bond Lengths Used in the ASED Calculation[55-58] (Å)

Ni—C	1.85	C—H	1.10
Ni—P	2.15	Pt—Cl	2.305 (cis)
Ni—olefin	1.90		2.327 (trans)
Ni—Cl	2.21	Pt—olefin	2.05
C=C	1.37		

In the early 1960s, Cossee proposed a mechanism for polymerization of α-olefins.[17-19] The Cossee mechanism (Figure 1) involves coordination of the olefin to a metal center followed by migration of an alkyl group to the olefin, forming a carbon–carbon bond. Four conditions were postulated for the reaction: (1) a nearly octahedral six coordinate metal atom; (2) an empty or nearly empty set of t_{2g} orbitals; (3) at least one alkyl group in the coordination sphere of the metal; and (4) at least one vacant coordination site. Conditions 1 and 2 apply specifically to the early transition metals that have a limited number of electrons. However, in its most general form this mechanism can be extended to the reactions with any of the transition metals. Here we consider specifically the d^8 nickel complexes such as those involved in the oligomerization and polymerization of olefins.[2,6,14] Our interest in olefin binding to the d^8 metals goes back to the early sixties and studies of Zeise's salt.[20]

Method of Calculation

Calculations were performed by using the atom superposition and electron delocalization technique.[21-23] This theory adds together an atom–atom pairwise repulsion energy, E_R, and an electron delocalization energy, E_D. As has been shown,[21] these energies, which come from integrating the forces on each nucleus as the atoms are brought together to form a molecule, yield the system energy E:

$$E = E_R + E_D \tag{1}$$

For each pair of atoms, the contribution to E_R is the Coulombic potential energy of the nucleus in the field of the other atoms. As each atom is added to the molecule, there is a contribution to E_D that is the integrated electrostatic force on the nucleus of the new atom due to bond charge formation. While E_D would ordinarily be practically impossible to obtain in this manner, it has been found to

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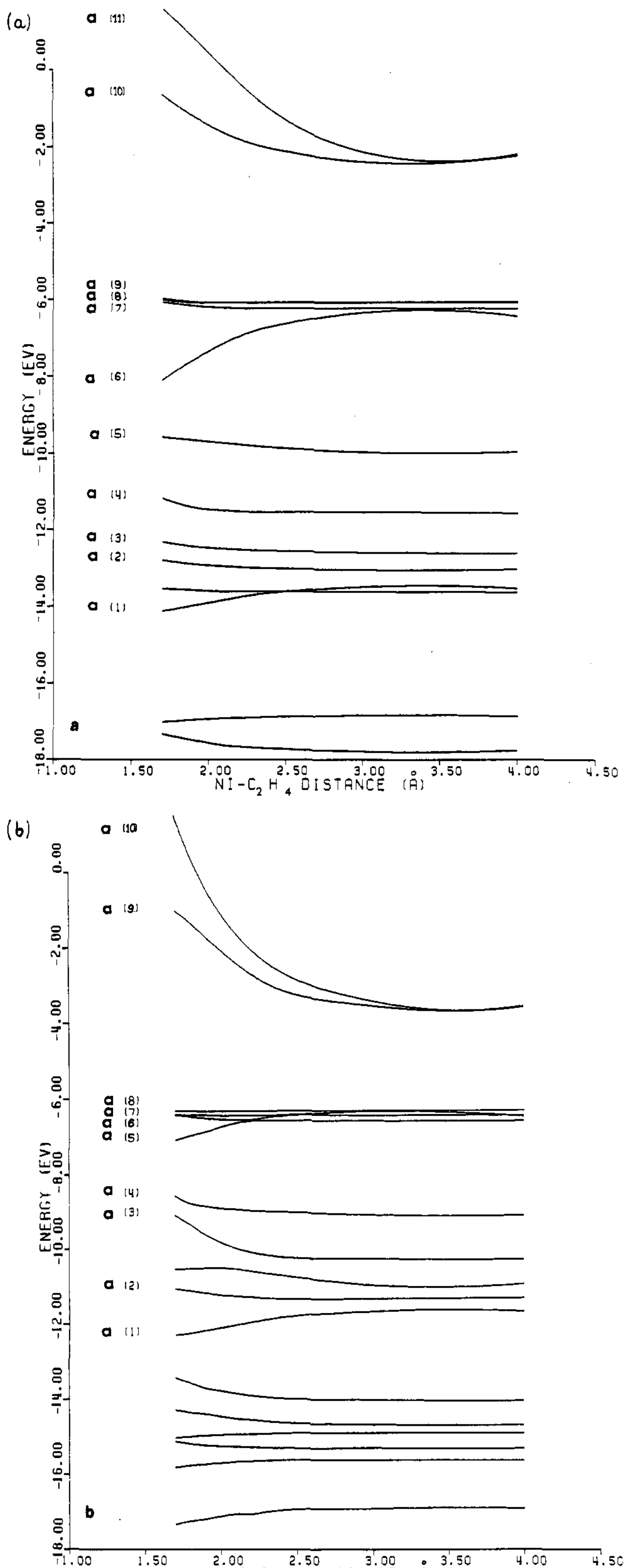

Figure 2. Correlation diagrams: (a) olefin perpendicular to the plane of the other ligands; (b) olefin in plane with the other ligands. The energy scale has an arbitrary zero. Only those orbitals with substantial metal character are labeled.

be well approximated as a one-electron molecular orbital energy E_{MO}: $E_{\mathrm{D}} \simeq E_{\mathrm{MO}}$. Diagonal Hamiltonian matrix elements, H_{ij}, are equal to the adjusted atom ionization energies, and off-diagonal elements, H_{ij}, are given by the formula

$$H_{ij} = 1.125(H_{ii} + H_{jj})S_{ij} \exp(-0.13R) \qquad (2)$$

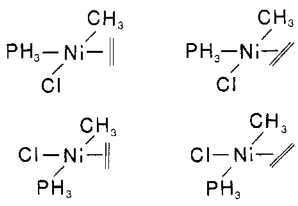

Figure 3. Model compounds used in the ASED calculation.

where S_{ij} is an atomic overlap integral and R is an internuclear distance. Experience has shown that $E_{R_{ij}}$ is better taken as the interaction between the nucleus of the less electronegative atom with the charge distribution of the more electronegative atom when the molecular orbital approximation to E_{D} is used. Parameters used are listed in Tables I and II.

This method proves to be particularly useful for calculating barriers to rotation of olefins.[24,25,29] The orbitals were derived by starting with an ML_4 model with D_{4h} symmetry and removing one of the ligands to obtain the ML_3 fragment. Such geometry was discussed previously by Burdett[32] and by Hoffmann.[33,34] In this model, three of the d orbitals are essentially nonbonding with respect to the olefin. The $d_{x^2-y^2}$ orbital combines with the olefin to form a σ donor bond and its antibonding counterpart (Figure 2). The d_{xz} orbital is available for π back-bonding as in the Dewar–Chatt–Duncanson[35,36] model.

The correlation diagram for the ethylene coordination to the ML_3 fragment is in Figure 2. The unsubstituted olefin is perpendicular to the plane of the ML_3 fragment as the experimental studies demonstrate.[14,37] Steric constraints present in substituted or cyclic olefins may offer some distortion from the idealized geometry.[38,39]

Results and Discussion

In the metal–olefin complex in its equilibrium (perpendicular) geometry (Figure 3), the distance between the carbon atoms in the olefin and the carbon atom of the alkyl group is large (2.7 Å). There is no significant interaction between the R group and the olefin. Rotation of the olefin into the plane of the molecule not only brings the carbon atoms from the olefin and the polymer chain closer together (2.2 Å) but also provides orbitals of appropriate symmetry for bonding overlap between the two carbon

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[25] To relate the barrier to the rotation of olefin to compounds for which experimental results have been obtained, the barrier to rotation in Ziese's anion [PtCl$_3$ (C$_2$H$_4$)$^{1-}$] was calculated. The result compares rather favorably with experimental data in similar complexes (calculated 75 KJ mol^{-1}, experimental 60–67 KJ mol^{-1}).[26-28]

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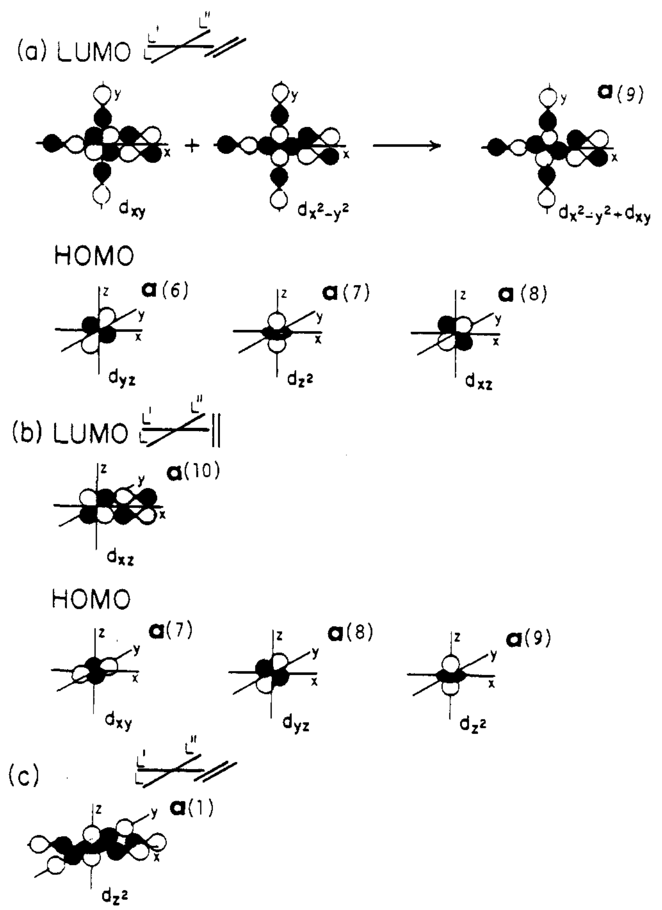

Figure 4. The most relevant orbitals: (a) HOMO and LUMO from planar complex; (b) HOMO and LUMO from perpendicular complex; (c) other significant orbitals facilitating bonding. Metal orbitals used in forming the molecular orbitals are labeled as atomic d orbitals.

atoms (Figure 4). Thus rotation is an essential first step in the carbon–carbon bond formation. Once the three carbon atoms and the metal center are in plane, orbitals for the formation of a new bond are readily available. The key metal atom orbitals are $d_{x^2-y^2}$ and d_{z^2}. They provide optimum delocalization and allow for positive overlap between the p orbitals on the appropriate carbon atoms. Upon rotation of the olefin, the orbitals are rearranged such that they either directly promote or are in a position to contribute to the carbon–carbon bond formation (Figure 4). The a(1) and a(9) orbitals (Figures 2b and 4b,c) have appropriate symmetry to form C–C bonds. Also several even lower energy predominantly ligand p and π orbitals are now in a position to form a bonding overlap between the last carbon of the polymer chain and the olefinic carbon.

As described in Chatt's classical lectures[40,41] explaining reactivity of transition-metal complexes and in accord with the Cossee mechanism,[16] lowering the HOMO–LUMO separation increases the reactivity of the complex. In this particular case, promotion of an electron from the HOMO to the LUMO has a dual effect. It weakens the metal–alkyl group bond by taking an electron out from a bonding orbital. By placing an electron into the LUMO, one initiates the carbon–carbon bond formation while introducing more antibonding character onto the metal atom (Figure 4a).

The need to form a planar configuration involving the metal atom, the two carbon atoms of the olefin, and the alkyl group (or hydrogen atom) that migrates to the olefin was established earlier by Hoffmann and Thorn,[42] who studied ethylene insertion into a metal–hydride bond in square-planar platinum complexes. On the basis of the above argument, a first step in the reaction is the rotation of the olefin around its bond to the metal atom. The barrier to this rotation as well as the HOMO–LUMO separation can be controlled by other ligands, some of which are Lewis acids, phosphines, and halides. Catalyst modification has been achieved in this way.[14]

The rotation is not only essential from the molecular orbital standpoint, but it is also needed in order to bring the carbon atoms closer together. Once the plane containing the three carbon atoms and the metal center is established, the carbon atoms from the ethylene and from the polymer chain are within distance comparable to the sum of their van der Waals radii (2.2 Å)[43] and only small further rearrangement must occur to form the new C–C bond. Analysis of the possible vibrational motions suggests that the energy to move the olefin is lower than the energy required to shift the methyl group. The reaction is likely to have some combination of these two motions with some preference for movement (or slippage)) of the olefin, although we have not explored this energy surface in detail.

A recently reported structure determination of dichloro(5-methylenecycloheptene)platinum(II) that has two olefins coordinated to the metal atom shows both C–C and M–C bond lengthening and a slight displacement of the in plane olefin when compared with the olefin in the perpendicular, preferred configuration.[38,39] The Pt–olefin bond is lengthened by 0.1 Å. Calculations for nickel show a bond lengthening of 0.2 Å upon rotation of the olefin into the plane of the complex. This difference from the experimental results for the platinum complex may be explained by greater steric crowding around the smaller nickel atom. In general, the olefin rotation around the bond with nickel is a higher energy process than rotation around the bond with platinum, suggesting that steric effects play a major role in Ziegler–Natta catalysis.

To examine the importance of the steric effect relative to the electronic effect in the olefin rotation process, the chlorine atom cis to the olefin was protonated. The proton was placed (1) such that Cl–H bond was parallel to the *x* axis and the Cl–H vector was pointing toward the olefin and (2) the proton was removed from the olefin by placing the Cl–H bond along the *z* axis (Figure 5). The barrier to rotation was calculated in both configurations. If the electronic effects were the major factor, the influence of the proton should be small. The calculations show that the proton raised the barrier to rotation by $\simeq$0.7 eV at a HCl distance of 1.3 Å when the proton is in the Cl–H–olefin plane (Figure 5). The barrier to rotation has been calculated for other H–Cl distances. As expected for a steric effect, this function has a maximum at a point representing closest contact with olefinic hydrogen atom.

Electronic effects are more pronounced with changes in the atom in the trans position. A π-acid ligand in a trans position completes for the back-bonding electrons from the metal d orbitals. Calculations performed for four configurations of the phosphine, halide, and the olefin (parallel and perpendicular to the coordination plane (Figure 6)), show that phosphine in the *trans* position lowers the

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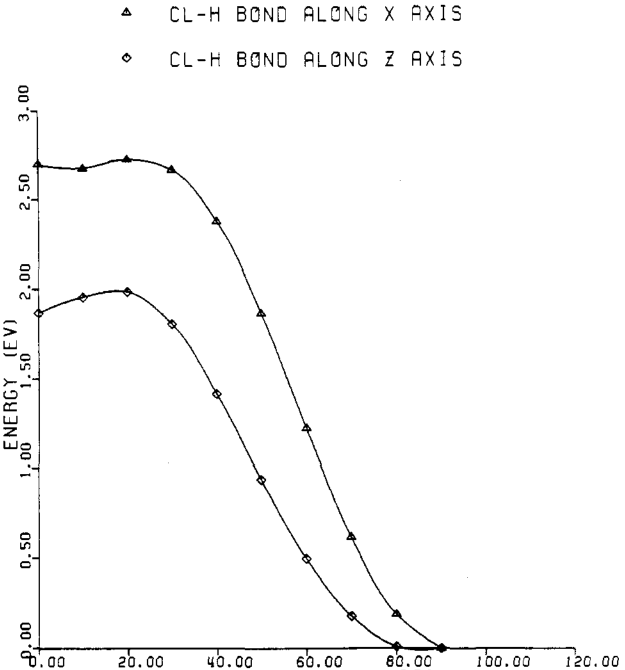

Figure 5. Barrier to rotation in the protonated complex.

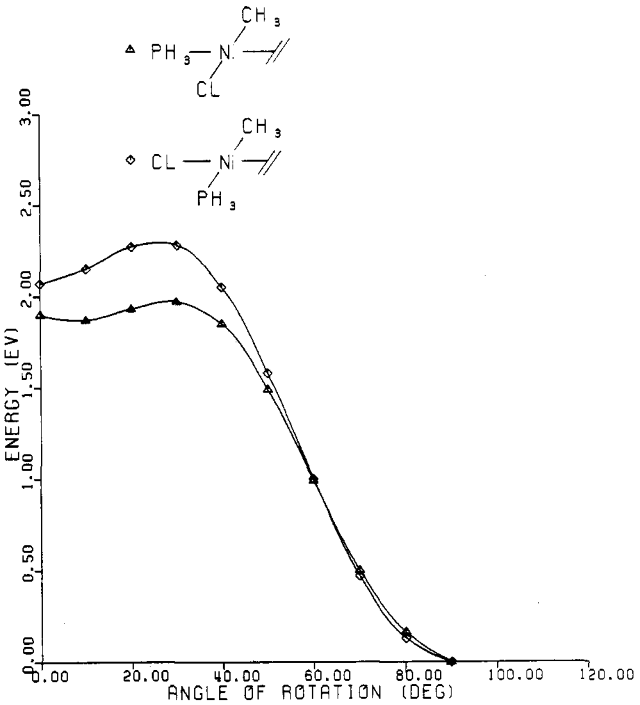

Figure 6. Barrier to rotation as a function of ligands.

barrier to rotation. Trans halide raised this barrier (Figure 6). On the other hand, bulky groups in the cis position cause steric effects to dominate. For example, the PH_3 ligand raises the barrier to rotation by 0.3 eV in our model. *Such differences in energy are sufficient to change the rate of the reaction by three to four orders of magnitude.*[44]

Cossee suggested that before a second step in the oligomerization could occur the polymer chain should migrate back to the position of the original R group.[17] However, this postulate has not been proved. A rearrangement of the "T-shaped" three-coordinate species is expected to take place with only a small barrier, at least according to other calculations for d^8 complexes.[45]

An alternate mechanism involving a five-coordinate intermediate may be envisioned. However, calculations show that placement of the olefin in the apical position of a square pyramid results in a weak bonding to the metal and disfavors a geometry in which it is in plane with the Ni–C(polymer) bond. Therefore, it seems unlikely that a five-coordinate (18-electron) intermediate plays an important role in the reaction.

McKinney performed similar calculations for the d^0–d^2 titanium systems.[46] He found evidence that a metallacycle mechanism, as suggested by Green,[10,47] might play a role in the polymerization and concluded that the mechanism varies with the oxidation state of the metal atom. In the d^8 nickel system different orbitals participate in the metal–olefin bonds. Metallacycles involving nickel have been well established both theoretically[48] and experimentally,[48,49] because the orbitals for the formation of a metallacycle are readily available. However, metallacycle formation does not lead to chain propagation, and consequently we have not examined these species further.

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Registry No. $Ni(C_2H_4)(CH_3)(PH_3)Cl$, 88129-83-3.

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