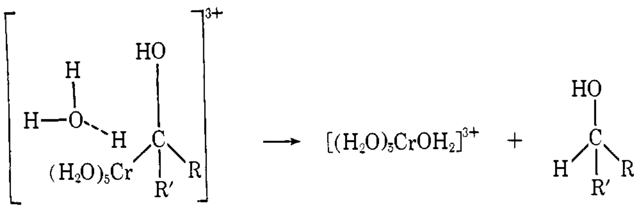

(9)

A similar mechanism appears reasonable for those ligands which contain no hydroxyl function. The kinetics for the chromium complexes containing these ligands have only one path and that is first order in hydrogen ion. If the activated complex involves a solvent molecule cis to the organic ligand, steric effects would be expected to be important. Thus, although the carbon in the methyl ligand is more positive than that of the alcohols, its rate constant for aquation, k_2, is larger. This may well be due to the ease with which a hydronium ion could approach the face of the octahedron on the side containing the methyl ligand. The relatively low amount of CH_3D ($\sim$55% of the D_2O concentration) found on aquation of the methylchromium ion would also be in the direction of the isotope effect expected for a path which involved the participation of a solvent molecule in the activated complex. The relatively slow rate of hydrolysis of the diethyl ether ligand could be due primarily to steric effects. Not only are there no substituents (hydroxy groups) to assist a solvent molecule by hydrogen bonding, but the methyl group and the ethyl ester groups, not being strongly hydrophilic, would interfere with the approach of a solvent molecule.

The activation parameters found by Coombes and coworkers[7] ($\Delta H^{\ddagger}$'s 30–40 kcal/mol and generally positive $\Delta S^{\ddagger}$'s up to 37 eu) for the acid hydrolysis of the pentaaquo(pyridiomethyl)chromium(III) ions are significantly different from those found in the current study and those of Kochi and Buchanan.[5] However, their experiments were done in the presence of oxygen, and their primary product was a pyridine aldehyde. Based on our preliminary experiments with the carbon-bonded Cr(III) complexes and various oxidizing agents, it is quite probable that the reaction under these conditions is different from the aquation reaction observed in an oxygen-free environment.

Acknowledgment. Financial support for this research by the National Institutes of Health, Grant No. 13638, and the Committee on Research, University of California, Grant No. D-207, is gratefully acknowledged.

Orbital Symmetry Restraints to Transition Metal Catalyzed [2 + 2] Cycloaddition Reactions

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Contribution from Shell Development Company, Emeryville, California 94608.
Received June 29, 1970

Abstract: Suprafacial [2 + 2] cycloaddition reactions can be catalyzed by certain transition metal complexes. One mechanism for the process involves an exchange of electron pairs between the metal center and the transforming ligands. This process would effect a spatial redistribution of metal valence electrons within the complex which can introduce energy barriers due to the ligand field of the nonreacting ligands. These barriers can, conceivably, be significant, playing a dominant role in the chemistry of metal-catalyzed [2 + 2] valence isomerizations. Coordination geometries describing restrictive and nonrestrictive ligand fields are discussed. Metal complexes capable of coordination geometries of a nonrestrictive nature are suggested as models for catalytically active metal systems. Examples include metals capable of six- and seven-coordination of C_{2v} symmetry.

Orbital symmetry conservation places significant restraints on the modes of transformation open to organic molecules.[1] Certain transition metal complexes are known to dramatically catalyze symmetry-forbidden transformations,[2] and a mechanism involving the removal of symmetry restrictions has been proposed.[3] Organic ligands coordinated to transition metal complexes, however, are not totally removed from symmetry restrictions; molecular transformations along certain modes of reaction can experience restraints due to the nature of the transforming ligands[4]

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(1) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(2) (a) H. Hogeveen and H. C. Volger, *J. Amer. Chem. Soc.*, **89**, 2486 (1967); P. G. Gassman, D. H. Aue, and D. S. Patton, *ibid.*, **90**, 7271 (1968); (b) H. C. Volger, H. Hogeveen, and M. M. P. Gaasbeek, *ibid.*, **91**, 218 (1969); T. J. Katz and S. H. Cerefice, *Tetrahedron Lett.*, 2509, 2561 (1969); (c) G. N. Schrauzer, *Advan. Catal.*, **18**, 373 (1968); M. Green and D. C. Wood, *Chem. Commun.*, 1062 (1967); *J. Chem. Soc.*, 1172 (1969); A. Greco, A. Carbonara, and G. Dall'Asta, *J. Org. Chem.*, **35**, 271 (1970); P. Heimbach and W. Brenner, *Angew. Chem., Int. Ed. Engl.*, **6**, 800 (1967); (d) R. L. Banks and G. C. Bailey, *Ind. Eng. Chem., Prod. Res. Develop.*, **3**, 170 (1964); M. Calderon, E. A. Ofstead, J. P. Ward, and K. W. Scott, *J. Amer. Chem. Soc.*, **90**, 4133 (1968); (e) H. C. Volger and H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, **86**, 830 (1967); N. Merk and R. Pettit, *J. Amer. Chem. Soc.*, **89**, 4788 (1967); (f) G. N. Schrauzer, R. K. Y. Ho, and G. Schlesinger, *Tetrahedron Lett.*, 543 (1970); (g) W. Reppe, O. Schlichting, K. Klager, and T. Towpel, *Justus Liebigs Ann. Chem.*, 560, 1 (1948); G. N. Schrauzer, *Angew. Chem., Int. Ed. Engl.*, **3**, 185 (1964); (h) for a general discussion and review of some of this chemistry, see F. D. Mango, *Advan. Catal.*, **20**, 291 (1969).

(3) F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, **89**, 2484 (1967); F. D. Mango, *Tetrahedron Lett.*, 4813 (1969); a forbidden-to-allowed description of the [1,3] suprafacial sigmatropic transformation has also been postulated[2h] and a similar treatment of disrotatory ring opening of cyclobutenes has been described.[2e,h]

(4) F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, **91**, 1030 (1969).

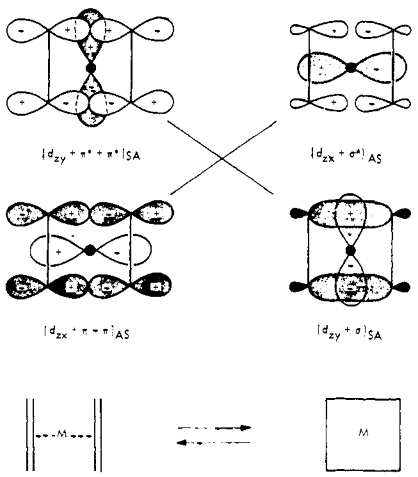

Figure 1. The removal of symmetry restrictions through a relocalization of ligand–metal AS and SA electron density. In this perspective, the *z* axis passes upward from the metal through the plane containing the four carbon atoms of the bisolefin system. The *x* axis is horizontal and the *y* axis vertical. The shaded orbitals represent the centers of maximum electron density in the respective molecular orbitals.

or the ligand field defined by the nonreacting ligands. In the forbidden-to-allowed[2h] catalytic process, orbital symmetry restraints due to restrictive ligand-field effects can conceivably dominate the overall chemistry. In this paper we introduce this aspect of forbidden-to-allowed catalysis as it applies to [2 + 2] cycloaddition reactions.

Bisolefin → Cyclobutane

The symmetry restrictions associated with the concerted fusion of two π bonds to two σ bonds in a suprafacial manner stem from the crossing of two of the four molecular orbitals in the bisolefin system.[1] The forbidden-to-allowed catalytic function of a transition metal can very simply be described in terms of certain operations performed by the metal on the two crossing molecular orbitals.[2h] This process is illustrated graphically in Figure 1. The orbital combinations are symmetry assigned relative to the preserved symmetry elements (the *zy* and *zx* planes in Figure 1). The important feature in this process is the redistribution of the metal's valence electrons, which necessarily proceeds with the forbidden-to-allowed process. In the model system in the figure, for example, the metal undergoes a reordering of its valence electrons which can be described $[d_{zy}(2), d_{zx}] \rightarrow [d_{zy}, d_{zx}(2)]$. It is this feature to the catalytic process—the spatial redistribution of metal valence electrons—which can create symmetry restrictions tending to restrain the reacting ligands (*e.g.*, the bisolefin system in Figure 1) from proceeding along the reaction coordinate. In considering this aspect of the forbidden-to-allowed process, we are concerned with the nonreacting metal ligands, their spatial configuration about the metal, and the corresponding ligand field. Since we specifically address the redistribution of d-electron density within one pair of metal orbitals (*e.g.*, the d_{zy} and d_{zx} in Figure 1), our attention here is on their relative energies within a given ligand field described by the nonreacting ligands.

Three situations exist for the splitting of the two critical d orbitals by the nonreacting ligands: case 1, they are left degenerate; case 2, the AS orbital is of higher energy; and case 3, the SA orbital is of higher energy. In case 1, there are no symmetry restraints to the [2 + 2] ligand transformation described in Figure 1; d-electron density can move in and out of the respective d orbitals without significantly altering the energy of the metal–ligand (nonreacting) bonding network. For case 2, cyclobutanation of the olefin ligands concentrates d-electron density in d_{zx}, the higher energy orbital. This is an energetically unfavorable process which, necessarily, means an energy barrier to ligand transformation. The barrier may not be large, depending on the extent of d-orbital splitting. For moderate energy barriers, and where the [2 + 2] ligand transformations are thermodynamically favorable, systems can either cross adiabatically to ground-state product complexes, or, conceivably, generate excited-state complexes.[5] In either case, ligand transformations experience energy barriers reflecting the strength of the ligand field described by the nonreacting ligands.

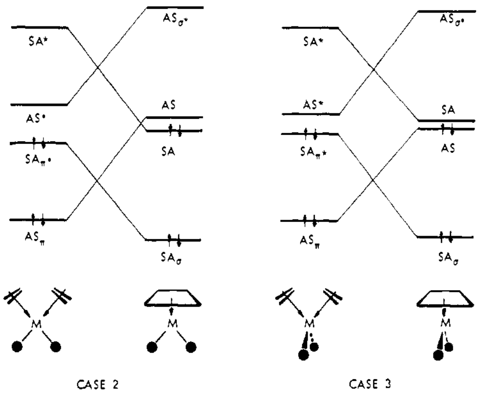

Figure 2. Correlation diagrams illustrating the orbital crossings in case 2 (square planar) and case 3 (tetrahedral). The complexes are hypothetical, with the ligands described as simple localized centers of electron density. Energy differences between the two complexes are not implied.

Case 3 is similar to case 1 in that symmetry restrictions to ligand transformations do not exist; moreover, the relocalization of metal d-electron density into a spatial configuration within the complex which is energetically more favorable than the original one may provide driving force for the ligand transformation. Examples[6] of cases 2 and 3, involving the transformation of hypothetical square-planar and tetrahedral complexes, respectively, are illustrated in Figure 2.

The orbital crossing occurring in case 2 places that transformation formally in the symmetry-forbidden category. Since there are a number of conceivable situations where the actual energy barrier to reaction would not constitute a significant restriction, the concept of "forbiddenness" appears inappropriate here; this situation seems better described in terms of "energy restraints" due to ligand-field effects. Moreover, the ligand transformation (*i.e.*, bisolefin → cyclobutane) is best considered symmetry allowed. The d-orbital crossing noted does not alter the "allowedness" of the

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(5) C. Zener, *Proc. Roy. Soc., Ser. A*, 140, 660, 696 (1933).

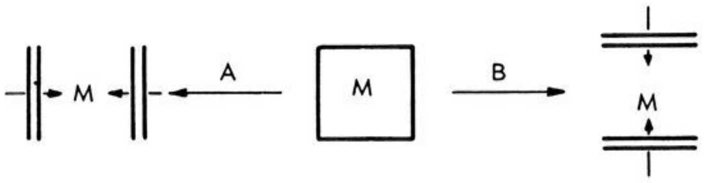
(6) The two examples illustrated in Figure 2 should not be considered as generally applicable to all four-coordinate metal complexes. Each system is best treated separately, considering both the bonding characteristics of the nonreacting ligands (*e.g.*, the donor and back-bonding properties, their ligand-field strengths, etc). and the number of valence electrons in the metal.

olefin fusion. The ligand transformation may be visualized as ground state across the reaction coordinate. The required exchange of electron pairs between transforming ligands and metal places electron density into a spatial configuration within the complex which is energetically unfavorable, creating transformation restraints and introducing the possibility of generating a complex in an excited state. But the olefin cyclobutanation, viewed alone, is continuously ground state throughout the transformation.

Cyclobutane → Bisolefin

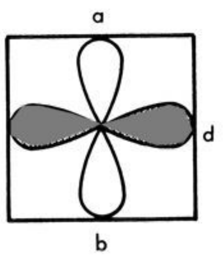
Ligand-field symmetry factors play a somewhat different role in the opening of a cyclobutane ring than in the reverse process. There is the effect of a given distribution of d-electron density on the direction of ring opening and the ligand-field restrictions that might accompany ring opening. We shall consider both factors as they apply to the ring opening of a symmetrical, metal-coordinated cyclobutane ring.

The coordinated ring can conceivably open in either one of two directions (eq 1). The ordering of the two critical d orbitals (*e.g.*, the d_{zx} and d_{zy}) can play an important role in the direction of ring opening. Where they are degenerate, and assuming two metal valence electrons distributed between them, the probability of opening along A or B is essentially the same. Here there are no ligand-field restrictions to ligand transformations. The cyclobutane ring is free to ring open in either direction without placing metal valence electrons in an energetically unfavorable spatial configuration. A ring vibration along one reaction mode (*e.g.*, A or B in eq 1) should localize the metal valence electron pair in one d orbital, thus opening the symmetry-allowed path along that mode of transformation.

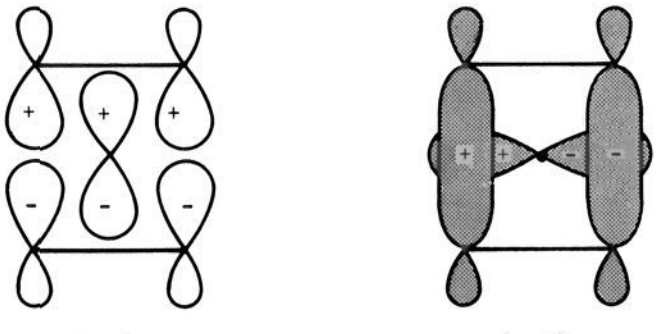


(1)

When the ligand field splits the critical d orbitals, the propensity to ring open along one mode of transformation becomes greater than that along the other. Moreover, ligand-field restrictions will be encountered along that mode of transformation possessing the greater propensity for reaction. Consider the cyclobutane I exposed to the indicated spatial distribution of d-electron density (*i.e.*, $d_{zx}(2)$, d_{zy}). The ring can either open through breaking bonds ab to the olefin pair cd (path A, eq 1) or through breaking bonds cd to the olefin pair ab (path B, eq 1). In the absence of the metal, the symmetry restrictions to opening in either direction stem from the fact that a filled σ orbital in the cyclobutane ring correlates with a π^* orbital in the olefin product and an empty cyclobutane σ^* correlates with a product π combination (*cf.* Figure 1). These restrictions can be removed by continuously increasing electron density in the cyclobutane σ^* orbital (thus generating π bonding in the π orbital of the product) and withdrawing electron density from the σ orbital (avoiding antibonding π^* character with ring stretch). For the direction of ring opening illustrated in Figure 1, electron density would be injected into $[\sigma^*]_{AS}$ and removed from $[\sigma]_{SA}$. A metal with the d-electron distribution illustrated in I is prepared to do precisely this, but only for one mode of ring opening (path A, Figure 1). The propensity to open in the other direction (path B) would not be significantly altered. The two orbitals in I (d_{zx} and d_{zy}) have the proper symmetry to interact with the appropriate orbitals in the cd bond system, but they are populated in the opposite way to that required to effect the necessary exchange of electron pairs, *i.e.*

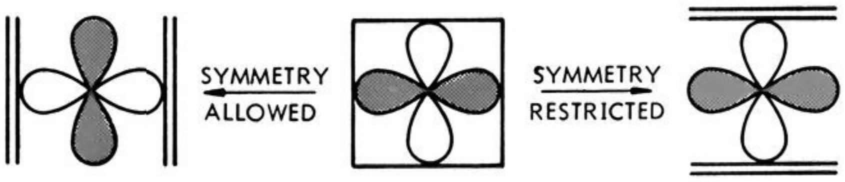


I



$\sigma^* + d_{zy}$ $\sigma^2 + d_{zx}^2$

This kind of orbital interaction, moreover, is essentially nonbonding with respect to the cd bond pair (the bonding resulting from the interaction of two filled orbitals of the same symmetry is essentially negative). The net result from the interaction of a cyclobutane ring with a metal center displaying the d-electron distribution illustrated in I should be a greater propensity to ring open along path A than along path B. Further, transformation along A, in this example, proceeds with symmetry conservation (*e.g.*, case 3), while transformation along B encounters an orbital crossing (*e.g.*, case 2). This qualitative description can be summarized



The ligand transformation along path B in the above example is symmetry restricted primarily because it retains the forbiddenness of the metal-free transformation. It should be noted that a redistribution of metal valence electrons does not proceed with reaction and thus this process does not receive forbidden-to-allowed assistance from the metal. Reaction can conceivably proceed in this direction through configuration interaction.[7]

Ligand transformation along the symmetry-allowed path (A) can encounter energy barriers due to the redistribution of metal valence electrons. An electron pair will, necessarily, be moved from a lower energy d orbital to a higher energy orbital with respect to the ligand field of the nonreacting ligands. The bisolefin–ligand product, however, splits the two critical d orbitals in a way opposite to that of the nonreacting ligands. When the ligand field of the nonreacting ligands is weak relative to that of the bisolefin–ligand system, ligand-field restrictions to transformation along path B are less significant. When the opposite is true, energy barriers to re-

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(7) W. Th. A. M. van der Lugt, *Tetrahedron Lett.*, **26**, 2281 (1970).

action emerge, reflecting the energy differential separating the respective ligand fields. Strong-field ligand systems (nonreacting), then, which split the critical d orbitals, will create in the coordinated cyclobutane ring a propensity to transform along the symmetry-allowed path, but transformation along that path may very well be blocked by the attending ligand-field restrictions. These systems should be significantly less active, catalytically, than their weak-field counterparts.

The propensity of a coordinated cyclobutane ring to transform along one mode of reaction in preference to another can be illustrated through simple semiempirical molecular orbital calculations. Calculations[8] have been carried out on certain hypothetical cyclobutane–metal complex models selected to reflect differences in the propensity of a cyclobutane ring to react along the two paths in eq 1. Given a distribution of d-electron density indicated in I, for example, bonds ab might be expected to have a lower bond order than bc [illegible] cd. With this d-orbital ordering and electron distribution, bonds ab are the bidentate centers of coordination and, as such, should suffer a loss in carbon–carbon bonding character due to the $\sigma(2) \rightarrow d_{zy}$ donor interaction, and a gain in antibonding character due to the metal-to-ligand back-bonding interaction, $d_{zx}(2) \rightarrow \sigma^*$. Both interactions would tend to diminish the bond order of bonds ab relative to bonds cd which do not interact with the metal system in this way.

Metal dicarbonyl and dihalide systems[9] were selected as models in the molecular orbital calculations. The calculations were carried out on d^6 ($FeCl_2$), d^8 ($NiCl_2$ and $Fe(CO)_2$), and d^{10} ($Ni(CO)_2$) cyclobutane and bisethylene models. In each of the cyclobutane complexes the d_{zy} orbital, aligned with the halogen or carbonyl ligands, was significantly higher in energy than the remaining d orbitals. In the d^6 and d^8 cyclobutane complexes, the d_{zx} was populated with valence electrons and the d_{zy} was not; in the d^{10} complex, the highest occupied orbital was the d_{zy}.[10] The symmetry-allowed directions are thus path B for the d^{10} system and path A for the d^6 and d^8 complexes (*e.g.*, eq 2, where M = Ni for path B and Fe for path A).[11] The distribution of metal va-

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[8] Molecular orbital calculations were done by the self-consistent charge and configuration (SCCC) modification of the iterative extended-Hückel method [see, *e.g.*, H. Basch, A. Viste, and H. B. Gray, *J. Chem. Phys.*, **44**, 10 (1966)]. Diagonal elements of *H* are approximated as

$$H_{ii} = I_i^0 - A_{iq} - B_{iq}^2$$

where the I_i^0, A_i, and B_i parameters give the valence orbital ionization potential (VOIP) as a function of the net charge, *q*, on the atom. In our calculations *q* is computed using Löwdin's orthogonalized atomic orbitals [P. O. Löwdin, *ibid.*, **18**, 365 (1950)].

$$H_{ij} = kS_{ij}(H_{ii} + H_{jj})/2.0 \qquad k = 1.80$$

[9] SCCC–MO calculations were carried out for $(CO)_2M(CH_2{=}CH_2)_2$ and $(Cl)_2M(CH_2{=}CH_2)_2$ in the square-planar and tetrahedral forms and for $(CO)_2M$–c-C_4H_8 and $(Cl)_2M$–c-C_4H_8 with M = Ni and Fe. The following interatomic distances (*R*) and bond angles have been assumed: $R(M{-}CO) = R(M{-}Cl) = 1.82$ Å, $R(M{-}(CH_2{=}CH_2)) = 2.0$ Å, $R(C{-}O) = 1.13$ A, $R(C{-}C) = 1.53$ Å, $R(C{=}C) = 1.33$ Å, $R(C{-}H) = 1.09$ Å, $\angle HCH$ in $CH_2{=}CH_2 = 120°$ The ligands were placed at the corners of the "tetrahedron" or "square." The cyclobutane ligand was assumed to be square planar with the CH_2 groups perpendicular to the plane and bisecting the corners ($\angle HCH = 109.47°$). Atomic orbitals for Ni and Fe were taken from Richardson and Niewpoort [J. W. Richardson, W. C. Niewpoort, R. R. Powell, and W. F. Edgell, *ibid.*, **36**, 1059 (1962); J. W. Richardson and W. C. Niewpoort, *ibid.*, **38**, 796 (1963)]. Orbitals for C, O, and Cl were obtained from the work of Clementi [E. Clementi and D. L. Ralmondi, *ibid.*, **38**, 2686 (1963)]. For H we used a Slater 1s orbital with an exponent of 1.2. The VOIP parameters for Ni and Fe were obtained from H. Basch, A. Viste, and H. B. Gray, *ibid.*, **44**, 10 (1966). For carbon, oxygen, chlorine, and hydrogen we use the following relations

$$H_{ii}(C_{2s}) = -19.52 - 11.75q - 1.15q^2$$

$$H_{ii}(C_{2p}) = -9.75 - 10.86q - 1.55q^2$$

$$H_{ii}(O_{2s}) = -32.30 - 15.35q - 1.49q^2$$

$$H_{ii}(O_{2p}) = -14.61 - 14.77q - 2.17q^2$$

$$H_{ii}(Cl_{2s}) = -25.23 - 11.48q - 0.70q^2$$

$$H_{ii}(Cl_{2p}) = -13.92 - 10.44q - 0.24q^2$$

$$H_{ii}(H_{1s}) = -13.60 - 16.65q - 3.80q^2$$

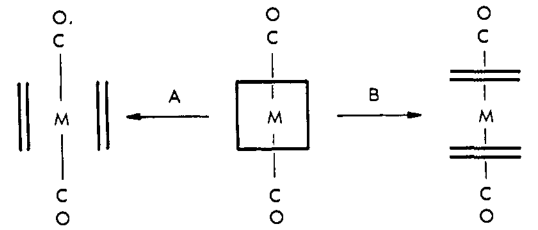
Calculations were carried to a self-consistency of 0.005 electron in charge and configuration.

[10] In the d^{10} metal complex where the entire d band is filled with metal valence electrons, the simple "filled" and "empty" d-orbital model for predicting the allowed path of transformation can be misleading. In the molecular orbital approximation of a metal complex, mixtures of metal atomic orbitals of the appropriate symmetries combine with ligand orbitals of matching symmetries yielding the set of molecular orbitals. The electrons (both ligand and metal) are distributed among the lowest energy orbitals. In most complexes, all of the metal atomic orbitals will be "mixed" into the occupied molecular orbitals, some to a greater degree than others, depending on symmetry and energy factors. A given metal atomic orbital will be "occupied" with electrons to the extent to which it contributes to the composition of the occupied molecular orbitals. Generally speaking, those metal atomic orbitals which symmetry-match the bonding ligand orbitals (*i.e.*, occupied with ligand valence electrons) will be populated to a lesser degree than those which symmetry-match the ligand antibonding (unoccupied) orbitals. The former, then, can be considered empty and the latter filled. This simplified picture still applies in the d^{10} system; however, the role of "pure" d orbitals is significantly diminished. In all d systems combinations of metal atomic orbitals of the same symmetries contribute to the respective molecular orbitals. In the forbidden-to-allowed process, attention is focused on the molecular orbitals of SA and AS symmetries. Metal d_{zy}–p_y combinations contribute to SA molecular orbitals and d_{zx}–p_x combinations contribute to AS orbitals. Because of their higher energy, the p orbitals make only minor contributions to the lower energy molecular orbitals and greater contributions to the molecular orbitals of higher energy. In the d^{10} system discussed here, the highest occupied molecular orbital has SA symmetry and is composed of a metal d_{zy}–p_y hybrid. There also exists an AS molecular orbital of lower energy composed of a similar d_{zx}–p_x combination. In the description adopted here, the SA dp hybrid interacts with an antibonding ligand orbital and can thus be considered filled, and the AS dp hybrid interacts with a ligand bonding orbital and can be considered empty. The exchange of electron pairs, therefore, can proceed through the metal hybrids of SA and AS symmetries. The important feature in the forbidden-to-allowed transformation, of course, is that all occupied molecular orbitals in the starting complex correspond in symmetry to the occupied molecular orbitals in the product complex, and this is the case here. Fortunately, full correlation diagrams are not always essential if the highest occupied AS or SA molecular orbital is known.

[11] The symmetry-allowed directions noted here were confirmed with full correlation diagrams. Symmetry assignments for all occupied molecular orbitals in the complexes follow (the numbers of occupied orbitals in the various symmetry categories are tabulated).

	$Ni(CO)_2$ (d^{10})	$NiCl_2$ (d^8)	$Fe(CO)_2$ (d^8)	$FeCl_2$ (d^6)
Path A	10 SS	8 SS	9 SS	8 SS
Bisethylene	6 AS	6 AS	6 AS	5 AS
(tetrahedral)	7 SA	6 SA	7 SA	6 SA
	4 AA	4 AA	4 AA	4 AA
Cyclobutane	10 SS	9 SS	10 SS	8 SS
	5 AS	5 AS	5 AS	5 AS
	8 SA	6 SA	7 SA	6 SA
	4 AA	4 AA	4 AA	4 AA
Path B	10 SS	9 SS	10 SS	8 SS
Bisethylene	5 AS	4 AS	4 AS	4 AS
(square	8 SA	7 SA	8 SA	7 SA
planar)	4 AA	4 AA	4 AA	4 AA

For each metal complex, the symmetry-forbidden direction of transformation shows the characteristic crossing of SA and AS molecular orbitals. The crossing molecular orbitals noted here are primarily ligand (cyclobutane) in character and reflect the retained "forbiddenness" of the isolated cyclobutane → bisethylene reaction. Orbital crossings are also noted along the symmetry-allowed direction (path A) in both d^8 complexes. These are, however, primarily d-level crossings and reflect the orbital splitting patterns of the d^8 systems. The correlation along path B, in contrast, showed the expected steep crossing of ligand AS and SA molecular orbitals. For $NiCl_2$, the d-level crossing along path A was 0.18 eV, while the crossing along path B was 4.05 eV; the crossings in $Fe(CO)_2$ were 0.65 (path A) and 3.55 eV (path B). The greater crossing along path A noted for $Fe(CO)_2$ reflects the difference in d-orbital splitlence electrons alters the bond order in the coordinated cyclobutane rings (basis Mulliken population analysis[12])



(2)

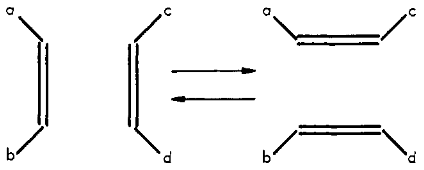
in the expected direction. The Mulliken population analysis for the cd and ab bonds in the cyclobutane nickel–carbonyl complex were 0.750 and 0.774, respectively, indicating a propensity to transform along path B. For the cyclobutane ring on iron dicarbonyl, the ab bonds were 0.752 and the cd 0.760; for the dichlorides, the same bonds were 0.740 and 0.756 for iron and 0.749 and 0.763 for nickel, consistent with a propensity to ring open along path A.

These results are significant only insofar as they reflect a preference to transform along one mode of reaction rather than another resulting from interaction with a given distribution of d-electron density. A propensity to ring open in a given direction does not necessarily mean a likelihood of reaction in that direction. The metal–dicarbonyl models used here are good examples of significant energy barriers to ring opening along either direction. The strong splitting of the critical d orbitals creates a propensity to transform along one path in preference to the other, but it further means a barrier to that transformation due to the withdrawal of CO back-bonding electrons and the injection of valence electrons into a metal atomic orbital with significant antibonding M–CO character. It is unlikely, therefore, that metal systems similar in character to these will have catalytic activity of this kind.

Olefin Reactions

We have discussed above the possibilities of energy barriers to metal-catalyzed [2 + 2] cycloaddition processes stemming from the ligand fields of nonreacting ligands. These barriers, even if small (*i.e.*, a few kilocalories per mole), could conceivably preclude a cycloaddition reaction if that reaction has only marginal thermodynamic driving force or involves a relatively unfavorable ligand-to-metal change in bonding energy. Both of these factors would seem to apply in the cycloaddition of simple olefins (*i.e.*, ethylene, propylene, etc.). Significantly, no transition metal catalyst, to our knowledge, will cyclobutanize simple olefins. This can, in part, be attributed to the ligand-field restrictions (case 2) associated with the preferred geometries of many olefin–metal complexes (*e.g.*, square planar and octahedral). Catalysis of this kind might best be found with metal systems offering ligand geometries in the case 1 and case 3 categories and with metal systems possessing some affinity for cyclobutane coordination. Tetrahedral and trigonal-bipyramidal bisolefin complexes are examples of case 3 systems. Some examples approximating case 1 systems would include bisolefin complexes in which the metal–ligand (nonreacting) moieties possess a C_{3v} or C_{5v} axis of symmetry. A bis(olefin)iron–tricarbonyl complex is an example containing the metal–ligand (nonreacting) moiety with the C_{3v} symmetry axis.

Although transition metals are not now known to cyclobutanize simple olefins, there are metal complexes (mainly tungsten and molybdenum) which will interconvert olefins through the remarkable catalytic process, olefin metathesis.[2d] In this catalytic reaction, simple olefins are interconverted with striking ease, the reaction proceeding at room temperature and below. A broad body of work directed toward the mechanism of this process indicates a cyclobutanation step involving an intermediate cyclobutane–metal species, either as a transition state or a short-lived intermediate.[13] Cyclobutanes, however, are clearly not free intermediates since they do not react nor are they observed as distinct products.[14] If they intervene in this chemistry, they must, therefore, remain coordinated to their metal centers of formation. The change in ligand-to-metal coordinate bonding associated with the transformation of a bisolefin–ligand system to a cyclobutane–ligand system can be a critical factor in which the number of metal valence electrons can play a contributing role. The bisolefin–ligand coordinate bond is composed of four molecular orbitals: SS_{π}, AS_{π}, SA_{π^*}, and AA_{π^*}. Of these, the SS_{π} and AS_{π} are donor and the SA_{π^*} and AA_{π^*} are back-bonding in character. The electronic population of SS_{π}, AS_{π}, and SA_{π^*} is essential to the formation of a ground-state cyclobutane ligand, but the population of the AA_{π^*} (through the metal d_{xy}, for example) is not. The coordinate bonding, then, associated with the population of AA_{π^*} must essentially be lost with π-bond fusion to the cyclobutane ring. The energy barrier to reaction may be lowered by not populating the AA_{π^*} orbital in the bisolefin complex; this is best achieved in d^2 metal complexes. In a study of the tungsten hexachloride–*n*-butyllithium catalyst system for olefin metathesis, the oxidation state of IV(d^2) best fits the experimental observations.[15]



One model for the catalytic species in olefin metathesis would be a metal complex whose nonreacting ligands either left the two critical d orbitals degenerate (case 1) or were sufficiently labile to rearrange to that geometry with ligand transformation. The transition metal in this complex could contribute further to the smooth ligand transformation in an oxidation state providing two valence electrons (*i.e.*, d^2). The cyclobutane ligand, in this case, could transform to either bisolefin–ligand isomer through a molecular vibration along the appropriate reaction coordinate. Since the d orbitals would be essentially degenerate, the appropriate order-

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ting between the chloride and carbonyl ligand systems. The ordering of the d levels in the tetrahedral iron complex points to a significant energy barrier to ring opening along the symmetry-allowed path (A); the two metal valence electrons in the d_{zz} orbital (AS) are in fact carbonyl back-bonding electrons in the cyclobutane complex and thus not completely free to flow into the transforming ligand network.

(12) R. S. Mulliken, *J. Chem. Phys.*, 23, 1833, 1841 (1955).

(13) For a recent review see G. C. Bailey, *Catal. Rev.*, 3, 37 (1969).

(14) J. C. Mol, F. R. Visser, and C. Boelhouwer, *J. Catal.*, 17, 114 (1970).

(15) J. Wang and H. R. Menapace, *J. Org. Chem.*, 33, 3794 (1968).

ing for ring opening in either direction could proceed with the required ring vibration.

Attractive metal geometries for the metathesis reaction include the trigonal prism (six-coordinate) and the monocapped trigonal prism (seven-coordinate). Both complexes fall into the case 1 category. The seven-coordinate complex would be preferred. It can form from an octahedral complex in which the first olefin occupies an axial position. The two olefins in the seven-coordinate complex would occupy adjacent ligand positions on either side of the original axial position (*i.e.*, straddling the C_{2v} axis in the monocapped trigonal prism). Seven-coordination for metal complexes possessing a low number of valence electrons can be anticipated, and the monocapped trigonal prism might reasonably be expected to intervene in this highly labile seven-atom family of complexes.[16]

Other mechanisms for the metathesis reaction are difficult to draw. One alternative is a stepwise process involving an oxidative-cycloaddition step to a five-membered metallocyclo intermediate. To effect the metathesis reaction, however, the metal must somehow move from one ring position to another in order to scramble the alkylidene groups in a way demanded by the observed distribution of products. This can best be achieved through the extrusion of a cyclobutane ring followed by a second insertion step. Free cyclobutanes, however, are not distinct intermediates in this chemistry. The difficulty in drawing a reasonable mechanism for moving the metal center from one ring position to another without, at some point, generating a cyclobutane, very loosely attached to the metal center, casts some doubt on the oxidative-cycloaddition mechanism. The forbidden-to-allowed process, in contrast, generates the cyclobutane ring fully coordinated to the metal. The coordinated ring is only a vibration removed from either bisolefin valence isomer.

Valence Isomerizations

There is a variety of metal-assisted [2 + 2] valence isomerizations where a significant thermodynamic driving force for ligand transformation exists.[2] In those cases involving highly strained and essentially planar cyclobutane ring systems (quadricyclene and prismane,[2a] for example), the transition metal coordinate-bonding character of the cyclobutane ring should be significantly greater than that of the unstrained, nonplanar counterparts. Moreover, in those cyclobutane ring systems fused to cyclopropane rings (quadricyclene and prismane), the focal points of bidentate character are best centered at the σ bonds describing the base of the cyclopropane rings. The unsaturation reflected in the higher p character of the cyclopropane ring[17] should transmit to those ligand centers attractive metal-bonding properties. The asymmetry of these cyclobutane rings reflects differences in the bond energies of the two cyclobutane σ bond pairs (*i.e.*, ab and cd in I). These ligand systems should, consequently, impress upon a metal center a unique ligand field with the centers of bidentate bonding focused at the two higher energy bonds (in these examples, the cyclopropane bonds). This should further order the two critical metal d orbitals in a way creating a propensity to transform to the thermodynamically preferred valence isomer (*e.g.*, quadricyclene → norbornadiene).[18] Quadricyclene, then, coordinated to a transition metal center through its two cyclopropane σ bonds (*i.e.*, bonds ab in I) should experience a strong propensity to transform to a norbornadiene ligand which is fully coordinated to the metal center through its two π bonds. The energy released from this ligand transformation can compensate for possible attending energy barriers arising through ligand-field effects. Indeed, attending rearrangements or displacements of the nonreacting ligands are quite reasonable in the metal systems reported to catalyze this valence isomerization.[2a]

The nature of the bidentate coordinate bond is closely associated with the forbidden-to-allowed process. The metal center, through back-bonding, imparts to the coordinated ligand the bonding character of the ligand's excited state. The mixing in of the excited state tends to alter the structure of the ligand toward that of the excited system. In the case of quadricyclene, with the cyclopropane rings the centers of bidentate coordination, the excited configuration corresponds to the ground state of metal-coordinated norbornadiene. Considering the driving force to transform to norbornadiene, it seems doubtful that quadricyclene can survive bidentate coordination to most metal complexes. In fact, all that prevents a fully coordinated quadricyclene from complete relaxation to norbornadiene, with preservation of metal-to-ligand coordinate bonding,[15] are the ligand-field restrictions described above. For metal systems in the case 1 and case 3 categories, complete molecular relaxation to the thermodynamically preferred valence isomer would seem guaranteed. Particularly high levels of catalytic activity would be expected of those systems offering bidentate coordination through an expansion of coordination number. Octahedral complexes open to facile seven-coordination through the axial ligand position (giving a case 1 complex) are particularly attractive model systems. The higher levels of activity would, in this example, seem to be associated with the metal systems with fewer valence electrons (*i.e.*, d^2–d^4).

The importance of a ligand's bidentate coordination character in metal-catalyzed [2 + 2] valence isomerization is illustrated in the rhodium-catalyzed valence isomerization of cubane.[19] In a careful study of this system, it has been shown that the valence isomerization of cubane to *syn*-tricyclooctadienes proceeds through a nonconcerted mechanism involving the oxidative insertion of Rh(I) into a strained carbon–carbon bond of cubane. There are some features of this work pertinent to the points discussed here. First, the second-order rate constants for the diene catalysts ([Rh(diene)Cl]$_2$) differed significantly for different dienes, indicating that the diene originally present on a catalyst remained attached throughout the catalysts' lifetime. This strongly suggests that bidentate coordination was never opened to the cubane ligand, and that the seat of catalysis on the coordination sphere was centered at the single coordination position along the principal axis of the square-planar system. The relative bidentate coordi-

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(16) E. L. Muetterties, *Accounts Chem. Res.*, 3, 266 (1970).

(17) A. D. Walsh, *Nature* (*London*), 159, 165, 712 (1947); C. A. Coulson and W. E. Moffitt, *J. Chem. Phys.*, 15, 151 (1947).

(18) It can be shown that metal-to-ligand bidentate coordinate bonding is only preserved in those cases where the otherwise forbidden valence isomerization proceeds along the forbidden-to-allowed reaction path. This aspect of metal-catalyzed symmetry-forbidden reactions will be discussed in a subsequent communication.

(19) L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, 92, 3515 (1970).

nation properties of the cyclobutane ring in cubane are not known. It is, however, reasonable to expect cubane to be a poor competitor with most diene–ligand systems for bidentate positions of coordination. The well known ability of Rh(I) systems to undergo oxidative insertion[20] of the kind proposed in the cubane isomerization makes the stepwise mechanism, operating through the open coordination position on the d^8 system, most reasonable.[21]

Another kind of valence isomerization of interest here is that in which bidentate character in both valence isomers is fixed but significant thermodynamic driving force is absent.[2b] An example is the valence isomerization of the *exo*-tricyclooctene II to the tetracyclooctane III. Bidentate coordination of these ligand systems, of course, tends to focus the two critical metal d electrons in the spatial configuration allowing maximum back-bonding; this electronic configuration opens the symmetry-allowed path to the product valence isomer (*e.g.*, II → III).

II III

Concerted ligand transformations of this kind[22] would be more sensitive to ligand-field restrictions than those offering greater thermodynamic driving force. These metal-catalyzed valence isomerizations, however, should proceed with greater ease than direct cyclobutanation of simple olefins, since both starting and product valence isomers are good bidentate ligand systems.

Summary and Conclusions

We have proposed that symmetry-forbidden reactions can proceed, in a concerted manner, on the coordination spheres of certain transition metal complexes. We now have described certain controlling factors for this process which can, conceivably, serve to direct the attention of experimentalists to those metal systems offering the greatest promise for this special kind of catalytic activity. The ligand-field effects discussed here should not be looked upon as selection rules offering clear division between active and inactive systems. They should better serve as a broad framework containing general guidelines to the more active species in this special area of metal catalysis. Transition metal systems which prefer those geometries describing restrictive ligand fields should possess less catalytic activity than those capable of ligand configurations defining nonrestrictive ligand fields. In this respect the transition elements exhibiting high lability in their interconversions between polytopal isomers[16] should show catalytic activity above that associated with metals locked in restrictive ligand-field geometries (*e.g.*, square planar and octahedral). Metals capable of facile six–seven-coordination interconversion (with C_{2v} symmetry in seven-coordination) and possessing an appropriate number of valence electrons (d^2 and higher is preferred; for a d^1 case, *cf.* ref 2h, p 311) are particularly attractive catalyst candidates for [2 + 2] forbidden-to-allowed processes.

In describing the ligand-field effects associated with the nonreacting ligands we have, for simplicity, treated a given network of ligands as an essentially fixed set of localized centers of electron density. Ligand systems, of course, can exhibit complex donor and back-bonding behavior and these factors can be important in the chemistry of these systems. More important, however, is the lability of a given set of ligands. Here we refer to the ability of a ligand system to adopt new, nonrestrictive geometries either through intramolecular rearrangement or through the shedding or gaining of ligands. Molecular rearrangements of a highly labile set of ligands can either precede the [2 + 2] reaction or proceed in direct response to it. This latter case should be particularly applicable to [2 + 2] transformations possessing a pronounced thermodynamic driving force. The energy generated by the otherwise forbidden transformation would essentially serve to drive the rearrangement of the labile set of ligands.

Ligand-field restrictions can, in theory, be removed in other ways. One interesting possibility involves the use of photons. Photolytic excitation can conceivably support reaction through either effecting a ligand rearrangement to a nonrestrictive geometry or displacing restrictive ligands from the primary coordination sphere. Possible photolytic assistance of this kind is suggested in the photolytic cyclobutanation of norbornadiene using chromium hexacarbonyl.[24]

We have focused our attention on a very special kind of catalytic process in which an otherwise forbidden molecular transformation proceeds on the coordination sphere of a transition metal. It is, necessarily, a concerted ligand transformation since it mirrors the metal-free, symmetry-forbidden reaction. This does not mean, however, that symmetry-forbidden reactions cannot be catalyzed along other reaction paths. They unquestionably can. The experimental observation

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(20) J. P. Collman, *Accounts Chem. Res.*, 1, 136 (1968).

(21) Oxidative addition need not occur in this mechanism. Simple monodentate coordination of a carbon–carbon σ bond can release ring strain through reducing bond order with back-bonding. The coordinated bond, which retains carbon–carbon bonding, can then undergo complete cleavage concomitantly with the second carbon-carbon bond running parallel to it. This process would proceed with an exchange of electron pairs between the transforming ligand and the metal center; the metal back-bonding electrons (in an antisymmetric metal atomic orbital) would flow into a π–π combination and an electron pair from the coordinated σ bond would be returned to a metal symmetric atomic orbital. The breaking of the two carbon–carbon bonds would thus proceed in a concerted manner following simple monodentate coordination to the metal center. The metal, in this role, removes the orbital symmetry restraints to the concerted transformation in very much the same way that it operates through bidentate coordination. Both processes are forbidden to allowed in character and differ from the pure oxidative-addition description in that two bonds are broken in the critical step to product. In the oxidative-addition mechanism, one bond is first completely cleaved, yielding an intermediate which then undergoes a transformation involving cleavage of the second bond. A continuum very likely exists between the two extreme mechanisms.

(22) A stepwise mechanism has been proposed for the rhodium-catalyzed (tris(triphenylphosphine)rhodium(I) chloride) valence isomerization of II → III.[23] In this study, experimental evidence was presented which supports the intermediacy of a species "x" which transforms to the observed product III and a second isomer. Although the stepwise mechanism is attractive for this rhodium system, the concerted ligand transformation does not seem to be completely ruled out. Species x could conceivably be a metal complex in which the ligand (II) is coordinated to the metal in a bidentate manner. Failure to pass cleanly to a bidentate III could stem from an energy barrier due to the ligand-field restrictions defined by the nonreacting ligands of this particular catalyst system.

(23) T. J. Katz and S. A. Cerefice, *J. Amer. Chem. Soc.*, 91, 6519 (1969).

(24) W. Jennings and B. Hill, *ibid.*, **92**, 3199 (1970); see also R. Pettit, *ibid.*, 81, 1266 (1959); D. M. Lemal and K. S. Shim, *Tetrahedron Lett.*, 368 (1961).

that a symmetry-forbidden transformation proceeds in the presence of a transition metal catalyst should not imply the intervention of the forbidden-to-allowed process. Stepwise catalytic processes reasonably explain the nickel-catalyzed cycloaddition of butadiene[25] and the rhodium-catalyzed valence isomerization of cubane,[19] for example. The overall chemistry associated with the catalysis of symmetry-forbidden reactions will unquestionably involve a number of distinguishable stepwise processes in addition to the special case addressed here. In describing postulated stepwise reaction paths, particular attention has been directed toward the "nonconcertedness" of the catalytic process.[19,23] All molecular transformations to distinct intermediates, of course, are concerted processes, and orbital symmetry restraints necessarily intervene. In the catalysis of [2 + 2] cycloaddition, symmetry restraints similar in kind to those discussed here can appear.[26] The ligand-field restraints encountered by the stepwise cycloaddition process are essentially those that would be associated with the forbidden-to-allowed process proceeding *via* monodentate coordination.[21] The two paths thus exhibit quite similar orbital symmetry patterns in their modes of catalysis.

We feel that the forbidden-to-allowed process will play an important role in the catalysis of symmetry-forbidden reactions. Catalytic systems are presently known which are best interpreted through forbidden-to-allowed concepts;[2d,f] the striking ease of these catalytic transformations suggests that significant levels of activity are achievable with appropriate metal systems. Indeed, most unusual catalytic systems have been reported in which trace elements (apparently entrained during purification of reagents over stainless steel spinning bands) catalyze the valence isomerization of quadricyclene derivatives to norbornadiene products, and do so with remarkable facility.[27] The nature of these elements is unknown. However, the apparent high levels of activity pose some interesting questions regarding their mode of catalysis. The real breadth of the chemistry associated with the forbidden-to-allowed process is essentially unknown, remaining the subject of experimental research. The dynamics of this process would seem to depend on the thermodynamic driving force of the [2 + 2] ligand transformations, the changes in metal-to-ligand coordinate bonding, and the attendant energy barriers associated with the ligand fields of the nonreacting ligands.

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(25) P. Heimbach and H. Hey, *Angew. Chem., Int. Ed. Engl.*, **9**, 528 (1970).

(26) Consider the oxidative-cycloaddition mechanism proposed for both olefin cyclobutanation and cyclobutane ring-opening processes.[19] For the ring-opening path, the oxidative-addition step, to be symmetry allowed, should be considered a $[{}_d\mathbf{2}_a + {}_\sigma\mathbf{2}_s]$ process (l) (the subscripts d and a on the first term refer to a metal d orbital which is antisymmetric to the symmetry plane bisecting the two reaction participants). The metal thus supplies an electron pair through one of its antisymmetric atomic orbitals. The second step, however, corresponds to a $[{}_\sigma\mathbf{2}_s + {}_\sigma\mathbf{2}_s + {}_\sigma\mathbf{2}_s]$ process and the metal thus must withdraw from the transforming ligand system an electron pair through one of its symmetric (with respect to the plane of symmetry passing through metallo–ring) atomic orbitals. Orbital symmetry restraints due to the ligand-field effects discussed above could enter here, introducing energy barriers to the second step. The transition metal, however, has a larger number of symmetric atomic orbitals than antisymmetric and thus can be in a variety of ligand fields which split the d orbitals in a way allowing the unhindered introduction of valence electrons into a symmetric atomic orbital. This would particularly be the case for metal systems with fewer d electrons, where a broader number of symmetric atomic orbitals would be available to accommodate the returning electron pair. The reverse, however, is true for reactions proceeding in the opposite direction. The oxidative-addition step now is described $[{}_d\mathbf{2}_s + {}_\pi\mathbf{2}_s + {}_\pi\mathbf{2}_s]$ and the second step (extrusion) $[{}_\sigma\mathbf{2}_a + {}_\sigma\mathbf{2}_s]$. The second step, extrusion of a cyclobutane ring, can experience significant orbital symmetry restrictions due to ligand-field effects, particularly in the d-electron-rich metal systems, since the metal must withdraw an electron pair through an antisymmetric orbital.

(27) P. G. Gassman, D. H. Aue, and D. S. Patton, *J. Amer. Chem. Soc.*, **89**, 2486 (1967).

Preparation and Spectroscopic Properties of Methylamino Derivatives of Some Difluoro- and Bis(trifluoromethyl)phosphorus Compounds

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Received April 6, 1970

Abstract: The preparation and characterization of four new compounds of the type $(CF_3)_2P(E)N(H)CH_3$ and $F_2P(E)N(H)CH_3$ (E = O, S) by aminolysis of the appropriate chlorophosphorus compound is described. Infrared and nmr spectra of the compounds indicate that no conformational preference is adopted on the latter time scale although the presence of conformational isomers may be indicated by infrared. Some hydrogen bonding is indicated by infrared studies especially for the compound $F_2P(O)N(H)CH_3$, which appears to be strongly hydrogen bonded in all states. The nmr spectral behavior indicates the presence of coupling of the N–H proton to the methyl proton. Second-order intensity variations are observed when the N–H chemical shift is close to that of the CH_3 group. The nmr spectra of the phosphines $X_2PN(H)CH_3$ (X = F, CF_3) show the same features.

Recently much interest has developed in the structural properties of P–N compounds especially in connection with the question of π bonding and restricted rotation about the phosphorus–nitrogen bond in amino derivatives of trivalent phosphorus compounds.[1-6] As part of a continuing study on the prop-