bond delocalization, about 20%, but militate against describing the structure as aromatic. These distances may be compared with those of [14]annulene and [16]-annulene originally prepared by Sondheimer[5,6] and structurally elucidated by Paul.[7,8] The alternation of bond lengths observed in the 16π-electron system of our dihydrooctaaza[14]annulene complex are very similar to those observed in [16]annulene, which, however, is markedly nonplanar.[8] The bond lengths found in the structure of [14]annulene are essentially equivalent and consistent with aromatic character.

The double bonds, C(1)–N(2), N(3)–C(2), and C(3)–N(4), have distances of 1.313 (2), 1.316 (2), and 1.311 (2) Å, respectively, which are only slightly longer than those found in complexes having isolated imine linkages.[9] Supporting this alternating double bond arrangement is the C(2)–C(3) distance of 1.463 (2) Å which is slightly greater than the 1.435 (7) Å found in the bisglyoximato nickel(II) complex.[10] With this disposition of double bonds, the negative charges of the ligand formally reside on N(1) and N(1)′, a location which most effectively neutralizes the positive charge on nickel(II). This charge localization is probably responsible for the Ni–N(1) distance, 1.784 (1) Å being significantly shorter than normal for low-spin Ni(II)–N distances and even shorter than those found in the 13-membered ring macrocyclic nickel(II) complex, 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienatonickel(II) perchlorate.[11] Similarly the "bites" of the five- and six-membered chelate rings N(1)–N(3) = 2.428 Å and N(3)–N(1)′ = 2.664 Å are shorter than normal and indicate some degree of constriction of the nickel(II) by the highly conjugated ligand.

The greater stability of the C_{2h} structure, III, over the more symmetrical D_{2h} structure can be rationalized on the basis of the arguments given by Nyholm and Gillespie[12] and from the fact that the interior angles of five-membered chelate rings are smaller than those of six-membered chelate rings. The angles defined by C(1)=N(2)—N(4) and C(3)=N(4)—N(1)′, where N(2) and N(4) each contain a lone pair of electrons, are predicted to be less than 120°. In the five-membered rings, a comparatively small angle of 107.8° is observed for the atoms C(1)=N(2)—N(3) whereas a much larger angle of 118.3° is observed for the atoms C(3)=N(4)—N(1) in the six-membered rings. The angular strain of the D_{2h} structure which contains four C–N–N angles close to 120° can be relieved by the observed isomerization to the C_{2h} structure thereby incorporating two of the C–N–N angles into the five-membered chelate rings. It should be noted that a sharp angle, 111°, has also been recently observed for the N–N–C angle of a similar five-membered chelate ring formed by the addition of hydrazine to platinum(II) nitriles followed by air oxidation.[13]

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Supplementary Material Available. A listing of atomic coordinates and structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-73-5773.

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Structure of a Transition Metal Dicyanovinylidene Complex, $(C_5H_5)Mo[C{=}C(CN)_2][P(OCH_3)_3]_2Cl$

Sir:

Recently the reactions between the 1-chloro-2,2-dicyanovinylidenemolybdenum and -tungsten derivatives $[(NC)_2C{=}C(Cl)]M(CO)_3(C_5H_5)$ (where M = Mo and W) and trivalent phosphorus ligands were reported[1,2] to give complexes of the type $(C_5H_5)M[C{=}C(CN)_2](PR_3)_2Cl$ in which a novel terminal dicyanovinylidene (or dicyanomethylene carbene) ligand is formed by an unusual chloride migration from carbon to molybdenum. The dicyanovinylidene ligand is of particular interest because of its relationship to the carbonyl ligand by substitution of an oxygen atom with an isoelectronic dicyanomethylene group.[1–5] This communication reports the first structural details on such a transition metal dicyanovinylidene complex.

The compound $(C_5H_5)Mo[C{=}C(CN)_2][P(OCH_3)_3]_2Cl$ was recrystalized from a mixture of dichloromethane and hexane to give clear orange, square rods in the monoclinic space group C_{2h}^5-$P2_1/n$. The unit cell contains four molecules and has dimensions a = 9.127 (2) Å, b = 18.515 (2) Å, c = 12.923 (2) Å, and β = 91.56 (1)°. A total of 3037 absorption-corrected structure amplitudes with $F_o^2 > 3\sigma(F_o^2)$ were used in the solution and refinement of the structure. Hydrogen atoms were located on a difference Fourier synthesis and were included in the refinement as a fixed-atom structure factor contribution. The final cycle of anisotropic full-matrix least-squares refinement led

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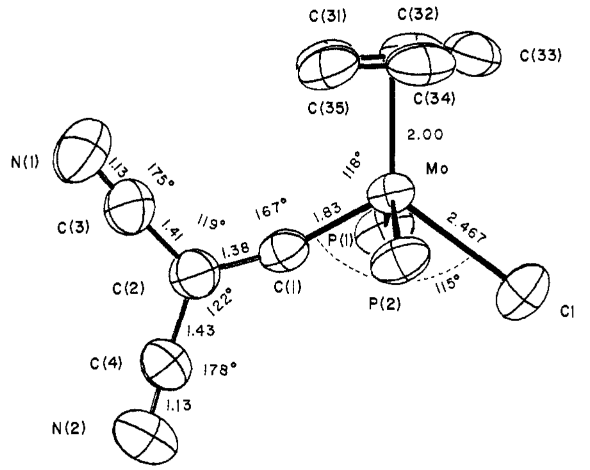

Figure 1. Coordination geometry about the Mo atom in $(C_5H_5)Mo(C{=}C(CN)_2)(P(OCH_3)_3)_2Cl$.

to a value of R of 0.043 (where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$). Final positional and thermal parameters along with the associated standard deviations as estimated from the inverse matrix have been deposited.[6]

The coordination geometry about the molybdenum atom is shown in Figure 1 and can be described as distorted tetragonal pyramidal with the cyclopentadienyl ring occupying the apical position. The cyclopentadienyl ring itself is slightly skewed with respect to the molybdenum atom with Mo–C(ring) distances of 2.270 (5), 2.331 (6), 2.411 (6), 2.361 (5), and 2.285 (5) Å for C(31) through C(35), respectively. The ring tilts toward the dicyanovinylidene ligand. The angle between the vector from Mo to C_5H_5 (center of gravity) and the normal to the C_5H_5 plane is 4.1°.

The molybdenum atom is 0.78 Å above the weighted least-squares plane defined by the atoms Cl, P(1), P(2), and C(1). Within the tetragonal plane the phosphite groups are trans to each other. The Mo–P distances are 2.461 (2) and 2.470 (2) Å for P(1) and P(2), respectively, while the P(1)–Mo–P(2) angle is 143.4 (1)°. The OCH_3 portions of both phosphite groups are disordered and bond angles and distances within these groups are not representative.

The dicyanovinylidene ligand exhibits a strong trans effect. Thus, the Mo–Cl distance of 2.467 (1) Å is long. Since the angle C(1)–Mo–C(33) is 148.2 (2)° it is possible that the cyclopentadienyl ring is skewed as a result of the trans influence on atom C(33).

The nearly planar dicyanovinylidene ligand is bound to the molybdenum atom as shown in Figure 1 with a Mo–C(1) distance of 1.833 (6) Å that is much shorter than Mo–C (carbonyl) distances of 1.93–1.99 Å found in comparable complexes.[7,8] The C(1)–C(2) distance at 1.378 (8) Å is longer than expected for a formal double bond (*ca.* 1.34 Å), but compares with the value of 1.386 (5) Å found for the somewhat analogous bond in the ketenimine ligand of $Ni(t\text{-}BuN{=}C{=}C(CN)_2)(t\text{-}BuNC)_2$.[9] The C(2)–$(CN)_2$ moiety is planar, with bond angles around C(2) of 118.6 (6), 121.9 (5), and 119.5 (6)°, which indicates a sp^2 hybridization of the C(2) orbitals. Thus the dicyanomethylene atom C(2) has only one remaining p orbital to form at most one π bond with the donor carbon atom C(1). There are two orthogonal p orbitals on the sp hybridized vinylidene carbon atom C(1); one with symmetry appropriate for a π bond with C(2), and one orbital which can enter into dπ–pπ back-bonding from the metal. These complexes can be compared with tetracyanoethylene (TCNE) complexes where the ligand consists of two sp^2 hybridized central atoms that are π bound to a metal without any additional p orbitals available. In this case the dπ–pπ back-bonding from the metal to the ligand can only go into π* orbitals, lengthening the central formal double bond to approximately 1.51 Å.[10] The remaining bond angles and distances in the $C(CN)_2$ moiety of the present study and of TCNE complexes are about the same.

An interesting feature of the present structure is that the planar dicyanovinylidene ligand is bent, with a Mo–C(1)–C(2) bond angle of 166.6 (4)°. The ligand bends toward the apical position. Since the shortest intramolecular contact distance (at 2.97 (1) Å) involving dicyanovinylidene ligand atoms is between atom C(1) and atom C(35) of the apical cyclopentadienyl ring, *i.e.*, in the direction of the bend, the bending may result from electronic rather that steric effects. In the comparable complex $(C_5H_5)Mo(CO)[P(C_6H_5)_2\cdot(CH_2)\cdot P(C_6H_5)_2]Cl$[7] the carbonyl ligand is bent in a similar manner, with a Mo–C–O angle of 169 (1)°.

The chemical and spectroscopic properties of both terminal[1,2] and bridging[4,5] dicyanovinylidene complexes have been interpreted[3] on the basis that the dicyanovinylidene ligand is a stronger π acceptor than the isoelectronic carbon monoxide ligand in accord with the stronger electron withdrawing properties of the dicyanomethylene moiety relative to an oxygen atom. The presently reported structure of $(C_5H_5)MO[C{=}C(CN)_2][P(OCH_3)_3]_2Cl$ supports this idea. The abnormally short molybdenum–carbon (dicyanovinylidene) distance indicates a relatively high molybdenum–carbon bond order in accord with the extremely strong π acceptor characteristics of the dicyanovinylidene ligand.

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Supplementary Material Available. A listing of positional and thermal parameters will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may by obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-73-5775.

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