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Geometry of Transition Metal Complexes with Ethylene or Allyl Groups as the Only Ligands

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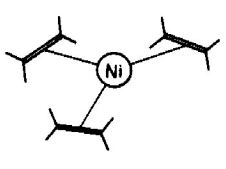
A theoretical study of M(ethylene)$_n$ (n = 2–4, M = Ni; n = 6, M = Cr) is carried out, with implications for the related M(allyl)$_n$ complexes discussed. The analysis relies on symmetry arguments supported by semiempirical molecular orbital calculations. $(C_2H_4)_3Ni$ is found to prefer a planar (2) to an upright (3) geometry, as a consequence of a symbiotic effect of σ and π bonding. $(C_2H_4)_2Ni$ shows little preference for a D_{2d} structure 8 over the D_{2h} 7. Three geometries of $(C_2H_4)_4Ni$—the quasicubical D_{2d} 11, the quasidodecahedral D_{2d} 12, both tetrahedrally coordinated, and the square-planar coordinated, upright D_{4h} structure 13—were studied, along with their modes of interconversion. The quasidodecahedral structure has the lowest energy, though close H-H contacts begin to obscure the true energetics of the various geometries. Existing complexes are with bidentate ligands which allow only the quasicubical geometry. It is suggested that ligands prepared for the quasidodecahedral coordination should be explored. Several octahedrally coordinated $(C_2H_4)_6Cr$ structures, of T_h, D_{3d}, T_d, and D_3 symmetry were also analyzed. In all systems the discrimination between various geometries rests on the symmetry-specific back-bonding of the ethylene ligand π^* levels. Making use of the analogous symmetry properties of a π-allyl ligand, we can construct a qualitative theory of the geometries of M(allyl)$_n$ systems, predicting significant rotational barriers for $(allyl)_2Ni$ and -Pt, and quasi-trigonal-prismatic, upright structures for $(allyl)_3Co$ or -Rh. The electronic structure and geometry of CrO_8^{3-} is also examined, with the finding of a low-energy pass from the equilibrium quasidodecahedral conformation to a D_4 upright structure.

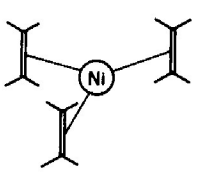
The recent synthesis of tris(ethylene)nickel(0)[2] was the primary stimulus for the present study. In this complex we are provided with a system which—due to its symmetry and the simplicity of the ligands—may serve as a model for a class of organometallic compounds where only CC double bonds coordinate to a transition metal. We will concentrate our investigations on the interaction of the π-electron systems of the ligands with the d electrons of the transition metal and the consequences thereof on the geometry of the complex. Simple molecular orbital (MO) arguments will be employed. After having worked out our arguments in some detail for the above-mentioned model system we will probe them by varying the number of ethylene ligands and the central atom and finally by testing them on complexes with other π-bonded ligands.

MO Treatment of Tris(ethylene)nickel(0)

Since our prime concern is in understanding the qualitative features of the molecular orbitals for various geometries of our model system $(C_2H_4)_3Ni$ (1), we start out by choosing various "reasonable" structures of high symmetry and constructing the corresponding molecular interaction diagrams. A trigonal-planar arrangement (2) of the three ligands around the central atom has been suggested,[2] in analogy to the structure assumed for (*all-cis*-1,5,9-cyclododecatriene)nickel(0)[3] and found in an X-ray diffraction study of tris[bicyclo[2.2.1]-heptene]nickel(0).[4,5] Another conceivable structure of 1 is also basically trigonal in coordination, but has the CC double bonds perpendicular to the coordination plane (3).



2, D_{3h}



3, D_{3h}

Both structures are of symmetry D_{3h} and finding a distinctive label for them exhibits a characteristic dilemma in dealing with coordination compounds where the ligands have additional orientational degrees of freedom. In the case at hand a distinction between the two structures could be attained by viewing the ethylene as a bidentate ligand. Compound 2 would then be planar hexagonal and 3 trigonal prismatic. But such a bidentate classification obscures the basic electronic features of metal–olefin bonding. Each ethylene carries a single donor orbital, its π orbital, not two. The primary coordination is set by the ligand donor orbitals. We have found it useful to specify the primary coordination (trigonal for 2 and 3) and supplement the incomplete geometrical description by group theoretical or colloquial descriptors. In this case both structures are D_{3h}, so let us call 2 "planar" and 3 "upright."

Although recent quantitative treatments show a somewhat more complicated bonding situation,[6-8] the metal–olefin bond is essentially well described by the Dewar–Chatt–Duncanson scheme.[9] Accordingly we consider electron donation from the π orbital of ethylene to an acceptor orbital at the metal and back-donation from the metal to the π^* orbital of the ethylene. The simplest interaction diagram, including only the 3d orbitals of the transition metal and the π and π^* levels of the three ethylene ligands, is shown in Figure 1 for the limiting structures 2 and 3.

The ethylene π levels subduce the same D_{3h} representations in 2 as in 3. Thus they should contribute in roughly equal measure to the bonding in the two geometries. The differentiation of 2 and 3 that does occur is due entirely to

(1) To whom correspondence should be addressed.
(2) K. Fischer, K. Jonas and G. Wilke, *Angew. Chem.*, 85, 620 (1973); *Angew. Chem., Int. Ed. Engl.*, 12, 565 (1973).
(3) K. Jonas, P. Heimbach, and G. Wilke, *Angew. Chem.*, 80, 1033 (1968); *Angew. Chem., Int. Ed. Engl.*, 7, 949 (1968).
(4) C. Kruger and Y.-H. Tsay, quoted in ref 2 and 5.
(5) K. Fischer, K. Jonas, P. Misbach, R. Stabba, and G. Wilke, *Angew Chem.*, 85, 1002 (1973); *Angew. Chem., Int. Ed. Engl.*, 12, 943 (1973).
(6) N. Rosch, R. P. Messmer, and K. H. Johnson, *J. Amer. Chem. Soc.*, 96, 3855 (1974).
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(8) J. H. Nelson, K. S. Wheelock, L. C. Cusachs, and H. B. Jonassen, *Chem. Commun.*, 1019 (1969); *J. Amer. Chem. Soc.*, 91, 7005 (1969); K. S. Wheelock, J. H. Nelson, L. C. Cusachs, and H. B. Jonassen, *ibid.*, 92, 5110 (1970); K. S. Wheelock, J. H. Nelson, J. D. Kelly, H. B. Jonassen, and L. C. Cusachs, *J. Chem. Soc., Dalton Trans.*, 1457 (1973).
(9) (a) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, 18, C79 (1951); (b) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2339 (1953).

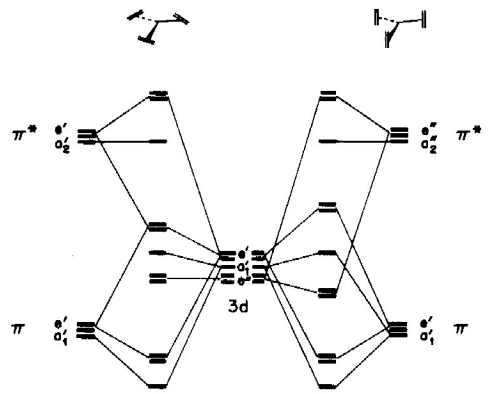
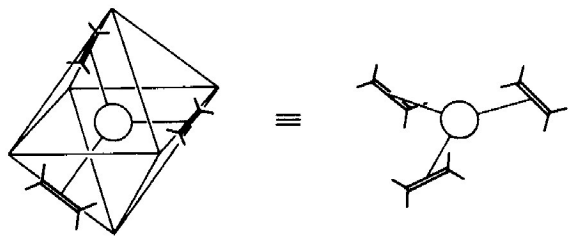


Figure 1. Schematic interaction diagram for $(C_2H_4)_3Ni$ in planar and upright geometries.

the π^* orbitals. In **2** these transform as $e' + a_2'$; in **3**, as $a_2'' + e''$. The degenerate orbitals find partners in the set of 3d functions of the metal. In the case of **2** the π^* e′ orbital stabilizes the metal $xy, x^2 - y^2$ set already destabilized by interaction with olefin π levels; in **3** the π^* e″ interacts with the corresponding symmetry set of metal xz and yz. It is not immediately clear which interaction is greater.

To gain some quantitative insight into the difference between **2** and **3**, as well as to examine a range of conformations spanning these two extremes of geometry, we carried out a series of molecular orbital calculations. A single motion taking **2** into **3**, while maintaining D_3 symmetry, was studied. This corresponds to rotating each ethylene subunit by the same angle and in the same sense around its coordination axis. The angle θ ranges from 0° in **2** to 90° in **3**. An interesting intermediate way point is the geometry **4**, θ = 54° 44′, which corresponds to a quasioctahedral (bidentate) coordination.



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The molecular orbital calculations which we used were of the extended Huckel type.[10] To estimate the one-electron Hamiltonian matrix elements for Ni we first performed a charge-iterative calculation for the intermediate geometry **4**. The distance from the Ni atom to the midpoints of the CC bonds was taken to be 2.0 Å, giving a Ni–C distance of 2.11 Å, which is very close to those found by X-ray diffraction of (*all-trans*-1,5,9-cyclododecatriene)nickel(0)[11] and bis(1,5-cyclooctadiene)nickel(0).[12] The ligands were taken in the equilibrium geometry of the free ethylene molecule and oriented with their plane perpendicular to the coordination direction. The basis set of valence atomic orbitals for Ni consisted of 3d, 4s, and 4p. Single Slater-type orbitals were used for the 4s and 4p functions, while the 3d wave function

Table I. Parameters Used in the Calculation of Model Nickel–Ethylene Complexes

Orbital	Orbital exponent 1	Orbital exponent 2	H_{ii}, eV
3d	5.75 (0.5683)[a]	2.00 (0.6292)[a]	−13.2
4s	1.50		−10.7
4p	0.86		−6.3

[a] Numbers in parentheses indicate the coefficient of the member of the contracted 3d function.

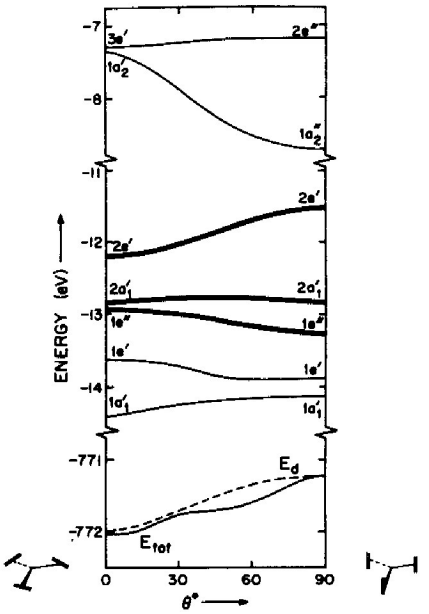

Figure 2. Individual energy levels (top) and total energy (bottom) for $(C_2H_4)_3Ni$ as a function of rotation of the ethylenes around the coordination axis. The darker lines are primarily metal 3d in composition. The dashed E_d line is the total energy of the ten electrons in just those 3d levels alone. Note two breaks in the energy scale. The numbering of the levels (1 e′, 2 e′ etc.) refers only to the levels in the diagram.

was taken as a contracted linear combination of two Slater-type wave functions. The various orbital exponents were taken from the work by Richardson, *et al.*[13] A quadratic charge dependence was assumed for the H_{ii} of nickel.[14] The H_{ii} for carbon and hydrogen were kept fixed; their values as well as the orbital exponents were the same as used in previous work.[10] The nickel parameters along with the final self-consistent H_{ii} values are summarized in Table I. For comparison we mention the energies of the π and π^* orbital of ethylene as obtained from a separate calculation of this molecule: the π energy is −13.2 eV; the π^* energy, −8.2 eV. All other calculations mentioned in this paper will be extended Huckel calculations using these parameters, unless specified otherwise.

The energy levels of $Ni(C_2H_4)_3$ as a function of θ were then computed by a simple noniterative extended Huckel calculation, using the parameters of Table I. Figure 2 shows our results. We plot the total energy and only those valence orbitals considered in Figure 1. We recognize that the perturbation arguments leading to these interaction diagrams were essentially correct. Above the levels originating from the π orbitals of ethylene (1 a_1' and 1 e′) we find the Ni 3d levels (1 e″, 2 a_1', and 2 e′). These levels are filled with a

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

(11) (a) H. Dietrich and H. Schmidt, *Naturwissenschaften*, 52, 301 (1965); H. Dietrich, *Acta Crystallogr., Sect. B*, 28, 2807 (1972); (b) D. J. Brauer and C. Kruger, *J. Organometal. Chem.*, 44, 397 (1972).

(12) H. Dierks and H. Dietrich, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, 122, 1 (1965).

(13) (a) J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, 36, 1057 (1962); (b) J. W. Richardson, R. R. Powell, and W. C. Nieuwpoort, *ibid.*, 38, 796 (1963).

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total of 16 valence electrons.[15] The lowest unoccupied molecular orbitals (1 a_2' and 3 e'; 1 a_2'' and 2 e'') are mainly of ethylene π^* character.

Structure **2** is favored over **3** by 0.74 eV. The rotational potential energy curve exhibits a noticeable hump at $\theta \approx 30°$. When we sum the energy of the d orbitals alone (dashed line in Figure 2), this hump is not apparent. This indicated to us that the perturbation causing the uneven energy curve was of steric origin. Indeed, in the course of the rotation we studied there occurs a close H-H contact of 1.92 Å at $\theta = 37°$. Were the ethylenes to have an electronic reason for preferring that geometry (which they do not), they would surely find a way to avoid the short H-H contact by bending the hydrogens away or by some other mode of relaxation. The mild steric difficulty exhibited here is but a harbinger of the troubles to be encountered when we pack more ethylenes around a metal atom.

What makes the "planar" configuration **2** more stable than the "upright" structure **3**? If one accepts the hypothesis that the interaction leading to σ bonding is equally strong in both cases, the difference has to come from the mechanism leading to the formation of π bonds, *i.e.*, the different role of the ethylene π^* orbitals. Let us, for the sake of the argument, switch on these two interactions consecutively in both structures and neglect all orbitals whose bonding character (σ *vs.* π) is unchanged in both geometries. This is done in Figure 3. We see that the Ni e' level is being pushed up due to σ interaction. In structure **3** it stays there because there is no π^* level of appropriate symmetry to interact with it. In case **2**, however, the Ni e' level is subject to a strong π interaction with an ethylene π^* orbital of the same symmetry, as a consequence of which it gets pushed down again. In this geometry the Ni e'' orbital has no interaction partner and stays at the same energy, whereas in **3** it shifts down due to interaction with a π^* orbital. But this shift is smaller than the "π" shift of the e' orbital in **2** because the e'' orbital is further away in energy from the ethylene π^* orbital than the e' orbital that has been lifted due to the σ interaction. Close inspection of Figure 2 confirms these statements. The movement of the Ni e' orbital upon rotation of the ethylene ligands dominates over that of the Ni e'' orbital. Thus we can rationalize the calculated preference for the "planar" structure **2**.

The importance of back donation can also be seen through an analysis of the various orbitals. As one goes from the "planar" to the "upright" structure, the charge on Ni, according to a Mulliken population analysis, decreases from 0.839+ to 0.624+. In structure **2** the occupation of each back-donating Ni orbital $x^2 - y^2$ and xy is 1.73 charge units, whereas in structure **3** we find 1.81 electrons in xz and yz. Since all other metal orbital occupations stay approximately equal, these differences make up the largest part of the charge differential on Ni mentioned above. Consistent with this decreasing back-donation as one goes from **2** to **3** is the overlap population of the CC bond. It increases from 1.266 to 1.312. The corresponding value for free ethylene is 1.304, which leads one to predict, not unexpectedly, a somewhat elongated CC bond in structure **2**.

One way to probe these arguments concerning the relative importance of the back donation is to shift the H_{ii} of nickel to higher energy in order to bring the 3d levels closer to the ethylene π^* orbital. A calculation, using a shift of 2.0 eV, confirmed the above analysis as it increased every effect attributed to the different role of back-bonding. The relative stability of structure **2** over **3**, for instance, increased to 1.25 eV. A corollary of this numerical experiment is that if the ethylene ligands are substituted by π-electron acceptors, then the conformational preference for the "planar" geometry **2** should be increased.

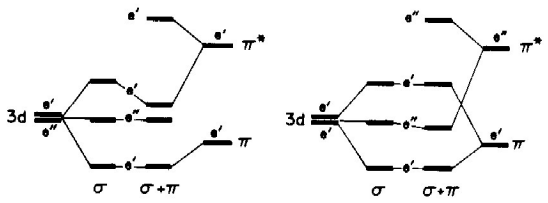


Figure 3. Schematic decomposition of π bonding in $(C_2H_4)_3Ni$. At left is the planar structure **2**; at right, the upright structure **3**. The orbital interactions are analyzed in stages. First, interaction with the ethylene π levels is turned on, in the columns marked σ. Second, the mixing with the ethylene π^* levels is added in, in the columns marked $\sigma + \pi$.

There is yet another way of looking at the preferred orientation of the ethylenes, which makes a connection to a recent theoretical discussion of bonding in trigonal-bipyramidal transition metal complexes.[16] It has been predicted that for d^{10} a π acceptor located at an equatorial position will prefer to have its acceptor orbital in the equatorial plane, as in **5**. This orientation is favored because the metal d orbitals in the equatorial plane are somewhat hybridized with the corresponding metal p orbitals. This increases their directional properties, leading to a better overlap with the π-acceptor orbital than the d orbitals perpendicular to the equatorial plane would offer. This argument is also valid for a trigonal-planar complex. The acceptor orbital of ethylene is, of course, the π^* orbital. Qualitatively then we would expect an orientation analogous to **5**, namely, **6**, which is what we have concluded above, from a different starting point.

5 **6**

Although there is as yet no published X-ray diffraction study on tris(ethylene)nickel(0), structures are known for several other nickel(0)–olefin compounds which confirm our analysis. The case of a single ethylene is illustrated by the structure of bis(*tert*-butyl isocyanide)(tetracyanoethylene)-nickel(0), where the CC bond is found to lie in the coordination plane.[17] A perfect planar structure has also been found for bis(ethylene)(tricyclohexylphosphine)nickel(0).[18] The "planar" arrangement analogous to **2** was found in tris[bicyclo[2.2.1]heptene]nickel.[4] Molecular models suggest this structure for (*all-cis*-cyclododecatriene)nickel(0). There is also some chemical evidence which suggests that (*all-trans*-cyclododecatriene)nickel(0) is less stable than its all-cis isomer.[3] The CC double bonds in the former macrocyclic ligand cannot all lie within the coordination plane, due to conformational constraints. The observed twist angle is 32°.[11b] Neglecting the various interactions within the ligand, the stability of the all-cis isomer relative to the all-trans is in

(15) C. A. Tolman, *Chem. Soc. Rev.*, 1, 337 (1972).

(16) A. Rossi and R. Hoffmann, to be submitted for publication. See also R. Hoffmann, J. M. Howell, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 94, 3047 (1972).

(17) J. K. Stalick and J. A. Ibers, *J. Amer. Chem. Soc.*, 92, 5333 (1970).

(18) C. Kruger and Y.-H. Tsay, *J. Organometal. Chem.*, 34, 387 (1972).

accord with our findings (Figure 2). In palladium chemistry there are several compounds which are relevant to our studies. A structure of tris(dibenzylideneacetone)palladium(0)[19a] shows trigonal coordination of the metal atom by three ethylenes, one from each ligand. The average twist angle is 18°. In tris(dibenzylideneacetone)dipalladium(0) each palladium atom is still trigonally coordinated, but in this more constrained structure the twist angles are 9, 17, 21, 37, 67, 80°.[19b]

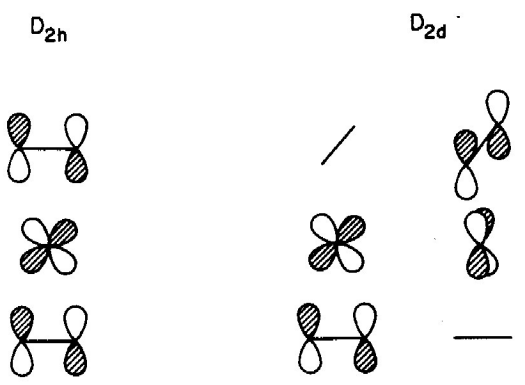
In summary we emphasize that it is the relative importance of the π back-bonding which determines the structure of tris(ethylene)nickel(0). Back-donation is maximized for the planar structure **2** due to a peculiar symmetry-allowed interplay with σ bonding as both types of bonding share metal orbitals of the same symmetry.

Geometry of Bis(ethylene)nickel(0)

We proceed to test our understanding of the bonding situation in olefin-nickel complexes by varying the coordination number of nickel. Consider two ethylenes linearly coordinated to a central nickel atom. Again we can distinguish two extreme structures, **7** and **8**, now of differing symmetry, D_{2h}

7, D_{2h} **8**, D_{2d}

and D_{2d}, respectively. The coordination axis is taken as the z axis, and the lower, fixed ethylene CC bond defines the x axis. As before, we compare the two structures by drawing the orbital interaction diagrams appropriate to each symmetry (Figure 4). These diagrams take into account overlap as well as symmetry arguments. The σ bond is formed through the z^2 orbital on the metal and is expected to be equally strong in both structures. The two metal orbitals in the xy plane, x^2-y^2 and xy, are nonbonding in **7** and **8**. The remaining metal orbitals xz and yz participate in back-bonding in structure **8** (D_{2d}), whereas in **7** (D_{2h}) only the xz orbital contributes, the yz orbital being nonbonding. However, in the latter case the overlap with the π^* orbitals involves the π^* levels of both ligands. This is shown in **9** and **10**.



9 **10**

It is in fact an interesting general question whether interaction **9** is equivalent to the net sum of both interactions in **10**. If we denote the ethylene orbitals as π_1^* and π_2^*, the metal orbitals xz or yz as d, and the interaction of a single π^* level with d as β

$$\langle d|H'|\pi_i\rangle = \beta$$

then the interaction in **9** is

$$\langle(1/\sqrt{2})(\pi_1^* + \pi_2^*)|H'|d\rangle = \sqrt{2}\beta$$

whereas in **10** we have two separate interactions, each of strength β.

We now must distinguish two limiting cases. In the first π^* and d are far apart in energy, so that nondegenerate perturbation theory is applicable. In that case the stabilization of the two electrons in the d level of **9** is given in second order by

$$\Delta E = 2\frac{(\sqrt{2}\beta)^2}{E_d - E_{\pi^*}} = \frac{4\beta^2}{\Delta E}$$

assuming the simplest perturbation theory without overlap, and neglecting π_1^*-π_2^* interaction. This ΔE is precisely the same that would be obtained for the four electrons in **10**.

The second case is that where d and π^* are close to each other in energy. In that case degenerate perturbation theory leads to a first-order correction of $2\sqrt{2}\beta$ for **9** and 4β for **10**. Interaction **10** is now preferred. We will return to a discussion of this problem below.

The results of an extended Huckel calculation as a function of ethylene rotation are shown in Figure 5. The parameters chosen are the same as in previous calculations on $Ni(C_2H_4)_3$ (Ni parameters from Table I, Ni–center of CC bond = 2.0 Å etc.).

The angle of rotation is measured from the D_{2h} structure. Note that the π level 1 b_{1u}, nonbonding in **7** with an energy −13.15 eV, lies above the metal xz level (1 b_{2g}) which has been lowered due to back-bonding. Otherwise the orbital energies behave as anticipated, giving rise to virtually no rotation barrier. The quasitetrahedral D_{2d} structure **8** is favored by only 0.07 eV (1.5 kcal/mol). There is almost no change in the charge on Ni (0.23+ in **7** *vs.* 0.28+ in **8**) nor in the overlap population of the CC bonds (1.278 in **7** *vs.* 1.272 in **8**).

The reason for the lack of discrimination in total energy between **7** and **8** is clear. The σ bonding is approximately equal, and there are no significant steric effects. Since π^* and metal d orbitals are well separated in energy, the perturbation analysis given above shows that the π-back-bonding effects also do not differentiate the D_{2d} and D_{2h} structures. We have probed in a numerical experiment the effect of reduction in the 3d–π^* energy separation. As expected, it produces an increasing favoring of the D_{2d} structure, through interaction **10** being more stabilizing than **9**.

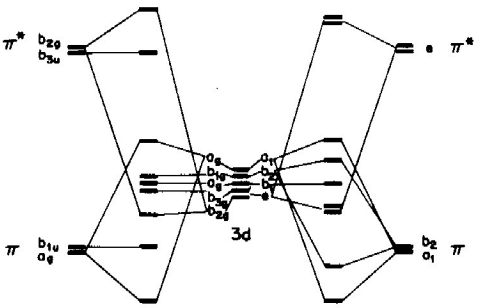


Figure 4. Interaction diagram for $(C_2H_4)_2Ni$. The D_{2h} structure **7** is shown at left; the D_{2d} **8**, at right.

(19) (a) M. C. Mazza and C. G. Pierpont, *Inorg. Chem.*, 12, 2955 (1973); (b) C. G. Pierpont and M. C. Mazza, *ibid.*, 13, 1891 (1974).

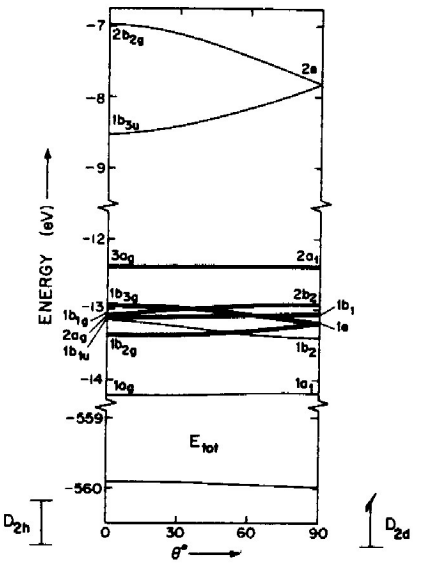


Figure 5. Calculated energy levels (top) and total energy (bottom) for $(C_2H_4)_2Ni$ geometries as a function of torsional angle. The darker lines are primarily of 3d character. Note two breaks in the energy scale. The numbering of the levels (1 a_g, 2 a_g etc.) refers only to the levels in the diagram.

Bis(ethylene)nickel(0) has not yet been synthesized, but there are compounds of Ni(0) where the metal atom may be coordinated to just two CC double bonds. The first ones synthesized were bis(acrylonitrile)nickel(0) and bis(acrolein)-nickel(0).[20] No X-ray diffraction studies on these compounds have been carried out, but from chemical and spectroscopic evidence a linear structure has been deduced, with simple metal-olefin coordination.[20] However this structural assignment has been disputed, and it appears that in the solid state Ni is probably further coordinated through the nitrogen lone pairs of other ligands.[21] A simple MO treatment of bis(acrylonitrile)nickel, in a structure analogous to 7, has been reported.[22a] The acceptor properties of the cyano group would lower the π^* orbital of the olefin, which might be the reason for the enhanced stability of the acrylonitrile complex. We should also mention a molecular orbital study of the coordination of two acetylenes to a transition metal atom.[22b]

Tetrakis(ethylene)nickel(0)

Nickel(0) coordinated to four CC double bonds satisfies the 18 electron rule. The fact that this structure is a particularly stable one may also be concluded from the number of known compounds of this type.[21b,23] The two primary geometries for four-coordination are tetrahedral and square planar. For a d^8 transition metal complex a square-planar arrangement is usually favored, whereas for a d^{10} complex a tetrahedral structure is usually found. We will consider both primitive coordination geometries. For each, one can further distinguish two conformations of high symmetry. For the tetrahedral coordination one has a "quasicubical" structure **11** and a "quasidodecahedral" **12**, both of idealized D_{2d}

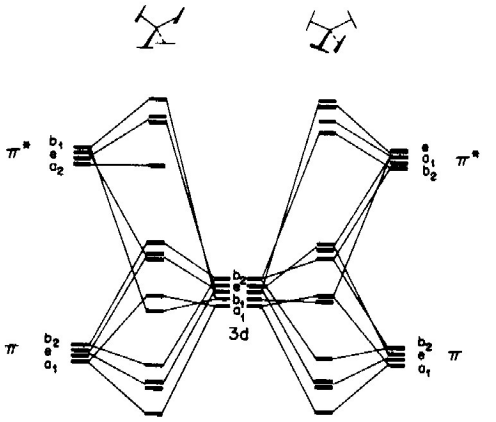


Figure 6. Interaction diagrams for quasicubical, **11**, and quasidodecahedral, **12**, geometries of $(C_2H_4)_4Ni$, both of D_{2d} symmetry.

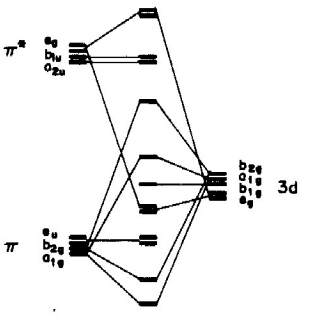
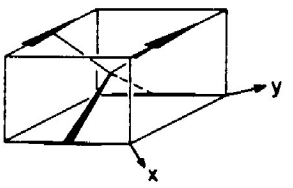


Figure 7. Interaction diagram for the upright geometry, **13**, of $(C_2H_4)_4Ni$.



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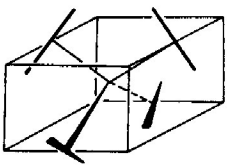
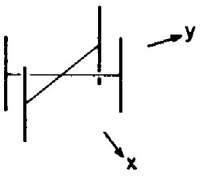


12

symmetry. The trivial descriptors focus on the polyhedra generated by the carbons. Similar to the three-coordinate case discussed at the beginning, two possible extreme orientations of the ethylenes in the square-planar type are "upright," **13**, and "planar," **14**, both of D_{4h} symmetry.



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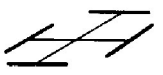


14

As before, the ethylene planes are taken perpendicular to the coordination axis, with a metal–CC center distance of 2.0 Å. Note the somewhat unconventional coordinate system for **13**, introduced to follow a motion relating **13** and **12** which we will describe below. Structure **14** may be eliminated on steric grounds. With normal ethylene units it leads to two H-H contacts of 1.09 Å for every pair of vicinal ethylenes. Interaction diagrams for the remaining structures are shown in Figures 6 and 7.

Let us first analyze and compare the bonding in the tetrahedral structures **11** and **12**. If we momentarily neglect π bonding and adopt as a working hypothesis equally strong σ bonding, we expect the familiar splitting of metal orbitals

(20) (a) G. N. Schrauzer, *J. Amer. Chem. Soc.*, 81, 5310 (1959); (b) G. N. Schrauzer, *Chem. Ber.*, 94, 642 (1961); (c) H. P. Fritz and G. N. Schrauzer, *Chem. Ber.*, 94, 650 (1961).

(21) (a) D. P. Tate, A. A. Buss, J. M. Augl, B. L. Ross, J. G. Graselli, W. M. Ritchey, and F. J. Knoll, *Inorg. Chem.*, 4, 1323 (1965); (b) G. N. Schrauzer, *Advan. Organometal. Chem.*, 2, 1 (1965).

(22) (a) D. A. Brown and G. N. Schrauzer, *Z. Phys. Chem. (Frankfurt am Main)*, 36, 1 (1963); (b) E. M. Shustorovich, G. I. Kagan, and G. M. Kagan, *Zh. Strukt. Khim.*, 12, 697 (1971).

(23) B. Bogdanovic, M. Kroner, and G. Wilke, *Justus Liebigs Ann. Chem.*, 693, 1 (1966).

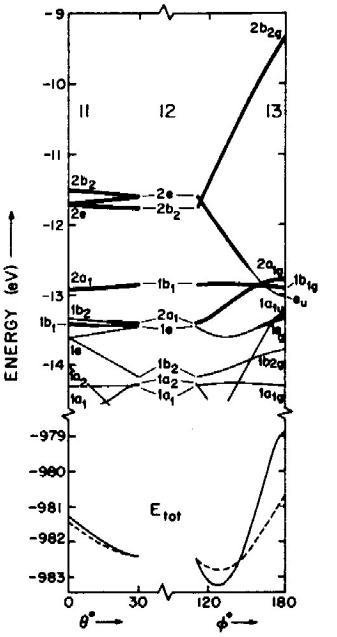
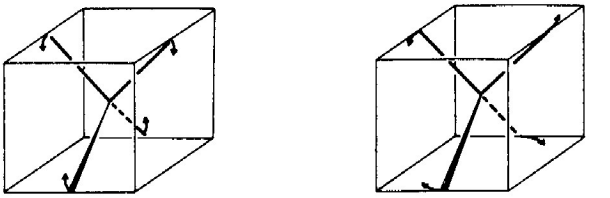


Figure 8. Computed energy levels (top) and total energy (bottom) of structures **11** (quasicubical), **12** (quasidodecahedral), and **13** (upright) of $(C_2H_4)_4Ni$. The interconversion of **11** and **12** is by a 30° twist of each ethylene, as described in the text. The interconversion of **12** and **13** occurs by a squashing mode, with ϕ the angle between the coordination directions. The darker lines are primarily 3d, and where lines are shaded they change in character from 3d (darker) to ligand (lighter). The solid E_{tot} curve is the total molecular energy as a function of the distortion, while the dashed line is the total energy of the electrons in only those orbitals which are primarily 3d or ligand π. Note the break in the energy scale.

in a tetrahedral field: z^2 and x^2-y^2 forming a twofold degenerate level below (a_1, b_1 in the reduced D_{2d} symmetry), xy, xz, and yz triply degenerate above (b_2, e). These levels then are split further according to the symmetries of the available π^* levels. Inspection of Figure 6 leads to a prediction of the following level order for the Ni d orbitals: $b_2(xy) > e(xz, yz) > a_1(z^2) > b_1(x^2-y^2)$ for structure **11** and $e(xz, yz) \simeq b_2(xy) > b_1(x^2-y^2) > a_1(z^2)$ for structure **12**. As in the case of three ligands, one would expect the downward shifts of the "upper" metal levels, metal-ligand σ antibonding, to be more pronounced because they are energetically closer to the π^* levels. A comparison of the the two interaction diagrams in Figure 6 shows that in structure **11** two "upper" and one "lower" metal d orbitals are affected by π back-bonding whereas in structure **12**, all three "upper" levels are pushed down, as well as one of the "lower" metal orbitals. One therefore might expect the quasidodecahedral structure **12** to be somewhat more stable than the quasicubical structure **11**.

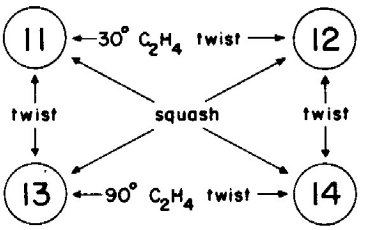
The characteristic sharing of metal orbitals between σ and π bonding is completely absent in the square-planar complex **13** (see Figure 7). In addition one expects a large destabilization of one metal orbital pointing toward the ligands. This is in our axis convention[24] the xy, b_{2g} orbital. Structure **13** should therefore be less stable than either **11** or **12**.

We turn to a discussion of the modes of interconversion of the various geometries. A tetrahedral arrangement is transformed into a square-planar one by distortion along either component of an e normal mode.[25] These motions may be colloquially described as "squashing" and "twisting" and are shown below. Both maintain D_{2d} symmetry.



"squashing" "twisting"

At first sight the interconversion of **11** and **12** would appear to involve a 90° rotation of each ethylene around the coordination axis. In fact the symmetry is so high that a simpler motion suffices--a rotation of each ethylene, in the same sense, by 30° around the coordination axis. The reader should convince himself of this point with models. The intermediate symmetry is D_2. Putting these modes together, we can summarize one set of interconversions of the various extreme geometries by the diagram



Our MO analysis did not explore all of these modes. For steric reasons, detailed above, paths leading to **14** are unproductive. We did study in some detail the 30° collective ethylene twist interconverting quasicubical and quasidodecahedral geometries, as well as the squashing distortion from the latter to the upright geometry **13**. The parameters of the calculation were again the same as for $Ni(C_2H_4)_3$. The resulting orbital energies are plotted in Figure 8. The horizontal coordinate in this complex figure covers two different rotations: that of the ethylene units (θ ranging from 0° in **11** to 30° in **12**) and that of the coordination axes in the course of the squashing mode (ϕ here is the angle between two "opposite" metal-CC bond directions). The range of ϕ is from 109° 28′ in **12** to 180° in **13**).

The orbital energy ordering clearly shows the basic features of the primary coordination–tetrahedral or square planar. The relative stability of the various structures is **12** > **11** > **13**. The influence of π bonding, along the lines analyzed in the discussion of Figure 6, is discernible in both the detailed level ordering and the general stability trend. But now the influence of steric factors cannot be avoided. With four ethylenes crowded around a metal atom there is no geometry which can escape destabilizing nonbonded overlaps. With our constraint to a planar ethylene geometry the closest H-H contacts are 1.54 in **11**, 1.85 in **12**, and 1.52 in **13**. We can see a consequence of this steric crowding in the appearance in Figure 8 of a high-lying orbital with ethylene σ character (1 a_2 or 1 a_{1u}). In an attempt to separate the valence contribution to the total energy from steric repulsion we can compare the sum over the filled "valence" level

(24) Our coordinate system is unconventional, in that it places the x and y axes between the ligands. We use the standard D_{4h} character table (*e.g.*, E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955, p 327), defining σ_v to contain the x and y axes and σ_d to pass between these axes and contain the coordination lines.

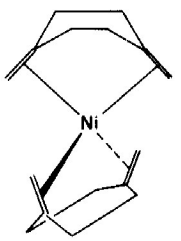
(25) The normal modes of vibration of a tetrahedral XY_4 system are described by G. Herzberg in "Molecular Spectra and Molecular Structure," Vol. II, Van Nostrand, Princeton, N. J., 1945, p 100. See also E. L. Muetterties and L. J. Guggenberger, *J. Amer. Chem. Soc.*, 96, 1748 (1974); R. Hoffmann, R. W. Alder and C. F. Wilcox, Jr., *ibid.*, 92, 4992 (1970).

energies (mainly ethylene π or metal character) with the sum of all levels. This is done at the bottom of Figure 8. The relative order of stability remains unchanged although the differences are decreased. Nevertheless, our total energy curves and the conclusions drawn therefrom must be treated with caution. We do not know if the extended Huckel procedure provides a proper balance of steric and electronic factors, nor did we allow the ligands the opportunity to change their geometry in response to the steric strain.

The absolute energy minimum is obtained for the quasidodecahedral structure **12** at an angle ϕ of 128° between the coordination directions to opposite ethylene subunits. Part of the energy decrease with the opening up of the tetrahedral angle is of steric origin; part of it is due to a more efficient σ bonding before the destabilized 2 b_{2g} level starts to dominate the energy curve.

There are no simple ethylene ligands among the many known complexes where Ni(0) is coordinated to four double bonds. The most common ligands are 1,5-cyclooctadiene, duroquinone, cyclooctatetraene, and norbornadiene.[21b,23,26,27] The nature of these ligands is such that two double bonds are held parallel, and the possible steric interactions between two ethylene subunits in this arrangement are absorbed in the ligand geometry. Such bidentate ligands enforce either the quasicubical geometry **11** or the planar **13**. Despite the large number of these compounds there are only a few X-ray structure analyses. Bis(1,5-cyclooctadiene)nickel(0),[12] (cyclooctadiene)(duroquinone)nickel(0),[28] and bis(duroquinone)nickel(0)[29] all have the quasicubical structure **11**, confirming our analysis.[30]

Though we predict that the quasidodecahedral structure **12** has the lowest energy among the alternatives examined, no nickel–olefin complex with that geometry has been identified. If binding two ligands together is a good strategy to bypass some of the steric difficulties of this geometrical arrangement, then complexes of 1,4-dimethylenecyclohexane, **15**, and penta-1,4-diyne, **16**, might be synthetic goals.



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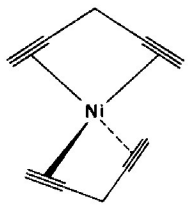
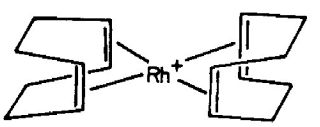


16

Insofar as the arguments we have deduced are based on symmetry considerations and not the detailed position of the transition metal levels our conclusions may be transferred to complexes with a different central metal atom. Of special interest would be compounds with two electrons less than Ni, *i.e.*, d^8 systems. Bis(1,5-cyclooctadiene)iron has recently been synthesized,[31] but structural details are not yet available. It is appropriate to note here the cationic Ir(I) and Rh(I) complexes with two norbornadienes or two cyclooctadienes[32-34] (*e.g.*, **17**) and the Rh(acac)$(C_2H_4)_2$ structure **18**.[35] For the former an all-upright structure, analogous to **13**, has been suggested.[32-34] For the latter the upright orientation of the ethylenes has been established in a crystallographic study.[35b]



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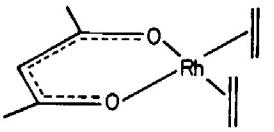
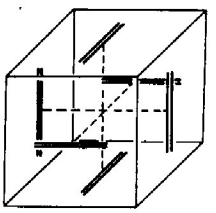


18

Hexakis(ethylene)chromium

We conclude our treatment of ethylene–transition metal model complexes with the analysis of hexakis(ethylene)chromium(0), **19**. Cr has been chosen instead of Ni in order to obey the 18-electron rule and to use a transition metal whose extended Huckel parameters are known.[5] But the molybdenum or tungsten analogs are more likely to exist as a consequence of their larger covalent radii. The number of possible structures with fairly high symmetry is, of course, even larger than in the previous case. The highest symmetry attainable is T_h, for an octahedrally coordinated structure, the ethylene ligands lying in the planes of a cube as shown in **20**.

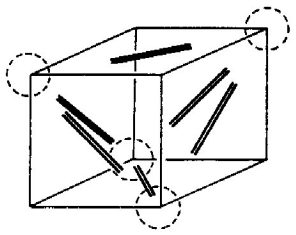


20

The metal d levels split in the quasioctahedral ligand field into an e_g level, moving high up due to σ antibonding, and a t_g level, shifted downward because of π back-bonding. The latter level is completely filled in the d^6 configuration of Cr(0). There is no "sharing of levels" between σ and π bonding. But neither would such sharing contribute to the stability of the complex, for the higher energy metal level is empty anyway and a σ contribution to the level involved in π bonding would only tend to destabilize it.

Further symmetric structures, obtained from **20** by different sequences of rotations of the ethylenes in the cube faces (thus maintaining octahedral coordination) are **21** (T_d), **22** (D_{3d}), **23** (D_{3d}), and **24** (D_3). The T_h structure **20** is not free from close ligand–ligand contacts, but the steric situation in **21–24** is worse. Particularly close H–H approaches occur in the areas indicated by circles. Construction of the various interaction diagrams presents no formal difficulty and is therefore not shown here. Structures **21–23** should on electronic grounds be of somewhat higher energy than **20** and **24**, since in the former there are σ-bonding ethylene π levels of the same symmetry as the 3d levels. The treat-

(26) G. N. Schrauzer and H. Thyret, *J. Amer. Chem. Soc.*, 82, 6420 (1960).
(27) G. N. Schrauzer and H. Thyret, *Chem. Ber.*, 96, 1775 (1963).
(28) M. D. Glick and L. F. Dahl, *J. Organometal. Chem.*, 3, 200 (1965).
(29) G. G. Aleksandov and Yu. T. Struchkov, *Zh. Strukt. Khim.*, 14, 1067 (1973).
(30) In a simple MO treatment of bis(duroquinone)nickel(0) no significant differences could be found between the quasicubical and the square-planar structure in explaining bonding and spectra: G. N. Schrauzer and H. Thyret, *Theor. Chim. Acta*, 1, 172 (1963).
(31) R. Mackenzie and P. L. Timms, *J. Chem. Soc., Chem. Commun.*, 650 (1974).
(32) J. F. Young, R. D. Gillard, and G. Wilkinson, *J. Chem. Soc.*, 5176 (1964).
(33) M. Green, T. A. Kuc, and S. H. Taylor, *Chem. Commun.*, 1553 (1970); *J. Chem. Soc. A*, 2334 (1971).
(34) R. R. Schrock and J. A. Osborn, *J. Amer. Chem. Soc.*, 93, 3089 (1971).
(35) (a) R. Cramer, *J. Amer. Chem. Soc.*, 86, 217 (1964); 89, 4621 (1967); (b) J. A. Evans and D. R. Russell, *Chem. Commun.*, 197 (1971).



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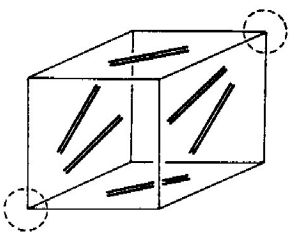

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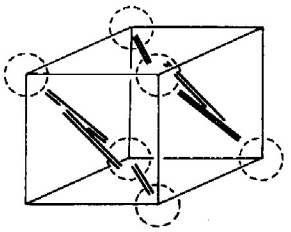

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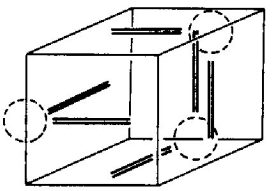
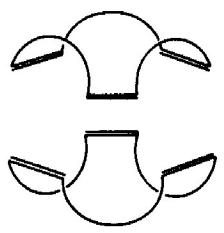


24

ment of **24** requires some care. The D_3 symmetry is lower than the pseudosymmetry which governs the true magnitude of the interactions. A detailed analysis shows that the 3d–ethylene interactions in **20** and **24** are of comparable magnitude. Extended Huckel calculations on these systems, with a Cr–CC midpoint distance of 2.1 Å, make **20** most stable, followed in order of increasing energy by **24**, **23** ~ **22**, **21**. If the energy of the d orbitals alone is computed, then **24** is of comparable energy to **20**.

Since the primary effect in determining the geometry of these molecules is steric, the relative stability order must be viewed with caution. One can imagine a number of ways in which the close H–H contacts of these structures could be relieved. For instance the ethylene hydrogens could be bent backward, away from the metal, as indeed one observes in many transition metal–olefin complexes. The same motion acts to increase back-bonding by lowering the π^* orbitals of the ligand. Further enhancement of back-bonding could be achieved by substitution of the ligand with π-accepting groups.

Another way to overcome the steric problem is by linking two or more CC double bonds together, to "remove" some H–H interactions. This has already been exploited in the known bidentate tetrakis complexes. We also note here the recent synthesis of tris(butadiene)molybdenum and -tungsten[36] but hesitate to predict the structure of these compounds. Structural types **23** and **24** are obviously amenable to improvement by preassembling three (*all-cis*-cyclododecatriene, triquinacene) or two (cyclooctadiene) olefins in one molecule, as shown in **25** and **26**. The same strategy leads to a number of structures based on trigonal-prismatic coordination, and not considered explicitly by us.



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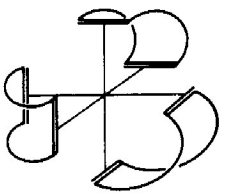
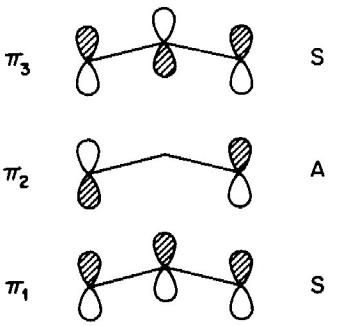


26

Geometries of Other π-Bonded Complexes, Especially Allyls

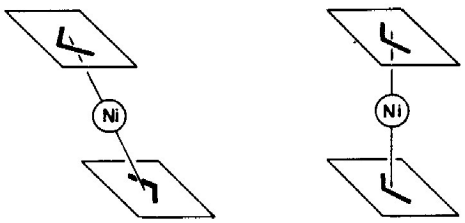
We are confident that the general features of our analysis, namely, the relative ordering of the levels and their slopes upon geometric distortion, will remain qualitatively unaltered as one changes the transition metal. Thus one should be able to use the same energy diagrams, changing only the number of electrons. Moreover, one should be able to carry the conclusions over to ligands which are not ethylenes but which engage in bonding through orbitals of the same symmetry type as ethylene.

Consider the pure allyl complexes of the transition metals.[37] The π-allyl group carries a familiar set of orbitals, shown below



The analogy we want to draw is the obvious one between π of ethylene and π_1 of allyl and between π^* of ethylene and π_2 of allyl. Since π_2 is likely to lie at lower energy than π^*, we should think of the maximum back-donation extreme of the metal–ethylene interaction diagrams that we have constructed. It is also important to keep the electron count straight—this is best demonstrated with an example.

Bis(π-allyl)nickel[37,38] has two more valence electrons than bis(ethylene)nickel. Reference to Figure 5 indicates that these two electrons will enter the 1 b_{3u} orbital. A clear preference for a "D_{2h}" structure follows, in agreement with the observed solid-state structure for bis(methylallyl)nickel.[39] If the D_{2d} structure is indeed at significantly higher energy, then an amusing corollary is that the interconversion of conformations **27** and **28** by a simple rotation around the allyl–



27 28

metal axis should be symmetry forbidden, a high-energy process. Nuclear magnetic resonance studies of bis(allyl)nickel, bis(allyl)platinum, and their 2-methyl derivatives have been interpreted in terms of the presence of two π-bonded forms such as **27** and **28**. The dynamic process which interconverts these isomers becomes important only at elevated temperatures, and there is no evidence that this process is a simple rotation around the coordination axis.[37,40,41]

(36) P. S. Skell, E. M. van Dam, and M. P. Silvon, *J. Amer. Chem. Soc.*, 96, 626 (1974).

(37) G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kroner, W. Oberkirch, K. Tanaka, E. Steinrucke, D. Walter, and H. Zimmermann, *Angew. Chem.*, 78, 157 (1966); *Angew. Chem., Int. Ed. Engl.*, 5, 151 (1966).

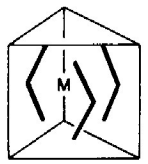
(38) G. Wilke and B. Bogdanovic, *Angew. Chem.*, 73, 756 (1961).

(39) R. Uttech and H. Dietrich, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, 122, 60 (1965).

(40) J. K. Becconsall and S. O'Brien, *J. Organometal. Chem.*, 9, P27 (1967); J. K. Becconsall and S. O'Brien, *J. Chem. Soc. A*, 423 (1967); S. O'Brien, *ibid.*, 9 (1970).

Both *ab initio* and semiempirical studies of the electronic structure of bis(allyl)nickel and -palladium have been performed.[42] The lowest ionization potentials are found in both methods to arise from levels with strong metal character, in agreement with the conclusions from photoelectron spectra.[43] Therefore the π_2 allyl orbital must lie below the metal orbitals. This is very different from the ordering of Figure 5, again cautioning us of the possible dangers in direct transfer of ethylene diagrams to the allyl case.

For tris(allyl)cobalt[44] and tris(allyl)rhodium[45] nuclear magnetic resonance spectra have been interpreted in terms of a "trigonal-prismatic" structure, **29**, analogous to the "upright" geometry, **3**. The d^9 metal has one electron less than nickel; the allyls counted as neutral three-electron ligands carry one electron more than ethylene. The net electron count is 2 more than in $Ni(C_2H_4)_3$. Reference to Figure 2 indicates population of the 1 a_2'–1 a_2'' level and a large preference for the upright geometry. In addition to **29** one finds experimental support for this preference in the structure of the conformationally constrained molecule **30**.[46] Theoretical arguments in favor of trigonal-prismatic coordination have been presented.[47]



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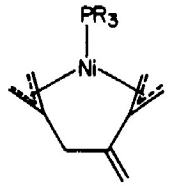

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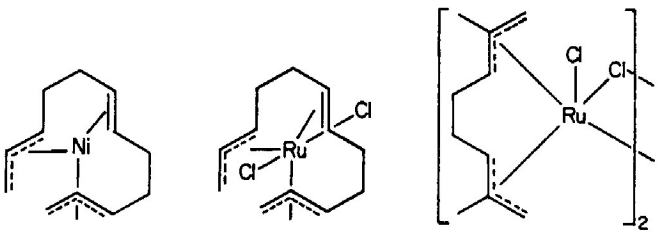
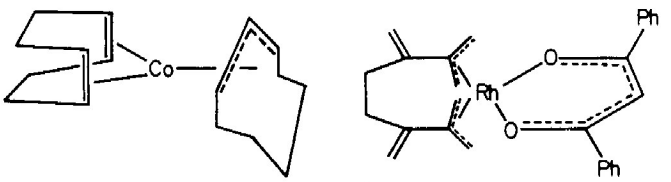
There is a brief report of the crystal structure of tris(allyl)-chromium, a molecule synthesized by Wilke and coworkers.[48] The geometry appears to be a slightly distorted variant of the upright conformation **3**. Our electron count of Cr d^6 + 3 electrons from the allyl groups makes this an interesting 9-electron case, which should have a soft potential surface for moving between the upright and planar extremes.

For four allyl groups around a metal atom a tetrahedral arrangement corresponding to **11** has been favored on steric grounds over a square-planar geometry like **13**.[37] Figure 8 shows that a molecule such as tetrakis(allyl)tungsten, which has the same number of valence electrons as $Ni(C_2H_4)_4$, should have a tetrahedral coordination structure but that molecules with two electrons fewer, for instance $Zr(C_3H_5)_4$, should prefer the square-planar geometry. Nuclear magnetic resonance studies of these species[37,49] do not reveal the basic structures, and crystallographic investigations are not yet available.

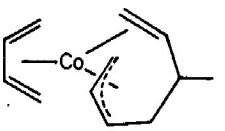
If one enlarges the scope of our considerations to include mixed ethylene and allyl complexes, one encounters a fascinating variety of structural types, represented by Wilke's intercepted butadiene trimer **31**,[5,37,50] **32**,[51] **33**,[52] **34**,[53] **35**,[54] and **36**.[55]



31 **32** **33**



34 **35**

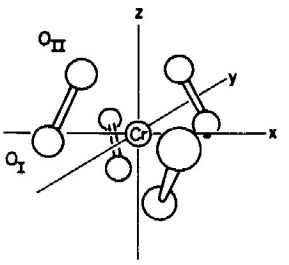


36

Geometry of Tetraperoxochromate(V), CrO_8^{3-}

Our analysis of the bonding in tetrakis-ethylene complexes led us naturally to other compounds in which four simple ligands orient themselves around a central metal atom. One such molecule is tetraperoxochromium(V), CrO_8^{3-}. The analogy to the ethylene case is a rather distant one, since we are dealing here with a formally d^1 metal and O_2^{2-} ligands which possess twice as many π orbitals, among them formally occupied π^* levels. The molecule is interesting in its own right, however, and so we have studied its geometry in some detail.

The coordinate system for CrO_8^{3-} is shown in **37**. The



37

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geometry of the ion is D_{2d}, quasidodecahedral. The "equatorial" oxygen atoms O_I are at a slightly greater distance (1.958 Å) from the Cr than the "axial" atoms O_{II} (1.882 Å).[56-60] The oxygen molecular axis is therefore tilted outward, the angle between the OO bond direction and the metal-center of OO bond axis (previously assumed 90°) is 86° 48′. The OO bond is at 1.466 Å, somewhat shorter than in the O_2^{2-} molecule, presumably due to charge transfer to the metal out of an antibonding orbital. Since there is an *ab initio* calculation available for this experimental structure,[56] we are able to make a comparison between the charge-iterative extended Huckel calculation[61] and the *ab initio* computation.

The bonding picture we derive is generally close to that of the *ab initio* calculations and qualitative ligand field arguments. The unpaired electron of Cr resides in a b_1 orbital. The O_{II} atoms are slightly more strongly bound to the metal than the O_I atoms, as judged by the respective overlap populations (0.283 *vs.* 0.217). The charges found in a Mulliken population analysis are as follows: Cr, 1.85+; O_I, 0.62−; O_{II}, 0.59−. The charge distribution in the *ab initio* study[56] was somewhat more polarized (Cr, 2.58+; O_I, 0.70−; O_{II}, 0.69−). The level ordering of the chromium orbitals $b_1(x^2-y^2) < a_1(z^2) < e(xz, yz) < b_2(xy)$ is in full agreement with the predictions of crystal field theory.[57] The main difference between our calculation and the *ab initio* calculation is the relative energy and the charge distribution in the b_1 orbital, occupied by the unpaired electron. In the latter calculation[56] this orbital was below two filled nonbonding orbitals and was found to be completely delocalized over the oxygen ligands. Here this orbital is the top occupied orbital, as it should be, and it is mainly localized on the metal (66%). This is in reasonable agreement with conclusions from esr measurements.[57]

Before studying deformations of the ion around its experimental structure, the geometry was idealized by orienting the O_2 molecules perpendicular to the bond direction metal-OO bond center, so as to make the structure similar to the one used in tetrakis(ethylene)nickel. The Cr-O distance thus became 1.92 Å. As a result, the total energy rose by 0.34 eV. This increase in energy is due to a deterioration of the important overlap between Cr z^2 and O_2 π^* orbitals. Two degrees of freedom were studied. The first was a deformation of the underlying tetrahedral coordination to square planar. This corresponds to a squashing mode (see **15**) or a variation of the angle ϕ in **37**. The second degree of freedom was a synchronous rotation, in the same sense, of the O_2 ligands around the coordination axis. Our calculated potential energy surface is displayed in Figure 9.

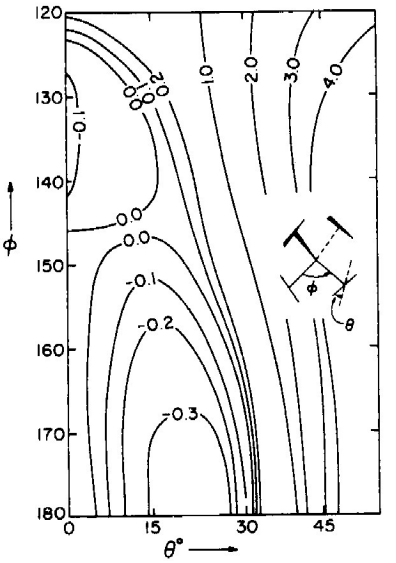

Figure 9. Potential energy surface computed for two degrees of freedom in CrO_8^{3-}. ϕ is the angle between the coordination directions, along the squashing mode. θ is the angle of twist of each O_2 group around the coordination direction. The contour intervals are in electron volts.

A minimum was found for the quasidodecahedral geometry at $\phi = 134°$, close to the experimental value of 131° 30′. However, this minimum was connected over a flat saddle point ($\Delta E \approx 0.25$ eV) with a second minimum for a square-planar coordination geometry of D_4 symmetry, where all the O_2 molecules were tilted from the vertical by 15° in the same sense. The energy of this conformation was lower than the first minimum by 0.11 eV. The tilting may be due to an attempt to minimize the mutual repulsion of nonbonded oxygen atoms. Both minima, however, have a higher energy than the experimental structure. The energy for a quasicubical geometry was always found significantly higher (at least 2.8 eV) than the corresponding quasidodecahedral structure. In a ligand arrangement such as structure **11** the π^* orbitals of O_2^{2-} lose their favorable overlap with the metal z^2 orbital, leading to a rise of the corresponding orbitals. The greater difference between structures **11** and **12** in this system, as compared to the nickel-ethylene analog, may also be viewed in light of the large angle between the Cr to ligand directions. This angle is 131° 30′ in the experimental structure, considerably larger than the tetrahedral angle of 109° 28′. Were the experimental angle to be taken over to the quasicubical geometry **11**, shorter OO distances would follow.

The most interesting conclusion from Figure 9 is that there is no clear advantage in CrO_8^{3-} for tetrahedral over square-planar coordination. The main reason for this is that most of the metal-ligand antibonding orbitals are unfilled. Or in another way of looking at this problem we can push the olefin analogy to the extreme by thinking of CrO_8^{3-} as a complex of Cr^{3-} with four neutral oxygen molecules, whose electronic structure is similar to that of an ethylene. Such a d^9 complex should, according to our considerations for $Ni(C_2H_4)_4$, be intermediate between the extremes of d^{10} (tetrahedral) and d^8 (square-planar) tetracoordination. This is what our surface for CrO_8^{3-} shows. Now the Cr atom is neither d^1 nor d^9, but at either extreme we can account for its geometrical preference.

The low-energy calculated for the D_4 structure suggests one obvious mechanism for interchange of O_I and O_{II} envi-

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(61) Because of the relatively large charge on the ion we allowed for a Madelung correction in the iterative scheme: J. C. Thibeault, to be submitted for publication. The final parameters were Cr (orbital 4s, Slater exponent 1.30, H_{ii} −12.1 eV; 4p, 0.775, −8.5), O_I (2s, 2.275, −32.7; 2p, 2.275, −18.2), O_{II} (2s, 2.275, −33.0; 2p, 2.275 −18.6). The Cr 3d orbital was taken as a linear combination of two Slater functions: one with exponent 4.95, coefficient 0.48761; the other with exponent 1.60, coefficient 0.72051. The corresponding 3d H_{ii} was −17.2 eV. All the Coulomb integrals are corrected for the Madelung shift of −17.2 eV.

ronments. It is also interesting to think about the species related to CrO_8^{3-} by one-electron reduction or oxidation. The b_1 orbital in which the lone electron resides is Cr–O antibonding and slightly O–O bonding. Thus CrO_8^{2-} should have a stronger metal–oxygen bond. To our knowledge this species is unknown. The NbO_8^{3-} ion in $KMgNbO_8 \cdot 7H_2O$ has been the subject of a crystallographic study.[62] It has a D_{2d} structure similar to that of CrO_8^{3-}, with Nb–O distances between 1.99 and 2.07 Å.

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Registry No. $(C_2H_4)_3Ni$, 50696-82-7; $(C_2H_4)_2Ni$, 52392-74-2; $(C_2H_4)_4Ni$, 52393-03-0; $(C_2H_4)_6Cr$, 52393-04-1; CrO_8^{3-}, 12526-97-5.