Nickelacyclopentane Complexes. A Theoretical Investigation

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Abstract: The relationships of geometry and coordination number to the degradation pathways of nickelacyclopentane complexes to cyclobutane or ethylene are explored and discussed in the light of the experimental observations of Grubbs and co-workers. The reductive elimination of cyclobutane from a square-planar four-coordinate complex is symmetry allowed. An unexpected four-coordinate trans complex (C_{2v} symmetry) is proposed to be an important intermediate in the degradation of five-coordinate nickelacyclopentane complexes to ethylene. In general, if metallacycle degradation to form cyclobutane is symmetry allowed, then the formation of ethylene will usually be symmetry forbidden, and vice versa.

Introduction

Metallacycles, exemplified by metallacyclopentanes, are easily formed and easily decomposed. They degrade to a variety of organic products (Scheme I), among them cyclobutanes, ethylenes, butenes, and butanes. It is clear that in these degradations just about every fundamental organometallic elimination reaction type occurs.

Following pioneering studies from the Whitesides group,[2] a substantive contribution to our mechanistic understanding of these reactions was made by Grubbs and co-workers on the nickelacyclopentane system with tertiary phosphine ligands.[3] A summary of their studies is shown in Scheme II. Nickelacyclopentanes of coordination number 3, 4, and 5 are in equilibrium with each other. For each complex there is a dominant reaction channel: the three-coordinate complex **1** yields butene, the four-coordinate complex **2** reductively eliminates cyclobutane, and the five-coordinate metallacycle **3** reductively fragments to give ethylene. Furthermore, kinetic evidence points to an equilibrium between **3** and $L_2Ni(CH_2)_4$, complex **4**, different from **2**, preceding the ethylene-forming step.

The reaction scheme is significantly simplified by these findings. Nevertheless, numerous mysteries remain. A partial list of these includes the detailed mechanism of butene formation, the degree of concert in the cyclobutane- and ethylene-forming steps, the nature of the bis(phosphine) complex **4**, and the fate of the metal fragments in the reactions. More generally one would like to understand the way in which ligand number and geometrical disposition influence the mode of degradation of these d^8 complexes. The complexity of several possible multistep pathways for butene formation has led us to exclude it from this theoretical study. However, we shall attempt to shed some light on the other questions. A previous study has already explored the relationship of some d^6 iron metallacyclopentane derivatives with bis(olefin) complexes.[4]

While we do know something about metallacyclopentane structures,[5] sad to say, little crystallographic information is available on the nickelacyclopentanes of interest to us. So we must

Scheme I
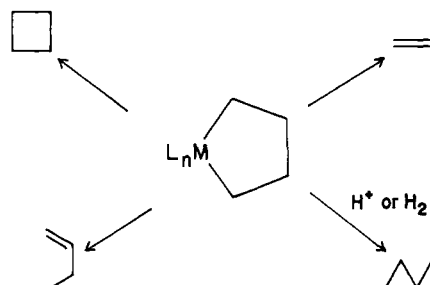
Scheme II
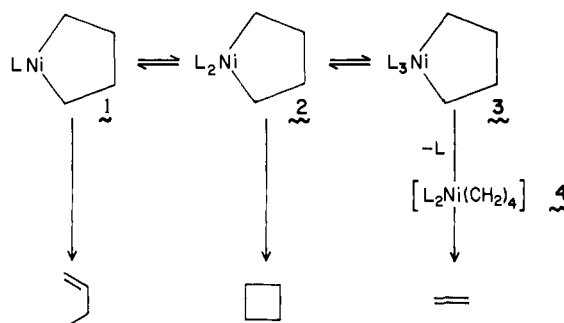
begin our study by estimating equilibrium geometries of reactants **1–3** and possible intermediates. We shall explore the degradation pathways available to each, independent of one another, and then in a concluding discussion attempt to correlate our findings with the observed reactivity.

Throughout this paper we use a semiempirical molecular orbital procedure. It is similar to the extended Hückel method[6] but contains a correction for two-body repulsion as suggested by Anderson.[7] Parameters are given in the Appendix, along with geometrical assumptions concerning ligands, the optimized geometries of various complexes explored, and the procedures used in calculating reaction surfaces. The phosphine we use is PH_3, electronically but certainly not sterically a model for the bulky phosphines of the Grubbs complexes.

Four-Coordinate L_2Ni Metallacycle Structures and Their Degradation

The central importance of the four-coordinate metallacycles, both from the synthetic viewpoint as well as the undefined nature of **4**, leads us to begin by exploring the potential energy surface of bis(phosphine) metallacycle complexes. Characteristic of four-coordinate Ni(II) complexes is a facile equilibrium between

(1) (a) Du Pont; Contribution No. 2840. (b) Cornell University. (c) Laboratoire de Chimie Organique Physique of the Université de Liège, Belgium.

(2) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976,** *98,* 6521–6528. McDermott, J. S.; Wilson, M. E.; Whitesides, G. M. *Ibid.* **1976,** *98,* 6529. Young, G. B.; Whitesides, G. M. *Ibid.* **1978,** *100,* 5808–5815.

(3) Grubbs, R. H.; Miyashita, A.; Liu, M.; Burk, P. *J. Am. Chem. Soc.* **1977,** *99,* 3863. *Ibid.* **1978,** *100,* 2418. Grubbs, R. H.; Miyashita, A. *Ibid.* **1978,** *100,* 1300, 7416, 7418.

(4) Stockis, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1980,** *102,* 2952.

(5) Krüger, C.; Tsay, Y.-H. *Cryst. Struct. Commun.* **1976,** *5,* 215. Jolly, P. W.; Krüger, C.; Salz, R.; Sekutowski, J. C. *J. Organomet. Chem.* **1979,** *165,* C39–42. Green, M.; Howard, J. A. K.; Mitsprachachon, P.; Pfeffer, M.; Spencer, J. L.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1979,** 306–314. Churchill, M. R; Youngs, W. J. *J. Am. Chem. Soc.* **1979,** *101,* 6462. Bringer, P.; Doyle, M. J.; Krüger, C.; Tsay, Y.-H. *Z. Naturforsch., Teil B* **1979,** *34,* 1289–1292.

(6) Hoffmann, R. *J. Chem. Phys.* **1963,** *39,* 1397. Hoffmann, R.; Lipscomb, W. N. *Ibid.* **1962,** *36,* 2179, 3489. *Ibid.* **1962,** *37,* 2872.

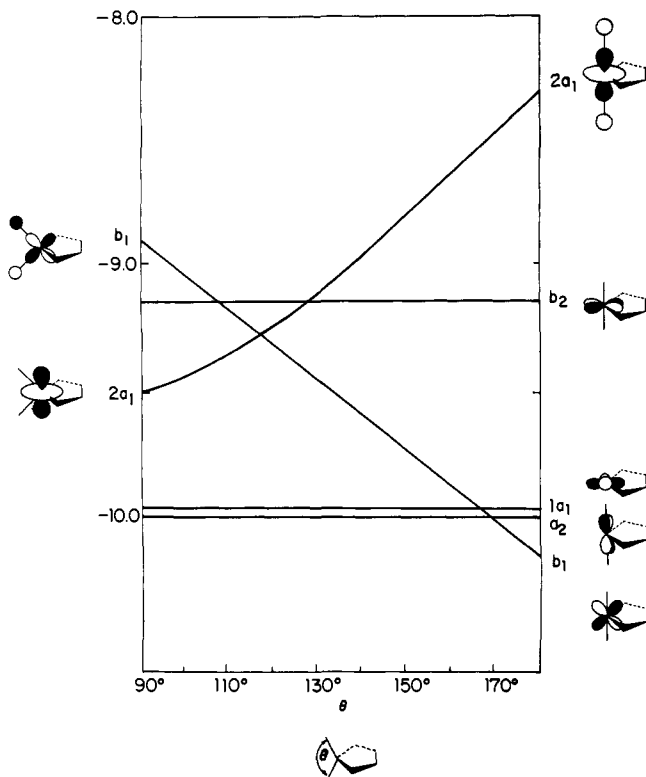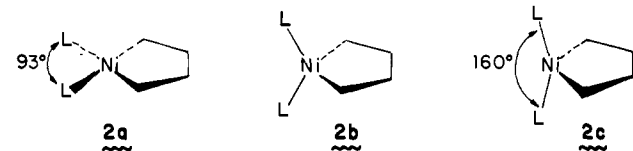(7) Anderson, A. B. *J. Chem. Phys.* **1975,** *62,* 1187.

Figure 1. A Walsh diagram for varying the interligand angle θ in Ni-$(PH_3)_2(CH_2)_4$, for $\alpha = 90°$ (see **5**). Only d-block orbitals are included.

low-spin square-planar and high-spin tetrahedral structures.[8] This suggests immediately the geometrical alternatives **2a** and **2b**.

Indeed these are important structures, but an unexpected contender, possessing a "trans" geometry, **2c**, turned up when we examined some modifications of the "tetrahedral" structure **2b**.

Our search for stable points on the four-coordinate metallacycle surface utilized two degrees of freedom. As defined in **5**, these

5
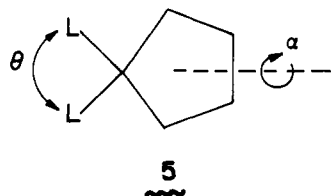
are the L–Ni–L (L = PH_3) angle θ and the torsion angle between P–Ni–P and C–Ni–C planes α. At $\alpha = 90°$, we calculated a Walsh diagram for varying the P–Ni–P angle θ. Figure 1 shows the d block as θ is varied. Indeed there is a typical tetrahedral ligand field splitting, two levels below three near the geometry that best approximates the tetrahedron, $\theta \sim 110°$. There will be three configurations, I–III, competing to be the lowest triplet, and presumably the ground state of the "tetrahedral" geometry.

I	$(a_2)^2(1a_1)^2(2a_1)^2(b_2)^1(b_1)^1$	$^{1,3}A_2$
II	$(a_2)^2(1a_1)^2(b_1)^2(2a_1)^1(b_2)^1$	$^{1,3}B_2$
III	$(a_2)^2(1a_1)^2(b_2)^2(2a_1)^1(b_1)^1$	$^{1,3}B_1$

The three competing low-spin configurations, IV–VI, all have $^1A_1$

(8) This well-established phenomenon has been studied by NMR (e.g., Que, L.; Pignolet, L. H. *Inorg. Chem.* **1973**, *12*, 156), photochemical perturbation experiments (McGarvey, J. J.; Wilson, J. *J. Am. Chem. Soc.*, **1975**, *97*, 2531), and most recently theoretically (Lohr, L. L., Jr. *Ibid.* **1978**, *100*, 1093).

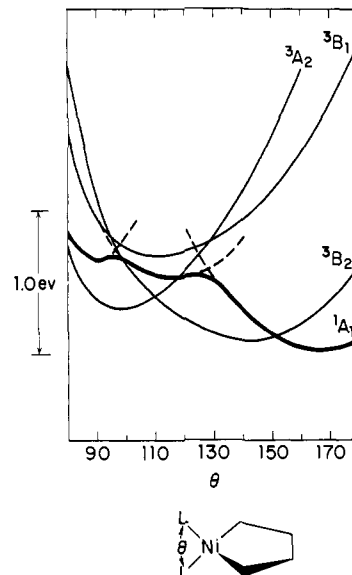**Figure 2.** Approximate changes in state energies of $Ni(PH_3)_2(CH_2)_4$ with the interligand angle θ. The energy of the $^1A_1$ state, relative to the triplet states, is assumed. Energies of the triplet states are taken directly from calculations performed with the appropriate configurations.

state symmetry, and no doubt will mix substantially, especially at intermediate θ. But each configuration will have its own geometrical preferences, with IV favoring low θ, V intermediate θ, and VI high θ.

IV	$(a_2)^2(1a_1)^2(2a_1)^2(b_2)^2$	$^1A_1$
V	$(a_2)^2(1a_1)^2(2a_1)^2(b_1)^2$	$^1A_1$
VI	$(a_2)^2(1a_1)^2(b_1)^2(b_2)^2$	$^1A_1$

These geometrical preferences arise from the marked change of two of the energy levels with θ. A substantial energy gap at high θ results from the falling slope of the b_1 level, **6**, which is stabilized

6   **7**
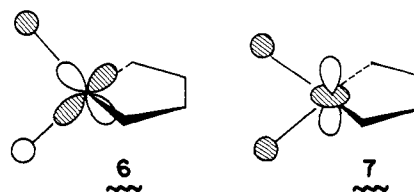
with increasing θ, and the rising slope of the $2a_1$ level, **7**, which is destabilized with increasing θ.

A deficiency of the extended Hückel method, which carries over to the method used here, is that only configuration energies, not state energies, can be calculated. Electron interaction is not explicitly included in our calculations. Configurations I–III will separate into higher lying singlets and lower lying triplets. Figure 2 summarizes the dependence of the configuration energies of the triplets upon θ. Also shown are the energies for configurations IV–VI, all of the same symmetry, which will mix to give a single, low-lying surface favoring high θ, as indicated by the boldfaced line in Figure 2. Of the states arising from configurations I–VI, it is likely that four will be at low energy, with preferred values of $\theta = 100°$ ($^3A_2$), 115° ($^3B_1$), 135° ($^3B_2$), and 160° ($^1A_1$). This spin-paired $^1A_1$ species with essentially trans phosphines is the unexpected contender **2c**.

All that is for the "tetrahedral" isomers. How do these curves connect up to the square-planar singlet? A correlation diagram for twisting, i.e., changing α in **5** for any θ, may be constructed from symmetry arguments. It is shown for $\theta \sim 90°$ in Figure 3.

The ground state of the square-planar form, $^1A_1$, correlates to configuration IV or V of the "tetrahedral" geometry, depending on θ, but it cannot correlate to configuration VI. While configurations IV, V, and VI will all mix, configuration VI will dominate the $^1A_1$ wave function, and it can be said that the *direct inter-*
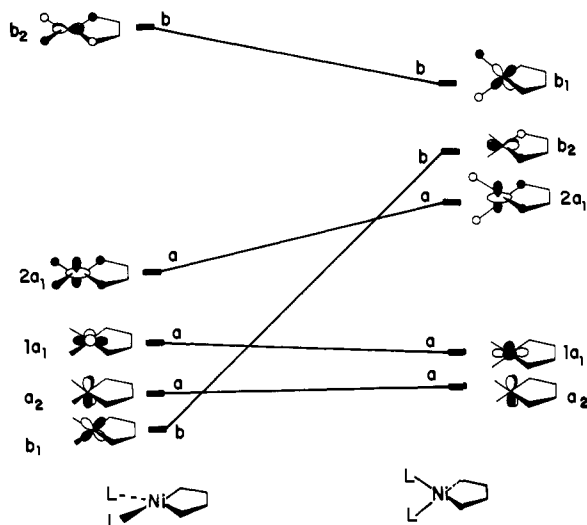
Figure 3. A correlation diagram for the interconversion of the square-planar form (left) of $Ni(PH_3)_2(CH_2)_4$ with a "tetrahedral" form (right) with $\theta = 90°$. C_2 symmetry is imposed throughout.

conversion of the trans structure **2c** *and the square-planar structure* **2a** *is a forbidden reaction.*

A complete elucidation of the intricacies of this potential energy surface will have to await more sophisticated calculations. For the present we propose that five states merit consideration: a ground-state square-planar singlet **2a** ($^1A_1$), three tetrahedral triplets **2b** ($^3A_2$, $^3B_1$, $^3B_2$), and a novel singlet **2c** ($^1A_1$), a "trans" isomer which is neither square planar nor tetrahedral. The new structure **2c** will play an important role in subsequent discussions.

Next we consider the possible degradation modes of the four-coordinate metallacycle. Let us begin with concerted reductive fragmentation processes, **2** → **8, 9, 10**, for olefin formation,
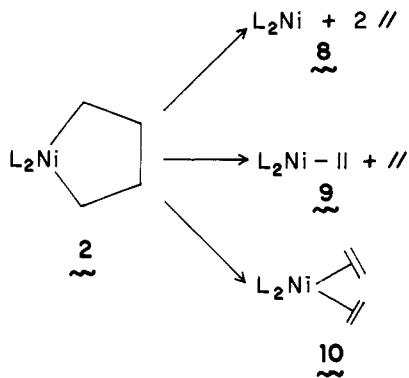

differing by whether the ethylenes are kept in the coordination sphere or not, and starting from the geometrical alternatives discussed above.

Correlation diagrams for splitting off two ethylenes, **2** → **8**, are constructed in Figure 4. As indicated by the HOMO–LUMO crossing in Figure 4a, the direct decomposition of square-planar **2a** to L_2Ni + two ethylenes in a least motion process is a forbidden reaction.[11] The orbitals of the metallacycle are given; they are those of a typical square-planar complex. The orbitals of an ML_2 fragment are available in the literature.[9] The fundamental problem in the reaction is that the symmetry of the breaking CC bond, a_1, is not matched by the symmetry of the extra metal orbital on the metal, b_2, that is filled as the metal goes from d^8 to d^{10}.

Assumming spin conservation, it will be impossible for a triplet state, **2b**, to correlate with L_2Ni and two ethylenes. There remains the new minimum energy structure we have located, the trans

isomer **2c**. Remarkably, the departure of two ethylenes from **2c** is a symmetry-allowed reaction, as Figure 4b shows. The difference between the two reaction pathways is to be traced to the very different orbital occupations as illustrated in Figure 4. In the d block, the three orbitals, a_1, a_2, and b_1 are similar in both fragments. This makes sense, for one can think of these molecules as octahedra minus two cis or trans ligands, and these three orbitals are derived from the t_{2g} set of the octahedron. One can think of the fourth orbital, $2a_1$ in **2a**, b_2 in **2c**, as being derived from the e_g set, and it is a very different orbital in each case, suitable to cis or trans geometry.

To evaluate the possibility of fragmentation of the metallacycle while maintaining bonding to the olefins, we first optimized the geometries of four different conformations of $L_2Ni(ethylene)_2$. **10a** and **10b** are square planar at Ni, while **10c** and **10d** are tetrahedral. Their relative energies (eV) are given in brackets.
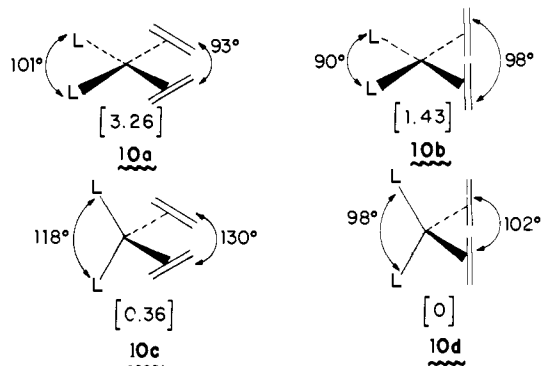
As anticipated these d^{10} complexes favor a tetrahedral coordination.[10] All structures with "coplanar" ethylenes are in steric difficulty; this shows up in the relative destabilization of **10c** relative to the calculated optimum **10d**. The tendency of the ethylenes to move into "upright" orientations, as in **10b** or **10d**, complicates the construction of reaction paths, because "coplanar" conformations are more closely related to the geometries of the metallacycles.

The evolution of the energy levels along a reaction path from the new minimum, **2c** to **10c** and then **10d**, is shown in Figure 5. The molecular energy for the system decreases throughout the reaction sequence. The procedure for defining the reaction coordinate for the transformation of the metallacyclopentane **2c** to the bis(ethylene) **10c**, as well as subsequent reaction coordinates, is described in the Appendix.

Metallacycle fragmentation with the expulsion of a single ethylene, **2** → **9**, is a process with inherently little symmetry. This discouraged us from computing a reaction path. However, $L_2Ni(ethylene)$ is observed in the reaction products, and this pathway cannot be discounted. This complex might also arise from ethylene dissociation from **10d**, and indeed this seems likely considering that the reverse reaction, addition of ethylene to $L_2Ni(ethylene)$, can result in metallacycle formation.[3]

Reductive eliminations of cyclobutane from the two likely singlet minima, **2a** and **2c**, are straightforward and correlation diagrams, drawn in Figure 6,[11] reveal that elimination from **2a** is allowed, but from **2c** is forbidden.

A surfeit of correlation diagrams has led us here. Perhaps it would be useful to summarize our findings; see Scheme III. We think that there are likely to be five accessible minima on the $L_2Ni(CH_2)_4$ surface: three tetrahedral triplets and two singlets (one square-planar, **2a**; one a distorted tetrahedral one with a large LNiL angle, **2c**). Allowed reactions lead from **2a** to cyclobutane, and from **2c** to two olefins, with or without tetrahedral inter-

(9) Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1977**, 602–610. *Adv. Organomet. Chem.* **1977**, *15*, 1–51. Hofmann, P. *Angew Chem.* **1977**, *89*, 551–553. Albright, T. A.; Hoffmann, R.; Tse, Y.-C.; D'Ottavio, T. *J. Am. Chem. Soc.* **1979**, *101*, 3812–3821, and references cited therein.

(10) Rösch, N.; Hoffmann, R. *Inorg. Chem.* **1974**, *13*, 2656–2666. Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel"; Academic Press: New York, 1974; Vol. 1, Chapter III.

(11) Braterman, P. S. *J. Chem. Soc., Chem. Commun.* **1979**, 70. Akermark, B.; Ljungquist, A. *J. Organomet. Chem.* **1979**, *182*, 59–75. Pearson, R. G. "Symmetry Rules for Chemical Reactions", Wiley-Interscience: New York, 1976; Chapter 5.
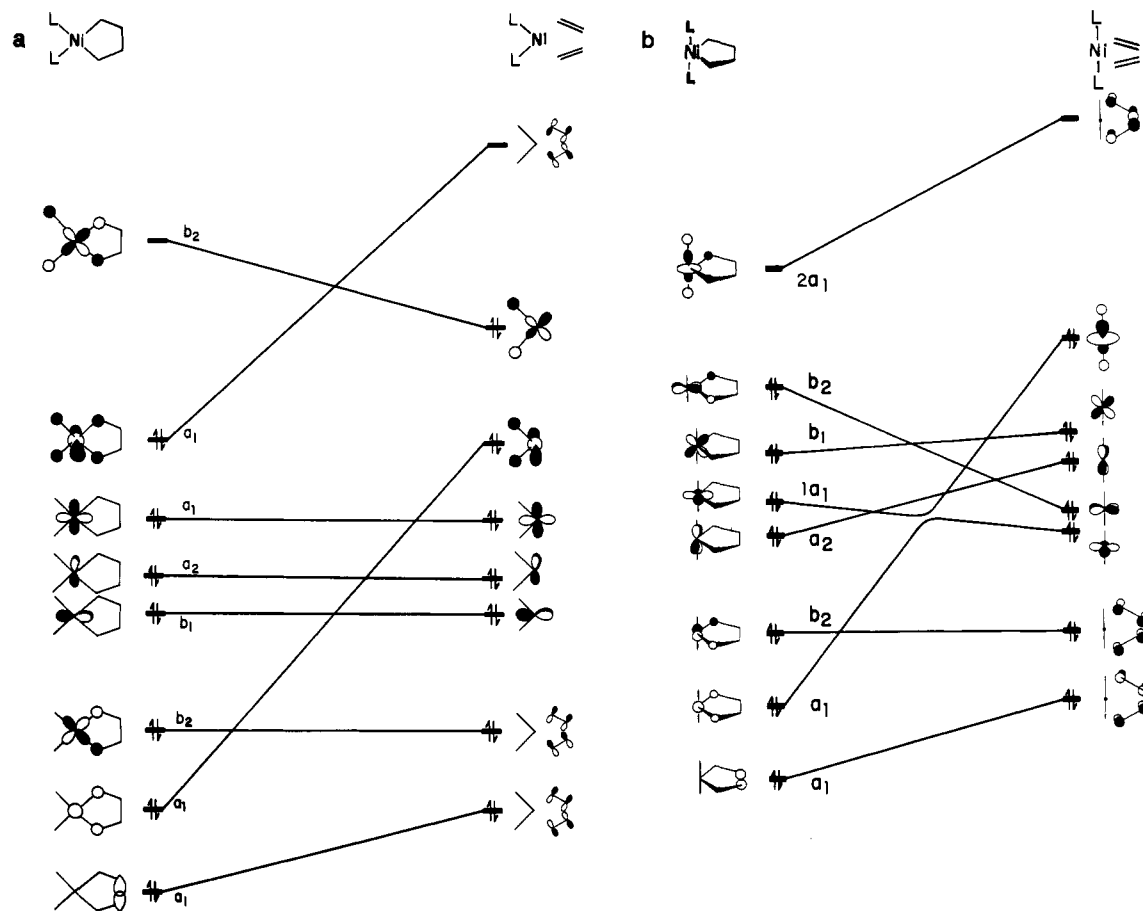
Figure 4. (a) A schematic correlation diagram for the reductive fragmentation of square-planar $Ni(PH_3)_2(CH_2)_4$, **2a** (left), into $Ni(PH_3)_2 + 2C_2H_4$ (right). C_{2v} symmetry is imposed throughout. (b) A schematic correlation diagram for the reductive fragmentation of the trans isomer of $Ni(PH_3)_2(CH_2)_4$, **2c** (left), into $Ni(PH_3)_2 + 2C_2H_4$ (right).
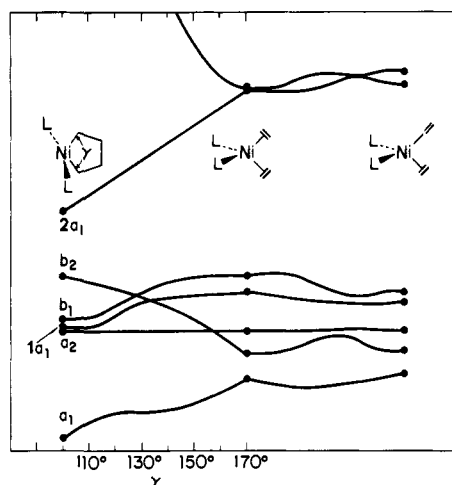

Figure 5. Evolution of the energy levels along the minimum energy reaction path from **2c** (left) through **10c** (middle) to **10d** (right). The reaction coordinate γ is defined in the Appendix.

mediates in which the olefins are bound, whereas it is forbidden for **2a** to fragment to ethylene and **2c** to eliminate cyclobutane. In fact, this is a general trend throughout our study: *If metallacycle degradation to form cyclobutane is symmetry allowed, then the formation of ethylene will usually be symmetry forbidden, and vice versa.* The metallacycle reactions, cyclobutane or ethylene formation, are formally "reductive elimination" processes. However, the formation of cyclobutane requires that the electron pair be transferred to the metal center via an orbital of b_2 symmetry, whereas the formation of two ethylene molecules takes place with electrons being transferred to the metal center via an a_1 orbital. That this should be so is graphically illustrated
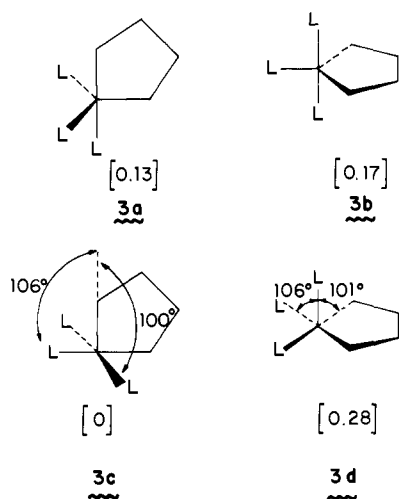
Scheme III
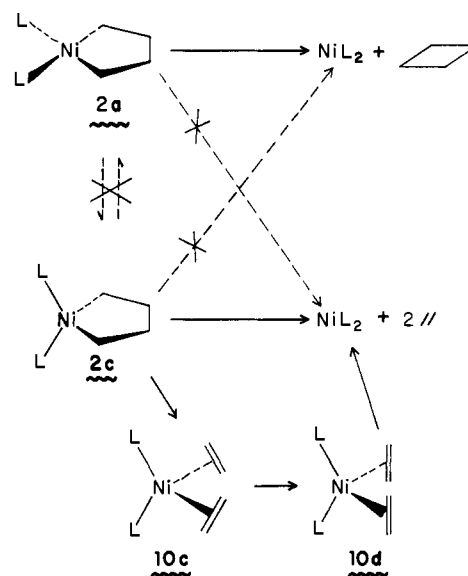
in Figure 7. In these d^8 complexes there is only one empty d orbital which, depending upon the geometry and coordination number, may be of a_1 or b_2 symmetry. Consequently, either cyclobutane or ethylene formation, but never both, will be an allowed reaction from any specified symmetrical geometry of the metallacycle complex.

Five-Coordinate L_3 Metallacycle Structures and Possible Degradation Pathways

Trigonal-bipyramidal **3a** and **3b** and square-pyramidal **3c** and **3d** are obvious candidates for the ground-state geometry of the

Nickelacyclopentane Complexes

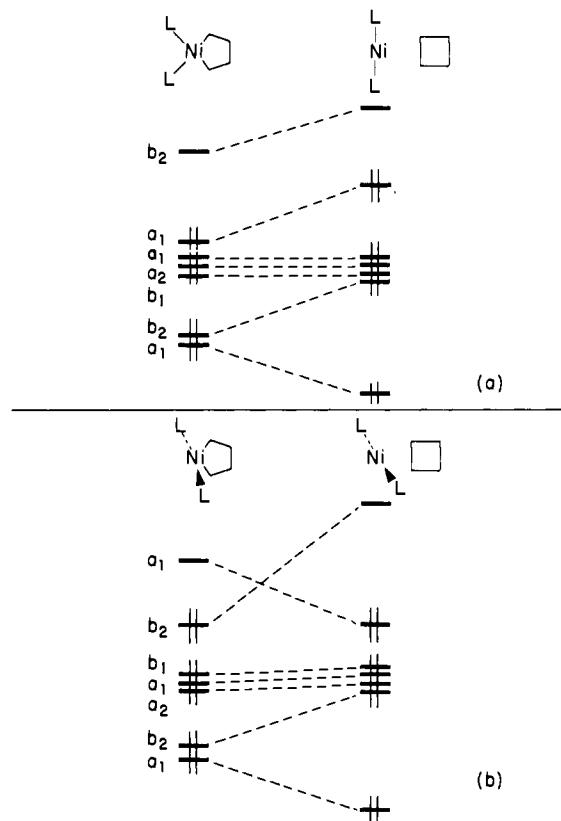*J. Am. Chem. Soc., Vol. 103, No. 10, 1981* 2599

Figure 6. (a) A schematic correlation diagram for the reductive elimination of cyclobutane from square-planar $Ni(PH_3)_2(CH_2)_4$, **2a**. (b) A schematic correlation diagram for the reductive elimination of cyclobutane from the trans isomer of $Ni(PH_3)_2(CH_2)_4$, **2c**.

five-coordinate complex. Geometry optimization gives the indicated energies as shown. The electronic and steric demands of the tetramethylene chelate appear to be best met in **3c**.[12] The other structures are not very much higher in energy. Most importantly we have found essentially no barriers between these conformers, along either Berry pseudorotation or turnstyle transits. Thus, in principle, the reaction could begin from any of these geometries.

We have considered reductive fragmentation to olefin from the five-coordinate complexes, again by two pathways: splitting ethylenes off directly and fragmentation while keeping them in the coordination sphere. Again we have not considered the intermediate possibility with one ethylene coordinated, because of the lack of symmetry. Also while $L_3Ni(ethylene)$ is a reasonable 18-electron complex, to our knowledge, it has not been observed among the products of the reaction.

Correlation diagrams for the splitting off of two ethylenes are constructed in Figure 8. While the symmetry of the (tetramethylene)(PH₃)₃ ligand set introduces a perturbation,[4] the primary features of the ligand-field splitting follows the well-known patterns for transition metal five-coordination.[12] In the trigonal bipyramid the occupied levels are b_1 (yz in this coordinate system; see Appendix), a_2 (xy), $1a_1$ ($x^2 - z^2$), b_2 (xz); in the square pyramid, $1a'$, $2a'$, $1a''$, and $3a'$. The orbitals of the pyramidal and T-shaped ML_3 fragments are available in the literature.[13]

Least-motion fragmentation from **3b** results in no level crossings and is an allowed reaction,[14] whereas the same process starting from **3d** is forbidden[10] despite the fact the products are still the same. Reaction paths from **3a** and **3c** do not retain symmetry elements passing through bonds made or broken, and so are more difficult to evaluate.[14] However, during fragmentation, the changes in energy levels for **3a** resemble those of **3d**, and **3c** those of **3b**.

Fragmentation while keeping both ethylenes in the coordination sphere leads to 20-electron complexes. These would be expected to be quite unstable. Indeed when we optimized several geometries, we obtained nearly dissociated olefins, weakly bound, with long Ni–C distances. Not unexpectedly, the correlation diagrams follow those deduced for complete fragmentation.

It is in this part of the discussion that we are most hampered by the lack of steric bulk in our model phosphines (as contrasted with the spatial extent of a typical ligand, PPh_3). Several metal–olefin complexes are found among the reaction products, e.g., $(Ph_3P)Ni(C_2H_4)_2$ and $(Ph_3P)_2Ni(C_2H_4)$.[3] These are both 16-electron complexes, a common electron count for Ni(0). But it could be that four-coordinate 18-electron complexes are not ob-
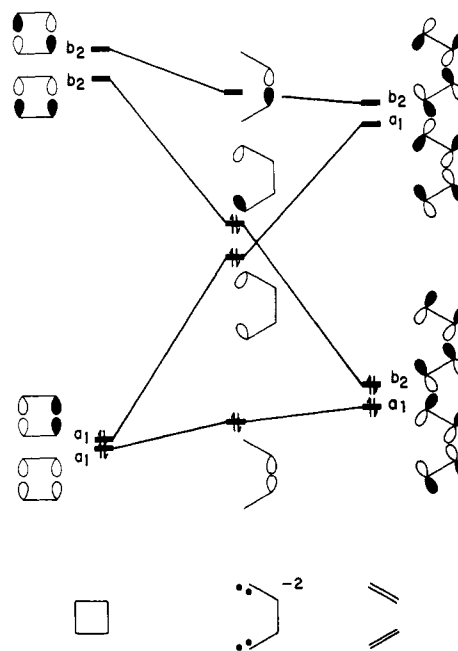
Figure 7. A schematic diagram illustrating the evolution of the orbitals of a $(CH_2)_4$ fragment. In the center is a tetramethylene dianion which is transformed into cyclobutane (left) or two ethylenes (right) with loss of two electrons.

served because of the combined steric demands of the bulky phosphines and olefins.

Correlation diagrams for the reductive elimination of cyclobutane from **3** are drawn in Figure 9. The elimination of cyclobutane from the highest symmetry structure **3b** is a symmetry-forbidden reaction, if the high symmetry (C_{2v}) is retained. Again this contrasts with the allowed nature of the elimination

(12) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365–374.

(13) Burdett, J. K. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1599–1613. Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058–1076. Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148–1155.

(14) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1970, and references cited therein.
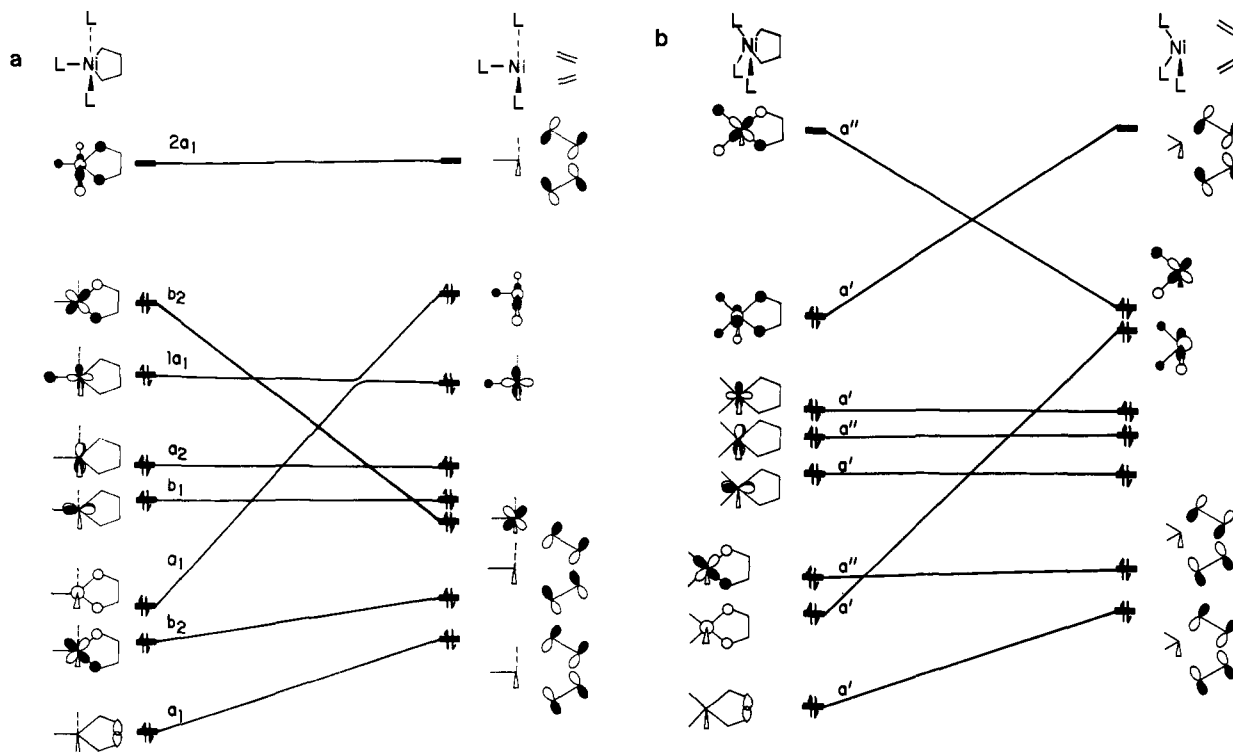
Figure 8. (a) A schematic correlation diagram for the reductive fragmentation of trigonal-bipyramidal $Ni(PH_3)_3(CH_2)_4$, **3b** (left), into T-shaped $Ni(PH_3)_3$ + $2C_2H_4$ (right). C_{2v} symmetry is retained. (b) A schematic correlation diagram for the reductive fragmentation of square-pyramidal $Ni(PH_3)_3(CH_2)_4$, **3d** (left), into pyramidal $Ni(PH_3)_3$ + $2C_2H_4$ (right). The symmetry is C_s.
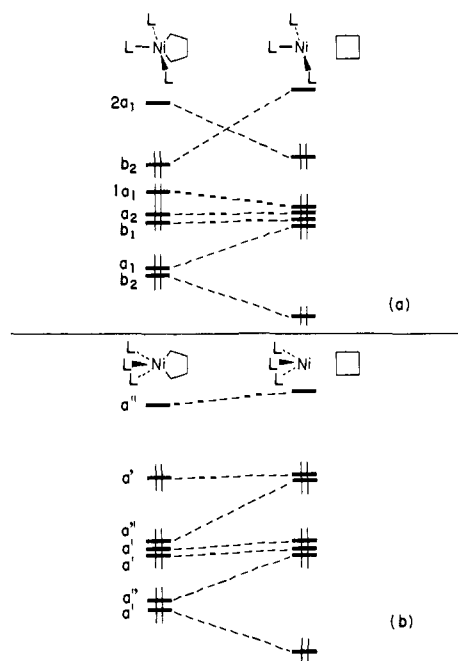

Figure 9. (a) A schematic correlation diagram for the reductive elimination of cyclobutane from trigonal-bipyramidal $Ni(PH_3)_3(CH_3)_4$, **3b** (left), to form T-shaped $Ni(PH_3)_3$ (right). C_{2v} symmetry is retained. (b) A schematic correlation diagram for the reductive elimination of cyclobutane from square-pyramidal $Ni(PH_3)_3(CH_2)_4$, **3d** (left), to form pyramidal $Ni(PH_3)_3$ (right). C_s symmetry is imposed throughout.

of ethylene from **3b** (see Figure 8).

We have computed potential surfaces for the elimination of cyclobutane from several of the conformers **3a–d**, permitting relaxation of the ML_3 fragment throughout the reaction path. Two pathways appear to be possible. Cyclobutane formation from **3c** along a reaction coordinate which has no symmetry elements through the relevant bonds is trivially symmetry allowed. Note that the C_{2v} isomer **3b** would also follow this reaction coordinate

after first undergoing distortion to **3c**. This changes a nominally symmetry-forbidden reaction, **3b** → cyclobutane, into the allowed transformation **3c** → cyclobutane.[4] The second pathway, **3d** → cyclobutane, is also allowed (as indicated in Figure 9b) and is roughly comparable.

To summarize, we find that several geometries are easily accessible for the five-coordinate metallacycle. Furthermore, allowed pathways exist for fragmentation to ethylene from some of these geometries and elimination of cyclobutane from other structures. This contrasts with the apparent lack of reactivity by these modes exhibited by $(Ph_3P)_3Ni(CH_2)_4$. This may, in fact, reflect the availability of lower energy pathways of reactivity, such as ligand dissociation, a point to which we will return.

Three-Coordinate Nickelacycle

This molecule, a d^8 ML_3 system, though asymmetrically substituted would be expected to retain an electronic "memory" of its origins from the symmetric system. A d^8 ML_3 molecule is a typical Jahn–Teller system which deforms from D_{3h} to T- and Y-shaped C_{2v} minima,[15] **11**. The constraints imposed by the
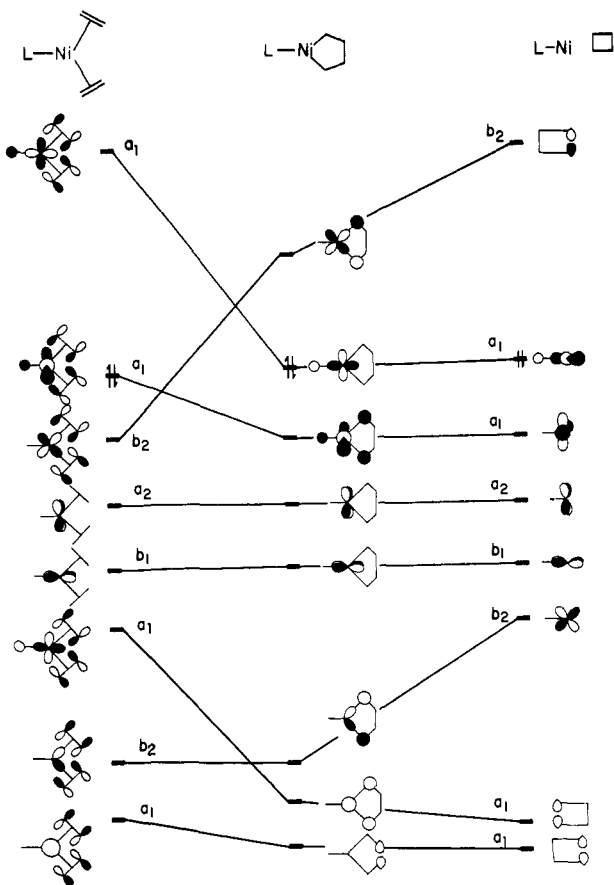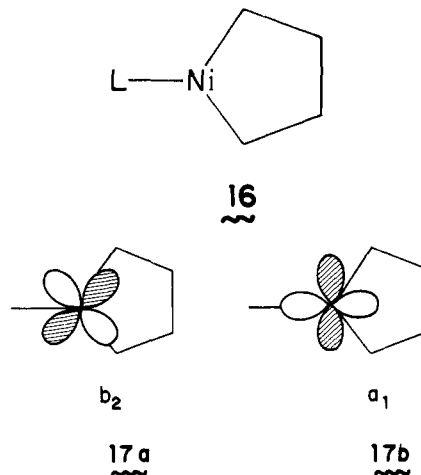

11
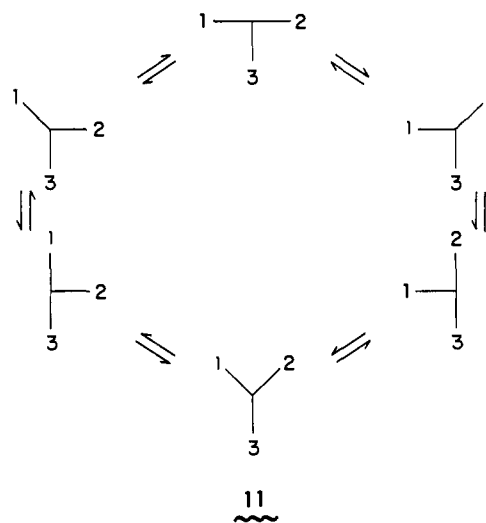
Figure 10. A schematic correlation diagram for the reductive elimination of cyclobutane from symmetrical $Ni(PH_3)(CH_2)_4$, **16** (center to right), and for the reductive fragmentation of $Ni(PH_3)(CH_2)_4$, **16**, into $Ni(PH_3)$ + $2C_2H_4$ (center to left).

tetramethylene chain are severe. If it spans positions 1 and 2 in **11**, it will effectively eliminate the upper half of the diagram and the Y-shaped structure at bottom as well. The optimized T-shaped structure, **12**, is 0.35 eV below a C_{2v} structure.

Once again we will consider three reaction channels for **12**, leading to **13–15**. The symmetry of the starting material is low,
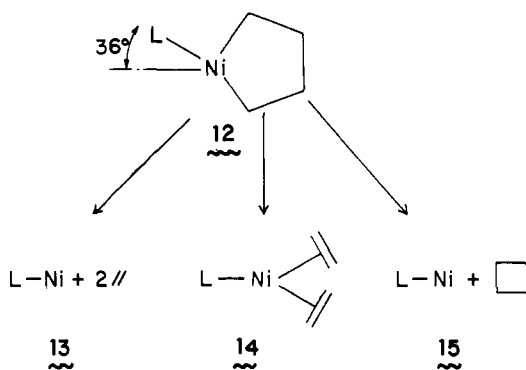

so that correlation diagrams beginning from **12**, which we have constructed, are not as informative as those which begin from the more symmetrical C_{2v} isomer, **16**. These correlation diagrams are shown in Figure 10. Their essence derives from the ordering of the two top d levels in the three-coordinate metallacyclopentane. These levels are descended from xz and x^2 and z^2 on the metal, with strong admixtures of x and z: **17a,b**. It is the Y distortion

(15) Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7255. Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K., submitted for publication.

from D_{3h} symmetry which puts b_2 above a_1. A hypothetical distortion to a T form would have reversed the ordering of these levels.

As it is, the reductive elimination of cyclobutane is allowed and the fragmentation to L–Ni + two ethylenes forbidden. The fragmentation step could be modified by (a) keeping the olefins in the coordination sphere and (b) fragmenting from the preferred "bent" geometry **12**. For the first possibility we computed optimum geometries for two $LNi(ethylene)_2$ conformers **14a** and **14b** and not unexpectedly found **14a** to be more stable.[10] A correlation from **16** to **14a** is still forbidden.
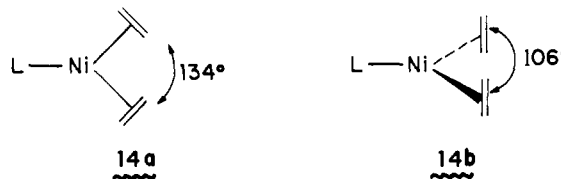
Fragmentation from the unsymmetrical bent form **12** removes the level crossing. The reaction remains effectively forbidden, for the avoided crossing that results is as effective in producing an activation energy as the real crossing. We have also computed a potential energy surface for the allowed reaction of reductive elimination of cyclobutane from the asymmetrical $LNi(CH_2)_4$, **12**. The energy surface very closely resembles that of the symmetrical reaction, illustrated in the schematic correlation diagram of Figure 10.

If reductive elimination of cyclobutane is an allowed reaction, why is it not observed as a reaction path? We think that this is a consequence of the extreme coordinative unsaturation of the product Ni–L, and the competing availability of other reaction paths.

Overall Reaction Scheme

We are now in a better position to evaluate the possible reactions of the several interrelated d^8 metallacyclic complexes, and to compare our computed reaction pathways with the experimental results. The results of our studies are conveniently summarized in Scheme IV. In this scheme, hypothetical reactions which we compute as having substantial activation barriers for reasons presented above are marked "—✗→". Qualitatively, the computational results are consistent with the experimental results[3] (see Scheme II).

One point of some interest is that the square-planar, cis bis(phosphine) metallacycle complex **2a** has only the reductive elimination of cyclobutane available to it as an allowed decomposition pathway. If excess phosphine is available and steric factors permit, a tris(phosphine) complex may exist. From the tris(phosphine) complex **3d** cyclobutane is the only allowed product, but if the tris(phosphine) complex undergoes isomerization to **3c** and loses a phosphine ligand, resulting in the formation of the trans bis(phosphine) complex **2c**, ethylene becomes the favored product. Hence, the availability of tris(phosphine) complexes **3d** and **3c** permits the formation and possible interconversion of the

Scheme IV
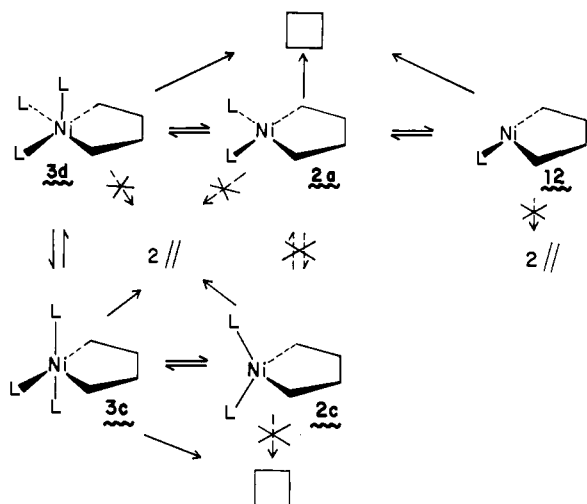
isomeric bis(phosphine) complexes **2a** and **2c**, *which themselves have no low-energy pathways for interconversion.* This is reminiscent of forbidden cis–trans isomerization of square-planar d^8 L_2NiX_2 complexes[16] and suggests that an associative process, with a five-coordinate intermediate, should be considered.

This finding enables us to rationalize the results of Grubbs and co-workers. Metallacycle degradation in the planar bis(phosphine) complex **2a** yields cyclobutane as the dominant product. But in the tris(phosphine) complexes **3**, phosphine elimination to give bis(phosphine) intermediate **4** appears to be competitive with metallacycle degradation. We believe the intermediate bis(phosphine) complex **4** is either the trans complex **2c** or the related bis(olefin) complex **10c** or **10d**, derived from **2c**. Ethylene may then be eliminated from **10** to give $L_2Ni(C_2H_4)$, a product which has been observed in the reaction mixture.

An interesting observation is that bis(phosphine) metallacyclopentane complex **2a** yields appreciable amounts of ethylene when photolyzed, and that a closely related bis(phosphine) platinum metallacyclopentane complex also produces ethylene when photolytically decomposed.[3,17] While ethylene formation from the ground state of the planar complex **2a** is symmetry forbidden, excited states of the planar metallacycle complex would have allowed pathways for ethylene formation. A possible alternative would be photochemical conversion of the planar complex **2a** to the trans isomer **2c** with subsequent allowed fragmentation to give ethylene.

The loss of phosphine from bis(phosphine) metallacycle complexes permits decomposition by yet another reaction pathway, resulting in the formation of 1-butene. We have not explored this reaction in our calculations, but we have examined the hypothetical reactions which could produce cyclobutane and ethylene and have reached the conclusion that cyclobutane is a symmetry-allowed product and ethylene is not. This finding is fully consistent with the large number of known phosphine bis(ethylene) Ni(0) complexes which do not themselves form metallacycles.[10,18]

Summary and Conclusions

A recurring observation in organotransition metal chemistry is that the ease of a reaction occurring in one portion of a metal complex depends strongly upon the number, nature, and location of the remaining ligands. Our efforts at unravelling the factors which are operating in the decomposition of Ni(II) metallacycles have resulted in a rather elaborate set of conclusions which have been schematically summarized in Scheme IV. We expect that the conclusions will be found to be applicable to decomposition reactions of metallacycle compounds of other d^8 transition metals.

(16) Eaton, D. R. *J. Am. Chem. Soc.* **1968**, *90*, 4272. Whitesides, T. H. *Ibid.* **1969**, *91*, 2395.

(17) Perkins, D. C. L.; Puddephatt, R. J.; Tipper, C. F. H. *J. Organomet. Chem.*, **1980**, *191*, 481–488.

(18) Jolly, B. W.; Wilke, G. "The Organic Chemistry of Nickel"; Academic Press: New York, **1974**; Vol. 1, Chapter V.

However, reactions at metal centers with different numbers of electrons and/or significantly different coordination geometries will require separate theoretical and, of course, experimental studies. This remains one of the exciting challenges of chemistry.

Appendix

Throughout this study a coordinate system, defined with respect to the metallacycle as shown in **18**, was used. Structures of C_{2v}


18
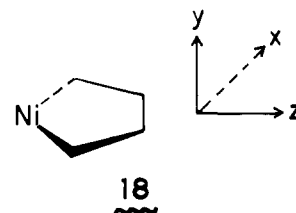
symmetry were prevalent in the study, and the character table shown below was used in assigning orbital symmetry.

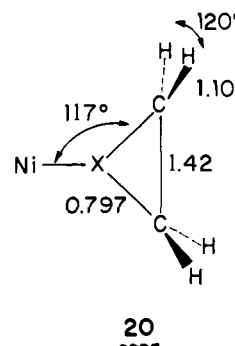| C_{2v}	E	$C_2(z)$	σ_{xz}	σ_{yz}
a_1	+1	+1	+1	+1
a_2	+1	+1	−1	−1
b_1	+1	−1	−1	+1
b_2	+1	−1	+1	−1

Atomic orbital parameters are those described previously.[19] Many calculations were repeated in which the atomic orbital energies of nickel were lowered by 2 eV. While minor differences in optimized geometry were found in some cases, relationships and conclusions remain the same.

The ligand PH_3 was used to model the tertiary phosphines. The P–H (1.40 Å) and Ni–P (2.20 Å) distances and the Ni–P–H angle (115°) were held constant in all calculations. The metallacycle is defined in **19**. X is a dummy point used to define the geometry.

19
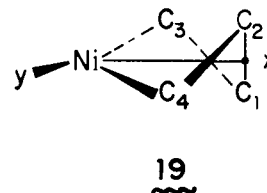
The distances X–C_1, X–C_2 (0.77 Å), C_1–C_3, C_2–C_4 (1.54 Å), C–H (1.10 Å), and angles Ni–X–$C_{1,2}$ (90°), X–C_1–C_3, X–C_2–C_4 (110°) were held constant. The distance Ni–X (2.65 Å) and the dihedral angles y–Ni–X–C_1 (148.8°) and Ni–X–C_1–C_3 (34.2°) as well as hydrogen positions were optimized for the square-planar complex $L_2Ni(CH_2)_4$ (**2a**). This metallacycle geometry was then held constant for most other geometry optimization. As an exception, the metallacycle of **2c** was reoptimized. Whereas only minor changes in the dihedral angles occurred, the Ni–X distance (2.39 Å) was significantly shortened.

For ethylene complexes, the geometry of the coordinated ethylene was defined as **20**. The Ni–X distance was optimized

20

for each complex. For complexes **10b–d**, optimization gave Ni–C distances of 2.09, 2.09, and 2.11 Å. In **10a** the ethylene was nearly dissociated (Ni–C, 2.66 Å). In the 20-electron complexes L_3-

(19) Pensak, D. A.; McKinney, R. J. *Inorg. Chem.* **1979**, *18*, 3407.

$Ni(C_2H_4)_2$ the ethylenes were held only very weakly in the coordination sphere with optimized Ni–C distances greater than 2.30 Å in all cases. The Ni–C distances for the three-coordinate complexes were 2.04 Å (**14a**) and 2.12 Å (**14b**).

The optimized angular disposition of the phosphines are given in the diagrams throughout the text.

The reaction coordinate for the elimination of cyclobutane was studied using the metallacycle framework **21**. The Ni–X distance

21
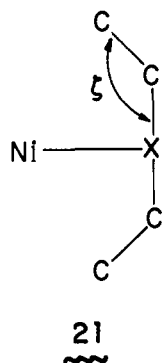
was increased stepwise and the angle ζ and the positions of the other ligands were optimized. The reaction coordinate for the fragmentation of the metallacycle to ethylene was studied using **22**, similar to that used by Stockis and Hoffmann.[4] The angle

22
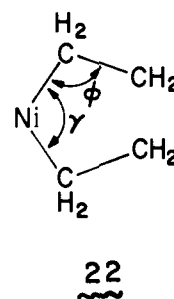
γ was opened stepwise and ϕ and ligand position were optimized.

Thermochromic Phase Transitions in Copper(II) Halide Salts. 1. Crystal Structure and Magnetic Resonance Studies of (CH3)2CHNH3CuCl3

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Abstract: $(CH_3)_2CHNH_3CuCl_3$ undergoes a thermochromic phase change at $T_{th} = 51$ °C changing in color from brown to orange. The low-temperature phase (II) is triclinic of space group $P1$ with $a = 11.692$ (8) Å, $b = 7.804(4)$ Å, $c = 6.106$ (3) Å, $\alpha = 79.00$ (4)°, $\beta = 122.60$ (4)°, and $\gamma = 116.47$ (4)° with $Z = 2$. The high-temperature phase (I) is orthorhombic $Pcan$ with $a = 17.589$ (7) Å, $b = 7.296$ (3) Å, and $c = 6.365$ (3) Å with $Z = 4$. Phase II contains bibridged linear chains of $Cu_2Cl_6^{2-}$ dimers; phase I contains tribridged chains of $(CuCl_3)_n^{n-}$ stoichiometry. The chain axes are coincident in the two phases. The $(CH_3)_2CHNH_3^+$ (IPA) ions are ordered in phase II but disordered in phase I. The ^1H NMR line width narrows at T_{th} to 4.5 G for the N-deuterated salt, consistent with a dynamic twofold disorder of the IPA ion. Single-crystal EPR data at 78 K are consistent with the structure of phase II. Susceptibility studies show the phase II linear chain consists of antiferromagnetically coupled dimers with an $S = 0$ ground state while the phase I linear chain is ferromagnetically coupled. A sharp break in the susceptibility occurs at T_{th}, indicating the existence of a first-order phase transition. Deuteration of the NH_3^+ moiety *raises* T_{th} by 10 °C, indicating the presence of weaker N–H···Cl hydrogen bonds in phase I. This weaker hydrogen bond allows the copper(II) ions to *increase* their coordination and form the more compact tribridged chain. Concomitantly, the barrier to rotation is lowered, and the cation becomes disordered.

The most easily detected solid-state phase transitions are those in which the color of the crystals change as the temperature is either raised or lowered. This thermochromism can be of two types. Continuous thermochromism is characterized by a gradual change in crystal color and is not indicative of a phase transition. On the other hand, discontinuous thermochromic phase transitions are evidenced by a dramatic change in crystal color at some temperature (T_{th}) and are symptomatic of a sudden change in crystal properties at T_{th}. In transition-metal complexes, thermochromism is a sign of a change in ligand coordination. These transformations may include alterations in atom connectivity, or they may only represent geometric distortions in the preexisting chemical entities.

Mori and co-workers[1] report studies on halogen-substituted dinitrodiamminecopper(II) compounds showing this thermo-

chromism to be a result of coordinate isomerization of the ambidentate NO_2 ligand. At low temperatures, the pure dinitrodiamminecopper(II) is purple and contains N-bonded NO_2 groups, while at high temperatures the green complexes contain O-bonded NO_2 ligands. As halides are doped into the salt, T_{th} is lowered until some critical halide concentration is reached and the green complexes are stabilized at all temperatures.

Various bis(*N*-alkylethylenediamine)copper(II) salts are also thermochromic.[2–5] The red, low-temperature phase contains

(1) Y. Mori, H. Inoue, and M. Mori, *Inorg. Chem.*, **14**, 1002 (1975).

(2) A. B. P. Lever, E. Mantovani, and J. C. Donini, *Inorg. Chem.*, **10**, 2424 (1971).

(3) L. Fabbrizzi, M. Micheloni, and P. Paoletti, *Inorg. Chem.*, **13**, 3019 (1974).

(4) J. R. Farraro, L. J. Basile, L. R. Garcia-Ineguez, P. Paoletti, and L. Fabbrizzi, *Inorg. Chem.*, **15**, 2342 (1976).

(5) J. R. Ferraro, L. Fabbrizzi, and P. Paoletti, *Inorg. Chem.*, **16**, 2127 (1977).