steric bulk of the BF_4^- group while the rings below the basal plane, R2, are bent inward (average Cu-P-C angle 106.8°). This distortion is responsible for the close inter-ring contacts below the basal plane and in turn for limiting the extent to which the bending back of the $P(C_6H_5)_3$ groups occurs. In $Ir(NO)(P(C_6H_5)_3)_3$, however, the Ir-P-C angle of the rings lying above the basal plane is normal (average Ir-P-C angle 114.1°) while that involving the rings lying below the basal plane is large (average Ir-P-C angle 121.2°). It is the expansion in this angle that allows for the greater bending back of the $P(C_6H_5)_3$ groups in $Ir(NO)(P(C_6H_5)_3)_3$. If one envisions a lever and fulcrum arrangement with the P atom as the fulcrum and R1 and R2 (Figure 2) on the lever arms, then it is the steric bulk of the axial ligand in $Cu(BF_4)(P(C_6H_5)_3)_3$ which is ultimately responsible for limiting the extent to which the bending back of the $P(C_6H_5)_3$ groups occurs.

The averaged structure of $Cu(BF_4)(P(C_6H_5)_3)_3$ and its comparison with its trigonal isomorphs also provide further support for our contention that the variation in the Cu-F(1) bond length is real. We note that molecule 2 which has the shortest Cu-F(1) distance (1) has the largest P-Cu-F(1) angle, (2) shows the largest deviation of the Cu atom from the plane of the three P atoms, (3) exhibits the largest conformational angle for the BF_3 group relative to the CuP_3 moiety, and (4) shows the largest fulcrum effect at the P atom.

In conclusion we have shown that the BF_4^- group in $Cu(BF_4)(P(C_6H_5)_3)_3$ is definitely coordinated, albeit weakly. But the factors responsible for the coordination of the BF_4^- group are not clear to us. Thus the related complex with tetramethylthiourea replacing the $P(C_6H_5)_3$ ligands, $[Cu(SC(N(CH_2)_2)_2)_3][BF_4]$,[45] contains a trigonal-planar Cu(I) cation and an uncoordinated BF_4^- anion. We believe that the trigonal-planar $Cu(P(C_6H_5)_3)_3^+$ cation should be isolable under the appropriate conditions since its isoelectronic analogs, $Pt(P(C_6H_5)_3)_3$[55] and CuL_3^+ (L = ethylenethiourea,[45] tetramethylthiourea,[45] and 2-picoline[44]), have been isolated and their structures determined. Perhaps the $Cu(P(C_6H_5)_3)_3^+$ cation exists as a discrete entity in $Cu(P(C_6H_5)_3)_3{\cdot}B(C_6H_5)_4$. A structure determination of this complex is clearly in order.

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Supplementary Material Available. A listing of structure factor amplitudes and reproductions of the infrared and Raman spectra of $Cu(BF_4)(P(C_6H_5)_3)_3$ and $CuCl(P(C_6H_5)_3)_3$ 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, 24× 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 $4.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1657.

(55) V. Albano, P. L. Bellon, and V. Scatturin, *Chem. Commun.*, 507 (1966).

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Structure of a Transition Metal Complex with a Terminal Dicyanovinylidene Ligand, $MoCl(\pi\text{-}C_5H_5)[C{=}C(CN)_2][P(OCH_3)_3]_2$

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The structure of (dicyanovinylidene)(π-cyclopentadienyl)-*trans*-bis(trimethyl phosphite)chloromolybdenum(II), $MoCl(\pi\text{-}C_5H_5)[C{=}C(CN)_2][P(OCH_3)_3]_2$, has been determined from three-dimensional X-ray data collected by counter methods. The clear orange compound crystallizes in space group $C_{2h}{}^5\text{-}P2_1/n$ of the monoclinic system with four molecules in a unit cell of dimensions $a = 9.127$ (2) Å, $b = 18.515$ (2) Å, $c = 12.923$ (2) Å, and $\beta = 91.56$ (1)°. The observed and calculated densities are 1.51 (2) and 1.58 g cm^{-3}, respectively. Full-matrix least-squares refinement led to a final value of the conventional R index (on F) of 0.043 for the 3037 reflections having $F^2 > 3\sigma(F^2)$. The structure consists of discrete monomers. The coordination geometry about the metal is distorted square pyramidal. The π-cyclopentadienyl ligand occupies the apical position while the dicyanovinylidene, chloro, and trimethyl phosphite ligands occupy the basal plane. The molybdenum atom is located 0.779 (3) Å from the basal plane. The trans trimethyl phosphite ligands are disordered. Some important bond distances (in Å) are as follows: Mo-C(dicyanovinylidene), 1.833 (6); Mo-P(1), 2.461 (2); Mo-P(2), 2.470 (2); Mo-Cl, 2.467 (1). An interesting feature of the structure is that the nearly planar dicyanovinylidene ligand is bent (Mo-C(1)-C(2) = 166.6 (4)°) toward the apical cyclopentadienyl ring which, in its own right, is tilted toward the dicyanovinylidene ligand. These structural features are consistent with an attractive "through-space" ligand-ligand interaction, as well as with an asymmetric metal-ligand π-back-bonding interaction.

Introduction

The binding of cyanocarbon ligands to transition metals has begun to be extensively studied because of the potential for stabilizing unstable and even unisolable hydrocarbon derivatives by replacement of hydrogen atoms with the cyano group.[2] Another feature of cyanocarbon chemistry is the close relationship between many compounds containing a dicyanomethylene [$:C(CN)_2$] group and the corresponding compound containing an oxygen atom in place of the dicyanomethylene group.[3] In particular the dicyanovinylidene lig-

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[1] To whom correspondence should be addressed.

(2) W. H. Baddley, *Inorg. Chim. Acta, Rev.*, 2, 7 (1968).

(3) H. Kohler, B. Eicher, and R. Salewski, *Z. Anorg. Allg. Chem.*, 379, 183 (1970).

and [:C=C(CN)$_2$] is of interest because of its relationship to the carbonyl ligand by substitution of an oxygen atom with an isoelectronic dicyanomethylene group.[4-8] Attempts to isolate free dicyanovinylidene have not yet been successful[9] but transition metal complexes have been characterized that contain dicyanovinylidene coordinated as either a bridging[5,6] or a terminal[4,7] ligand. These studies have shown that the analogy between the dicyanovinylidene ligand and the carbonyl ligand has severe limitations and that the dicyanovinylidene ligand is one of the strongest π-acceptor ligands presently identified in transition metal chemistry.[9]

In order to characterize further the novel dicyanovinylidene ligand we have determined and report here the X-ray structure of MoCl(C$_5$H$_5$)[C=C(CN)$_2$][P(OCH$_3$)$_3$]$_2$. The complex is prepared through a reaction of a 1-chloro-2,2-dicyanovinylmolybdenum derivative, Mo(CO)$_3$(C$_5$H$_5$)[ClC=C(CN)$_2$], and trivalent phosphorus ligands in which the terminal dicyanovinylidene ligand is formed by an unusual chloro migration from carbon to molybdenum.[4,7] A preliminary communication on this structure has appeared.[10] In addition the X-ray structure of a complex containing a bridging dicyanovinylidene ligand,[5,6] Fe$_2$(CO)$_2$(C$_5$H$_5$)$_2$(μ-CO)(μ-CC(CN)$_2$), has also been determined.[11]

Collection and Reduction of Intensity Data

Preliminary Weissenberg and precession photography of the *hkl*, 0*kl*, and *hk*0 nets showed that the clear orange crystals of MoCl(C$_5$H$_5$)[C=C(CN)$_2$][P(OCH$_3$)$_3$]$_2$ belong to the monoclinic system. The systematic absences observed for the reflections *h*0*l* with $h + l$ odd and 0*k*0 with *k* odd are consistent with space group $C_{2h}{}^5$-$P2_1/n$.[12] The crystal chosen for data collection was a needle approximately 0.3 mm thick which was cut to give a length of 0.4 mm. The faces were identified from optical goniometry as belonging to the forms {100}, {011}, and {021}. Cell parameters were determined at 21° from a least-squares refinement[13,14] of 23 intense high-order reflections, hand-centered on a Picker four-circle automatic diffractometer using Cu Kα radiation (λ 1.54056 Å) prefiltered through a 0.5-mil Ni foil and employing a tube takeoff angle of 1.1°. The cell parameters are $a = 9.127$ (2) Å, $b = 18.515$ (2) Å, $c = 12.923$ (2) Å, and $\beta = 91.56$ (1)°. The density calculated for four formula weights per unit cell is 1.583 g cm^{-3} and compares with that of 1.51 (2) g cm^{-3} measured for a microcrystalline sample by flotation in aqueous ZnCl$_2$.

The mosaicity of the crystal was examined by means of the narrow-source, open-counter, ω-scan technique. The peak width at half-height for a typical strong reflection was found to be approximately 0.2°. The crystal was mounted on the diffractometer with the *a* axis slightly offset from the spindle axis. Intensity data were collected as previously described[14,15] using Cu Kα radiation prefiltered through 0.5-mil nickel foil. The takeoff angle was set to 2.2°. The scan range was *ca.* ±0.9° in 2θ from the calculated positions of the Kα_1 and Kα_2 peaks. The scan speed was 2° min^{-1} and backgrounds were measured at each end of the scan for preset times of 10 sec for reflections with $2\theta < 80°$ and 20 sec for all higher order reflections. The receiving aperture which was positioned 32 cm from the crystal directly in front of the counter had its windows set such that the opening was 0.5 cm high and 0.4 cm wide.

The intensities of six standard reflections were measured every 100 reflections. They showed an average deviation from their average intensity of about $\pm 2.6\sigma$. Intensity data were collected for the unique *hkl* planes out to 2θ(CuKα_1) of 127° yielding 3718 reflections. In addition 241 Friedel-pair reflections were collected. The data were processed as previously described[13,14] using a value for *p* of 0.04. Of the unique reflections observed, 3037 reflections have $F^2 > 3\sigma(F^2)$ and only these reflections were utilized in the refinement of the structure. The linear absorption coefficient for the compound for Cu Kα radiation is 78.7 cm^{-1}. The data were corrected for absorption.[16] Upon making the absorption correction, the average deviation among the Friedel pairs improved from 2.4 to 1.6%. The maximum-minimum transmission factors were 0.292 and 0.151, respectively.

Solution and Refinement of the Structure

An origin-removed sharpened Patterson synthesis revealed the positions of the molybdenum and one phosphorus atom. Refinement of the positions of these atoms gave the agreement indices

$$R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

and

$$R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o{}^2]^{1/2}$$

of 0.44 and 0.52, respectively. Weights, *w*, were taken as $4F_o{}^2/\sigma^2(F_o{}^2)$. In this and succeeding full-matrix least-squares refinement the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. Atomic scattering factors for neutral molybdenum, chlorine, phosphorus, oxygen, nitrogen, and carbon were taken from the new tabulation.[17] Hydrogen atom scattering factors were those of Stewart, Davidson, and Simpson.[18] Anomalous dispersion effects were included in the calculation of F_c[19] using the values of $\Delta f'$ and $\Delta f''$ for molybdenum, chlorine, phosphorus, oxygen, and nitrogen calculated by Cromer and Liberman.[20]

Further three-dimensional difference Fourier syntheses revealed the positions of the remaining nonhydrogen atoms. The cyclopentadienyl atoms were treated as a rigid group[16] of D_{5h} symmetry (C–C = 1.42 Å) with an overall group temperature factor. Four cycles of isotropic least-squares refinement led to the agreement indices $R = 0.115$ and $R_w = 0.158$. Bond angles and distances within the phosphite group P(1) were not satisfactory at this point. A three-dimensional difference Fourier synthesis calculated without the phosphite atoms included in the structure factor calculation revealed peaks that could be interpreted as resulting from a disordering of two of the three phosphite P–O–CH$_3$ arms. Each of the two disordered arms has two conformations such that the oxygen atoms are distinct but the methyl groups are superimposed. The interpolated peak heights indicated an equal population between the disordered conformations. In order to account for most of the electron density in this phosphite group, each badly disordered arm was assigned two oxygen atom positions with a population parameter of 0.5. In the next two cycles of least-squares refinement all atoms were allowed to vibrate anisotropically except for the atoms in the disordered phosphite arms and the cyclopentadienyl ring atoms which had individual isotropic thermal parameters. The agreement indices dropped to $R = 0.057$ and $R_w = 0.081$. A three-dimensional difference Fourier synthesis revealed significant amounts of residual electron density in a torus about the cyclopentadienyl ring. Thus the thermal motion of this ring was not satisfactorily accounted for by the use of a rigid-body model employing individual isotropic thermal factors. Nevertheless all of the cyclopentadienyl hydrogen atoms could be located in reasonable positions, as well as most of the methyl hydrogen atoms on all but the two badly disordered phosphite arms. In addition electron densities of the order of the hydrogen atom densities were found that could be ascribed to multiple images of disordered phosphite arms for all arms in groups P(1) and P(2). In order to limit the

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(4) R. B. King and M. S. Saran, *J. Chem. Soc., Chem. Commun.*, 1053 (1972).

(5) R. B. King and M. S. Saran, *J. Amer. Chem. Soc.*, **94**, 1784 (1972).

(6) R. B. King and M. S. Saran, *J. Amer. Chem. Soc.*, **95**, 1811 (1973).

(7) R. B. King and M. S. Saran, *J. Amer. Chem. Soc.*, **95**, 1817 (1973).

(8) R. B. King, *Inorg. Nucl. Chem. Lett.*, **9**, 457 (1973).

(9) R. B. King, "Proceedings of the Conference on Horizons in Organometallic Chemistry," New York Academy of Sciences, New York, N. Y., Aug 1973.

(10) R. M. Kirchner, J. A. Ibers, M. S. Saran, and R. B. King, *J. Amer. Chem. Soc.*, **95**, 5775 (1973).

(11) R. M. Kirchner and J. A. Ibers, in preparation.

(12) The coordinates of equivalent positions are $\pm(x, y, z; {}^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$.

(13) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(14) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).

(15) See, for example, R. M. Kirchner and J. A. Ibers, *J. Amer. Chem. Soc.*, **95**, 1095 (1973).

(16) Programs and procedures used were as described previously.[15]

(17) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England, Table 2.2A, in press.

(18) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(19) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).

(20) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

expense of the refinement no additional disorder model was constructed to account for these small residual electron densities. The methyl hydrogen atoms of the four best behaved phosphite arms were idealized (C_{3v} symmetry, C-H = 1.0 Å) as well as the five cyclopentadienyl hydrogen atoms (D_{5h} symmetry, C-H = 1.0 Å) with individual temperature factors equal to those of the carbon atom to which each hydrogen atom is attached. The hydrogen atoms were included in ensuing refinements as a fixed-atom structure factor contribution. These refinements also included an extinction variable since an inspection of the data showed that for strong low-order reflections $|F_o|$ was consistently less than $|F_c|$, indicating possible secondary extinction effects. Two final cycles of full-matrix least-squares refinement with all atoms refined individually with anisotropic thermal parameters converged to final agreement indices of $R = 0.043$ and $R_w = 0.061$. The goodness of fit, the standard deviation of an observation of unit weight, is 2.21 e. The extinction coefficient refined to a value of 7.2 (6) × 10^{-6} e^{-2}.

A final difference Fourier map revealed peaks as high as 1.28(5) e $Å^{-3}$, which is approximately 20% the height of an oxygen atom in previous difference maps. The peaks above background are associated with disordered phosphite arms. From the residual electron density of the final difference Fourier calculation we estimate that 2 and 11% of the total electron densities of the phosphite groups P(1) and P(2), respectively, have been ignored by our final structural model. This small amount of residual electron density does not significantly affect the structural results obtained for the rest of the molecule. A comparison of $\Sigma w(|F_o| - |F_c|)^2$ for various classes of reflections based upon $|F_o|$, Miller indices, and the setting angles shows no unexpected trends.

The positional and thermal parameters obtained from the last cycle of least-squares refinement are given in Table I along with the associated standard deviations as estimated from the inverse matrix. The idealized hydrogen atom positions along with their assigned thermal parameters are given in Table II. Root-mean-square amplitudes of vibration of the atoms treated anisotropically are given in Table III. Final values of $10|F_o|$ and $10|F_c|$ in electrons are available.[21]

Description of the Structure

A perspective view of a single molecule, the asymmetric unit, is given in Figure 1 along with the atom-labeling scheme. Bond distances, selected bond angles, various weighted least-squares planes, and nonbonding distances are given in Tables IV-VII, respectively.

The coordination geometry about the molybdenum atom can be described as distorted square pyramidal, with the cyclopentadienyl group at the apex of the pyramid and the four other monodentate ligands at the corners of the tetragonal base. This geometry, sometimes referred to as a "piano stool" conformation, is illustrated in Figure 2. The molybdenum atom is 0.779 (3) Å from the weighted least-squares plane defined by atoms Cl, P(1), P(2), and C(1). Within the base of the tetragonal pyramid the phosphite ligands are trans to each other, with a P(1)-Mo-P(2) angle of 143.36 (5)°. The dicyanovinylidene ligand is trans to the chlorine atom, with a C(1)-Mo-Cl angle of 114.6 (2)°. These bond angles within the coordination sphere are typical for molybdenum(II)-cyclopentadienyl complexes that have the distorted square-pyramidal conformation, despite a variety of ligands in the basal plane. Reference to Figure 1, a projection of the molecule onto the cyclopentadienyl ring, shows that the dicyanovinylidene ligand is situated directly over the midpoint of a carbon-carbon bond of the ring whereas the chlorine atom is situated directly over a ring carbon atom. This conformation appears to be preferred for complexes of the type $Mo^{II}X(CO)_{3-n}(\pi\text{-}C_5H_5)L_n$, where X (a σ-bonded group) is situated directly over a C_5H_5 carbon atom while one of the carbonyl ligands is situated directly over the midpoint of a carbon-carbon bond of the ring.[22]

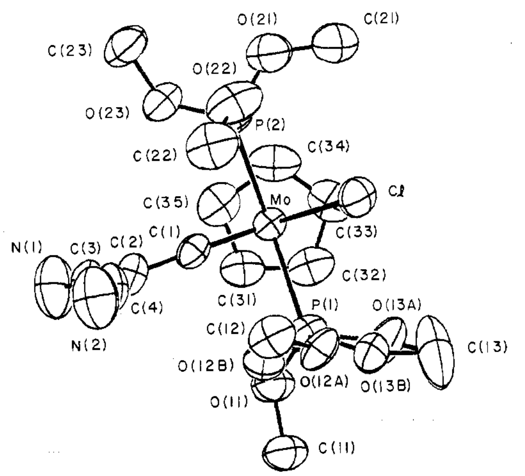

Figure 1. Projection of a molecule of $MoCl(C_5H_5)[CC(CN)_2][P(OCH_3)_3]_2$ onto the plane of the C_5H_5 ring. This is the asymmetric unit with the atom-labeling scheme. Hydrogen atoms have been omitted for the sake of clarity. The 50% probability vibrational ellipsoids are shown.

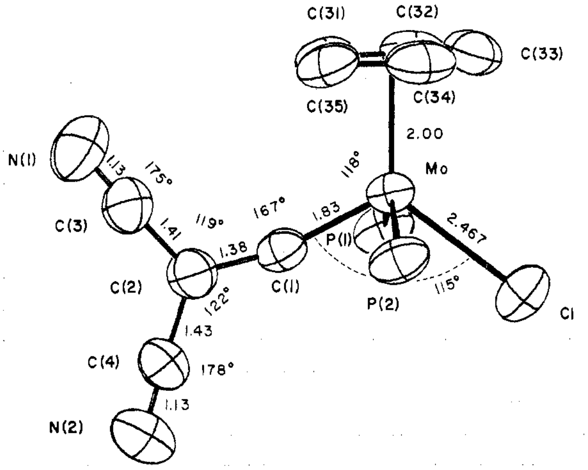

Figure 2. Perspective view of a single molecule of $MoCl(C_5H_5)[CC(CN)_2][P(OCH_3)_3]_2$. The OCH_3 portions of the phosphite groups and the hydrogen atoms of the cyclopentadienyl group are not shown. The 50% probability vibrational ellipsoids are shown.

The dicyanovinylidene ligand is bound to the molybdenum atom as shown in Figure 2 with a Mo-C(1) distance of 1.833 (6) Å that is much shorter than Mo-C(carbonyl) distances of 1.93-2.06 Å found in comparable complexes.[23-25] The ligand itself is nearly planar, as can be seen in Table VI. All of the bond distances and angles found here within the terminal dicyanovinylidene ligand agree with the average values for the bridging dicyanovinylidene ligand in $Fe_2(CO)_2(C_5H_5)_2(\mu\text{-}CO)[\mu\text{-}C{=}C(CN)_2]$.[11] 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 $Ni(t\text{-}BuN{=}C{=}C(CN)_2)(t\text{-}BuNC)_2$.[26] 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 indicate an 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

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(21) See paragraph at end of paper regarding supplementary material.

(22) K. W. Varnett and D. W. Slocum, *J. Organometal. Chem.*, **44**, 1 (1972).

(23) A. D. U. Hardy and G. A. Sim, *J. Chem. Soc., Dalton Trans.*, 1900 (1972).

(24) M. A. Bush, A. D. U. Hardy, Lj. Manojlovic-Muir, and G. A. Sim, *J. Chem. Soc. A*, 1003 (1971), and references therein.

(25) A. T. McPhail, G. R. Knox, C. G. Robertson, and G. A. Sim, *J. Chem. Soc. A*, 205 (1971).

(26) D. J. Yarrow, J. A. Ibers, S. Otsuka, and Y. Tatsuno, *J. Amer. Chem. Soc.*, **95**, 8590 (1973).

Table I. Positional and Thermal Parameters for $MoCl(C_5H_5)[C{=}C(CN)_2][P(OCH_3)_3]_2$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	0.20871 (4)[b]	0.37319 (2)	0.21413 (3)	0.01029 (6)	0.00248 (2)	0.00574 (3)	−0.00003 (2)	−0.00095 (3)	0.00044 (1)
Cl	0.2027 (2)	0.4265 (1)	0.0391 (1)	0.0195 (2)	0.0040 (1)	0.0064 (1)	−0.0013 (1)	−0.0007 (1)	0.0012 (1)
P(1)	0.2833 (2)	0.4984 (1)	0.2514 (1)	0.0160 (2)	0.0030 (1)	0.0083 (1)	−0.0014 (1)	−0.0025 (1)	0.0009 (1)
P(2)	0.0170 (2)	0.2989 (1)	0.1275 (1)	0.0149 (2)	0.0031 (1)	0.0078 (1)	−0.0012 (1)	−0.0033 (1)	0.0009 (1)
O(11)	0.3354 (5)	0.5047 (2)	0.3657 (3)	0.0225 (8)	0.0031 (1)	0.0079 (3)	−0.0013 (3)	−0.0010 (4)	−0.0003 (2)
O(12A)[c]	0.2085 (9)	0.5626 (4)	0.2012 (7)	0.0131 (11)	0.0027 (2)	0.0113 (7)	−0.0007 (4)	−0.0003 (7)	0.0019 (3)
O(12B)[c]	0.1360 (10)	0.5563 (4)	0.2746 (7)	0.0190 (15)	0.0027 (2)	0.0095 (7)	0.0008 (5)	0.0017 (9)	−0.0006 (3)
O(13A)[c]	0.4511 (10)	0.5109 (5)	0.1931 (9)	0.0111 (12)	0.0044 (4)	0.0151 (10)	−0.0011 (5)	0.0015 (9)	0.0016 (5)
O(13B)[c]	0.3575 (11)	0.5508 (5)	0.1825 (7)	0.0176 (14)	0.0037 (3)	0.0088 (6)	−0.0013 (5)	0.0026 (8)	0.0003 (3)
O(21)	0.0653 (6)	0.2387 (3)	0.0443 (4)	0.0260 (10)	0.0047 (2)	0.0098 (4)	−0.0026 (3)	−0.0001 (5)	−0.0009 (2)
O(22)	−0.1028 (6)	0.3357 (3)	0.0578 (4)	0.0210 (8)	0.0047 (2)	0.0137 (5)	−0.0009 (3)	−0.0081 (5)	0.0014 (2)
O(23)	−0.0585 (5)	0.2481 (2)	0.2064 (3)	0.0153 (6)	0.0037 (1)	0.0091 (3)	−0.0018 (2)	−0.0008 (3)	0.0008 (2)
N(1)	−0.0027 (8)	0.3360 (5)	0.5367 (5)	0.0267 (14)	0.0089 (4)	0.0096 (5)	0.0010 (6)	0.0026 (7)	0.0041 (4)
N(2)	−0.2588 (7)	0.4962 (5)	0.3496 (6)	0.0164 (10)	0.0085 (4)	0.0143 (7)	0.0044 (5)	0.0024 (7)	0.0018 (4)
C(1)	0.0552 (6)	0.3992 (3)	0.2947 (4)	0.0102 (7)	0.0029 (2)	0.0063 (3)	−0.0010 (3)	−0.0014 (4)	0.0009 (2)
C(2)	−0.0424 (6)	0.4099 (3)	0.3727 (5)	0.0112 (7)	0.0040 (2)	0.0079 (4)	−0.0006 (3)	0.0008 (4)	0.0012 (2)
C(3)	−0.0217 (7)	0.3712 (4)	0.4660 (5)	0.0144 (9)	0.0053 (3)	0.0083 (5)	−0.0004 (4)	0.0020 (5)	0.0014 (3)
C(4)	−0.1635 (7)	0.4581 (4)	0.3612 (5)	0.0115 (8)	0.0058 (3)	0.0089 (5)	0.0011 (4)	0.0020 (5)	0.0012 (3)
C(11)	0.3914 (8)	0.5698 (4)	0.4120 (6)	0.0209 (12)	0.0035 (2)	0.0103 (6)	−0.0012 (4)	−0.0001 (6)	−0.0011 (3)
C(12)	0.0448 (8)	0.5749 (4)	0.2009 (6)	0.0153 (10)	0.0040 (2)	0.0126 (6)	0.0009 (4)	−0.0013 (6)	0.0000 (3)
C(13)	0.5002 (9)	0.5475 (8)	0.1359 (6)	0.0180 (12)	0.0168 (8)	0.0098 (6)	0.0007 (8)	0.0046 (7)	0.0021 (6)
C(21)	0.1479 (9)	0.2530 (4)	−0.0398 (6)	0.0215 (13)	0.0045 (3)	0.0096 (6)	−0.0006 (4)	−0.0017 (7)	−0.0006 (3)
C(22)	−0.1818 (8)	0.3986 (5)	0.0855 (7)	0.0151 (10)	0.0052 (3)	0.0145 (8)	0.0025 (5)	−0.0035 (7)	0.0000 (4)
C(23)	−0.1856 (8)	0.2053 (4)	0.1783 (7)	0.0147 (10)	0.0039 (2)	0.0146 (7)	−0.0019 (4)	0.0014 (7)	−0.0007 (3)
C(31)	0.3463 (7)	0.3396 (3)	0.3550 (5)	0.0149 (9)	0.0035 (2)	0.0073 (4)	0.0008 (3)	−0.0038 (5)	0.0002 (2)
C(32)	0.4472 (7)	0.3571 (3)	0.2797 (6)	0.0119 (8)	0.0036 (2)	0.0112 (5)	0.0010 (3)	−0.0039 (5)	0.0000 (3)
C(33)	0.4342 (7)	0.3067 (4)	0.1984 (5)	0.0145 (9)	0.0045 (3)	0.0091 (5)	0.0030 (4)	−0.0011 (5)	−0.0005 (3)
C(34)	0.3228 (8)	0.2588 (3)	0.2224 (6)	0.0196 (10)	0.0030 (2)	0.0106 (5)	0.0027 (4)	−0.0049 (6)	−0.0007 (2)
C(35)	0.2672 (7)	0.2784 (3)	0.3207 (5)	0.0182 (10)	0.0034 (2)	0.0087 (4)	0.0006 (4)	−0.0024 (5)	0.0020 (2)

[a] The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{33}kl)]$. [b] The numbers given here are estimated standard deviations in the least significant figures. [c] This atom is part of the disorder model and has a population parameter of 0.5.

Table II. Hydrogen Atom Positional[a] and Thermal Parameters[b]

Atom	x	y	z	B, Å^2
H(31)[c]	0.3306	0.3664	0.4218	4.8
H(32)	0.5205	0.3987	0.2832	5.2
H(33)	0.4933	0.3058	0.1335	5.7
H(34)	0.2866	0.2160	0.1796	5.5
H(35)	0.1860	0.2535	0.3577	5.5
H(11A)	0.3049	0.5956	0.4166	5.4
H(11B)	0.4604	0.5975	0.3656	5.4
H(11C)	0.4397	0.5639	0.4811	5.4
H(21A)	0.2400	0.2700	−0.0200	7.0
H(21B)	0.1017	0.2915	−0.0869	7.0
H(21C)	0.1633	0.2087	−0.0844	7.0
H(22A)	−0.2656	0.4084	0.0509	6.8
H(22B)	−0.1176	0.4426	0.0794	6.8
H(22C)	−0.2094	0.3947	0.1617	6.8
H(23A)	−0.1672	0.1724	0.1179	5.3
H(23B)	−0.2724	0.2366	0.1601	5.3
H(23C)	−0.2145	0.1730	0.2387	5.3

[a] These are idealized positions and were not refined. [b] Hydrogen atoms were assigned temperature factors equal to those of the carbon atom to which each hydrogen atom is attached. [c] H(31) is attached to C(31); H(11A), H(11B), and H(11C) are attached to C(11); etc. No hydrogen atoms were included in the model for the disordered methyl groups C(12) and C(13).

Table III. Root-Mean-Square Amplitudes of Vibration (Å)

Atom	Min	Intermed	Max
Mo	0.1928 (6)	0.2072 (6)	0.2353 (6)
Cl	0.212 (2)	0.259 (2)	0.306 (2)
P(1)	0.213 (2)	0.230 (2)	0.305 (2)
P(2)	0.209 (2)	0.217 (2)	0.304 (2)
O(11)	0.224 (5)	0.259 (5)	0.316 (5)
O(12A)	0.190 (10)	0.236 (10)	0.325 (10)
O(12B)	0.208 (10)	0.276 (10)	0.297 (10)
O(13A)	0.205 (11)	0.272 (12)	0.366 (12)
O(13B)	0.225 (11)	0.269 (10)	0.299 (11)
O(21)	0.253 (6)	0.298 (6)	0.349 (6)
O(22)	0.224 (6)	0.280 (6)	0.401 (6)
O(23)	0.221 (5)	0.260 (5)	0.302 (5)
N(1)	0.233 (8)	0.333 (9)	0.426 (10)
N(2)	0.232 (8)	0.330 (8)	0.417 (9)
C(1)	0.193 (7)	0.201 (6)	0.264 (7)
C(2)	0.209 (7)	0.239 (7)	0.289 (7)
C(3)	0.224 (8)	0.267 (8)	0.318 (8)
C(4)	0.211 (8)	0.264 (8)	0.332 (8)
C(11)	0.229 (8)	0.301 (8)	0.306 (8)
C(12)	0.240 (8)	0.273 (8)	0.331 (9)
C(13)	0.229 (8)	0.319 (10)	0.543 (13)
C(21)	0.257 (8)	0.292 (8)	0.315 (9)
C(22)	0.216 (9)	0.314 (9)	0.365 (10)
C(23)	0.220 (8)	0.282 (8)	0.354 (9)
C(31)	0.191 (7)	0.251 (7)	0.297 (8)
C(32)	0.192 (7)	0.255 (7)	0.327 (8)
C(33)	0.205 (7)	0.270 (7)	0.318 (8)
C(34)	0.195 (7)	0.249 (7)	0.354 (8)
C(35)	0.190 (7)	0.276 (8)	0.313 (8)

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 which can enter into dπ-pπ back-bonding from the metal. This last orbital greatly enhances the ability of the dicyanovinylidene ligand to act as a π-acceptor ligand. This complex can be compared with tetracyanoethylene (TCNE) complexes where the ligand consists of two sp^2-hybridized central atoms that are π bound to the metal without any additional p orbitals available. Here 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.[27] The remaining bond angles and distances in the $C(CN)_2$ moiety and in the TCNE complexes are about the same. A curious feature of the planar dicyanovinylidene ligand is that the linkage to the metal is bent, with a Mo-C(1)-C(2) bond angle of 166.6 (4)°. This feature will be discussed later.

The cyclopentadienyl ligand is slightly skewed with respect to the molybdenum atom. As one goes around the ring there is a smooth and highly significant variation in molybdenum-carbon bond lengths, ranging from 2.270 (5) to 2.411 (6) Å.

[27] J. S. Ricci and J. A. Ibers, *J. Amer. Chem. Soc.*, **93**, 2391 (1971), and references therein.

Table IV. Bond Distances (Å)

Mo-Cl	2.467 (1)	
Mo-P(1)	2.461 (2)	
Mo-P(2)	2.470 (2)	
Mo-C(31)	2.270 (5)	2.332 (72)[c]
Mo-C(32)	2.331 (6)	
Mo-C(33)	2.411 (6)	
Mo-C(34)	2.361 (5)	
Mo-C(35)	2.285 (5)	
Mo-Cp cg[a]	2.003	
Mo-C(1)	1.833 (6)	
C(1)-C(2)	1.378 (8)	
C(2)-C(3)	1.411 (9)	
C(2)-C(4)	1.426 (9)	
C(3)-N(1)	1.131 (8)	
C(4)-N(2)	1.127 (9)	
P(1)-O(11)	1.543 (4)	1.61 (16)
P(1)-O(12A)[b]	1.508 (7)	
P(1)-O(12B)[b]	1.751 (9)	
P(1)-O(13A)	1.740 (9)	
P(1)-O(13B)	1.491 (8)	
P(2)-O(21)	1.619 (5)	1.578 (41)
P(2)-O(22)	1.555 (5)	
P(2)-O(23)	1.561 (4)	
O(11)-C(11)	1.434 (8)	1.36 (21)
O(12A)-C(12)	1.511 (10)	
O(12B)-C(12)	1.295 (11)	
O(13A)-C(13)	1.107 (12)	
O(13B)-C(13)	1.450 (11)	
O(21)-C(21)	1.365 (9)	1.410 (49)
O(22)-C(22)	1.420 (9)	
O(23)-C(23)	1.444 (7)	
C(31)-C(32)	1.395 (9)	1.406 (19)
C(32)-C(33)	1.407 (9)	
C(33)-C(34)	1.390 (9)	
C(34)-C(35)	1.428 (10)	
C(35)-C(31)	1.409 (9)	

[a] Cp cg = center of gravity of C_5H_5 ring. [b] The A and B refer to the two disordered orientations of a phosphite arm. [c] The number in parentheses for the average value is the standard deviation of a single observation estimated on the assumption that the quantities averaged are from the same population.

Table V. Selected Bond Angles (deg)

Cl-Mo-P(1)	78.54 (5)	Mo-P(1)-O(12B)	113.6 (3)
Cl-Mo-P(2)	79.03 (5)	Mo-P(1)-O(13A)	106.4 (4)
Cl-Mo-C(1)	114.6 (2)	Mo-P(1)-O(13B)	128.5 (4)
P(1)-Mo-P(2)	143.36 (5)	Mo-P(2)-O(21)	118.8 (2)
P(1)-Mo-C(1)	81.5 (2)	Mo-P(2)-O(22)	119.8 (2)
P(2)-Mo-C(1)	82.0 (2)	Mo-P(2)-O(23)	111.0 (2)
C(1)-Mo-C(31)	91.8 (2)	P(1)-O(11)-C(11)	124.0 (4)
C(1)-Mo-C(32)	123.2 (2)	P(1)-O(12A)-C(12)	123.8 (6)
C(1)-Mo-C(33)	148.2 (2)	P(1)-O(12B)-C(12)	121.2 (7)
C(1)-Mo-C(34)	123.6 (3)	P(1)-O(13A)-C(13)	138.4 (10)
C(1)-Mo-C(35)	91.7 (2)	P(1)-O(13B)-C(13)	130.4 (10)
Cp cg-Mo-Cl	126.9 (1)	P(2)-O(21)-C(21)	124.2 (5)
Cp cg-Mo-P(1)	107.5 (1)	P(2)-O(22)-C(22)	124.5 (5)
Cp cg-Mo-P(2)	109.1 (1)	P(2)-O(23)-C(23)	122.2 (4)
Cp cg-Mo-C(1)	118.5 (2)	O(11)-P(1)-O(12A)	118.5 (4)
Mo-Cp cg-C(31)	86.5 (3)	O(11)-P(1)-O(12B)	90.4 (4)
Mo-Cp cg-C(32)	90.3 (3)	O(11)-P(1)-O(13A)	98.8 (4)
Mo-Cp cg-C(33)	94.4 (3)	O(11)-P(1)-O(13B)	113.0 (4)
Mo-Cp cg-C(34)	91.7 (3)	O(12A)-P(1)-O(13A)	95.9 (5)
Mo-Cp cg-C(35)	87.2 (3)	O(12B)-P(1)-O(13B)	93.9 (5)
Mo-C(1)-C(2)	166.6 (4)	O(21)-P(2)-O(22)	96.7 (3)
C(1)-C(2)-C(3)	118.6 (6)	O(21)-P(2)-O(23)	98.8 (3)
C(1)-C(2)-C(4)	121.9 (5)	O(22)-P(2)-O(23)	109.1 (3)
C(3)-C(2)-C(4)	119.5 (6)	C(31)-C(32)-C(33)	108.9 (6)
C(2)-C(3)-N(1)	175.1 (9)	C(32)-C(33)-C(34)	107.6 (6)
C(2)-C(4)-N(2)	178.4 (8)	C(33)-C(34)-C(35)	108.5 (6)
Mo-P(1)-O(11)	109.5 (2)	C(34)-C(35)-C(31)	107.0 (6)
Mo-P(1)-O(12A)	122.6 (3)	C(35)-C(31)-C(32)	108.0 (6)

Table VI

Various Weighted Least-Squares Planes

Plane no.	Atoms[a]	Distance from plane, Å
1	[Cl	−0.038 (2)
	P(1)	0.049 (2)
	P(2)	0.042 (2)
	C(1)]	−0.540 (5)
	Mo	0.779
2	[C(31)	0.003 (5)
	C(32)	−0.005 (5)
	C(33)	0.007 (6)
	C(34)	−0.005 (6)
	C(35)]	0.001 (6)
	Mo	−1.997
	C(1)	−1.996
	P(1)	−1.950
	P(2)	−2.074
	Cl	−2.853
3	[C(1)	−0.006 (5)
	C(2)	0.010 (6)
	C(3)	0.023 (7)
	C(4)	0.003 (8)
	N(1)	−0.032 (9)
	N(2)]	−0.014 (9)
	Mo	0.040
	Cl	−0.080

Equations of the Planes of the Form $AX + BY + CZ = D$ (Crystal Coordinates)

Plane	A	B	C	D
1	7.413	−10.594	1.186	−2.932
2	6.051	−10.975	5.674	0.380
3	5.078	13.702	4.685	7.137

[a] Brackets enclose those atoms defining the plane.

The ring tilts symmetrically toward the dicyanovinylidene ligand. This tilting of the π-cyclopentadienyl ring seems to be a general feature of $Mo(\pi-C_5H_5)L_4$ molecules.[25,28] 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°. Only one similar complex,[25] $Mo(NCO)(CO)(C_5H_5)(PPh_3)_2$, has a tilt comparable to the present study, as evidenced by Mo-C(ring) distances ranging from 2.28 (1) to 2.43 (1) Å. The mean Mo-C(ring) distance of 2.33 (2) Å of the present study compares well with other mean Mo-C(ring) distances in similar complexes.[25,29] The C-C bond distances within the ring range from 1.390 (9) to 1.428 (10) Å but there is no systematic trend nor any correlation with the variation in Mo-C bond lengths. The mean C-C(ring) bond distance is 1.41 (2) Å which is typical of mean C-C(ring) distances in similar complexes.[25,29]

The Mo-Cl distance of 2.467 (1) Å is short, approximately 0.13 Å less than the predicted single-bond distance of 2.60 Å (calculated using the radii of 1.61 Å for Mo and 0.99 Å for Cl).[30] Churchill has suggested[30] that a contraction in the Mo-Cl length from its normal single-bond value may be due, partly at least, to d-orbital contraction on the metal atom. The very strong π-acceptor properties of the trans dicyanovinylidene ligand could result in a significant d-orbital contraction on the Mo atom. In comparison the Mo-Cl distance is 2.542 (9) Å in $MoCl(CO)_3(C_5H_5)$[31] and 2.541 (5) Å in

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(28) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **6**, 1213 (1967).

(29) J. Rajaram and J. A. Ibers, *Inorg. Chem.*, **12**, 1313 (1973).

(30) M. R. Churchill, *Perspect. Struct. Chem.*, **3**, 91 (1970).

(31) S. Chaiwasi and R. H. Fenn, *Acta Crystallogr., Sect. B*, **24**, 525 (1968).

Table VII. Selected Nonbonded Distances (Å)

Intermolecular Contacts			
H(23A)-H(11B)	2.35	N(1)-H(33)	2.91
H(33)-H(23B)	2.51	N(1)-H(23B)	2.93
H(31)-H(23A)	2.63	Cl-H(22B)	2.96
H(11C)-H(11C)	2.65	O(21)-C(11)	3.20 (1)
N(2)-H(32)	2.82	N(2)-O(13A)	3.29 (1)
O(21)-H(11B)	2.87	N(1)-C(34)	3.40 (1)
N(1)-H(34)	2.87	N(1)-O(12B)	3.40 (1)
C(32)-H(21C)	2.88		
Intramolecular Contacts			
C(1)-C(3)	2.398 (9)	P(1)-C(32)	3.032 (6)
C(1)-C(4)	2.450 (9)	C(1)-H(35)	3.05
C(2)-N(1)	2.54 (1)	Mo-H(33)	3.09
C(2)-N(2)	2.55 (1)	P(2)-C(34)	3.108 (7)
O(11)-H(31)	2.66	Cl-P(1)	3.119 (2)
O(21)-H(34)	2.67	Cl-P(2)	3.141 (2)
C(1)-P(1)	2.844 (5)	Mo-C(2)	3.189 (6)
C(1)-P(2)	2.863 (5)	Cl-O(22)	3.271 (5)
Mo-H(31)	2.88	P(1)-C(31)	3.275 (6)
Mo-H(35)	2.90	Mo-O(11)	3.312 (4)
P(2)-H(34)	2.96	P(2)-C(35)	3.359 (7)
C(1)-C(31)	2.962 (8)	Mo-O(23)	3.362 (4)
C(1)-C(35)	2.971 (8)	C(1)-N(1)	3.394 (9)
Mo-H(32)	3.00	C(1)-N(2)	3.472 (9)
Mo-H(34)	3.03	Cl-C(1)	3.635 (5)
C(1)-H(31)	3.03	P(1)-P(2)	4.681 (2)

$MoCl(CO)(C_5H_5)(PPh_2CH_2CH_2PPh_2)$.[24] These values indicate a much smaller contraction in the Mo-Cl distance, consistent with the observation that the ligands which are trans to the chlorine in these latter complexes are weaker π acceptors than the dicyanovinylidene ligand.

The trimethyl phosphite groups have Mo-P distances of 2.461 (2) and 2.470 (2) Å for P(1) and P(2), respectively. These values are between values for Mo-P(phosphite) bonds, 2.406 (9) Å in $MoI(CO)_2(C_5H_5)[P(OCH_3)_3]$[23] and 2.388 (8) Å in $MoI(CO)_2(\pi\text{-}CH_3C_5H_4)[P(OCH_3)_3]$,[23] and Mo-P(phosphine) bonds, 2.481 (5) Å in $MoI(CO)_2(C_5H_5)[P(C_6H_5)_3]$,[24] 2.497 (3) and 2.500 (3) Å in $Mo(NCO)(CO)(C_5H_5)[P(C_6H_5)_3]_2$,[25] and 2.473 (3) Å in $Mo(CO)_2(C_5H_5)(COCH_3)[P(C_6H_5)_3]$.[32] Metal-phosphite M-P bonds are significantly shorter by *ca.* 0.1 Å than the analogous metal-phosphine bonds,[23] and it has been suggested that this results from phosphite ligands being better π acceptors than phosphine ligands.[33,34] This argument must be viewed with caution, however, since the steric requirements of phosphite ligands are less than those of phosphine ligands.[35] The phosphite ligands of the present study must compete with each other as well as with the strong π-acceptor dicyanovinylidene ligand for metal dπ electrons. This probably explains why the M-P(phosphite) distances of the present study are longer than other M-P(phosphite) bonds, yet not as long as the analogous metal-phosphine distances.

Bond angles and distances within the trimethyl phosphite group P(1) are not representative because of disordering. The less disordered trimethyl phosphite group P(2) has mean Mo-P-O and O-P-O angles of 117 (3) and 102 (4)°, respectively, which compare with the mean values for the same angles in $MoI(CO)_2(C_5H_5)[P(OCH_3)_3]$ and $MoI(CO)_2(CH_3C_5H_5)[P(OCH_3)_3]$ of 117.3 and 100.6°,[23] respectively. The mean P(2)-O distance of 1.58 (4) Å of the present study is the same as the mean value of 1.59 Å in the two similar complexes. Hardy and Sim suggested that there is some double-bond character in these P-O bonds.[23] The badly disordered phosphite group P(1) seems to occupy an open channel in the packing arrangement of the molecules, as can be seen in the stereoscopic packing diagram of Figure 3.

Table VII gives selected nonbonded distances. There are no intermolecular contacts shorter than the sum of the van der Waals radii. The crystal structure of $MoCl(C_5H_5)[C{=}C(CN)_2][P(OCH_3)_3]_2$ consists of the packing of discrete molecules, as can be seen in Figure 3. There are no unusually short intramolecular contacts, but the values listed in Table VII are useful for determining the nature of the conformational distortion in the $MoCl(C_5H_5)[C{=}C(CN)_2][P(OCH_3)_2]_2$ molecule resulting from the presence of the very strong π-acceptor dicyanovinylidene ligand.

Discussion

The chemical and spectroscopic properties of dicyanovinylidene complexes[4-7] have been interpreted[8-9] on the basis that the dicyanovinylidene ligand is one of the strongest π acceptors presently identified in transition metal chemistry. It is a stronger π acceptor than the carbonyl ligand.[9] Reference to Cotton and Wing's scheme for relating Mo(II)-C bond lengths to bond orders[36] indicates that the dicyanovinylidene Mo-C bond length of 1.83 Å corresponds to a bond order of 3. Two of the possible consequences of this strong π-acceptor character have already been discussed, *i.e.*, the short Mo-Cl distance and the longer than expected Mo-P(phosphite) distances. In addition the tilting of the cyclopentadienyl ring and the bending of the molybdenum-dicyanovinylidene linkage may also be a consequence of this strong π-acceptor character.

The nearly 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 distances (at 2.962 (8) and 2.971 (8) Å) involving dicyanovinylidene ligand atoms are between atom C(1) and atoms C(31) and C(35) of the apical cyclopentadienyl ring, *i.e.*, in the direction of the bend, the bending may result from electronic rather than steric effects. In addition, as described above, the cyclopentadienyl ring tilts slightly toward the dicyanovinylidene ligand. There are no short intermolecular contacts for either of these two ligands so packing forces are presumed to be unimportant.

The nature of electronic effects important for ligand-ligand interactions in complexes similar to that studied here is not well understood. The electronic interactions are described as occurring *via* back-bonding with the central metal atom[37-39] or *via* "through-space" ligand-ligand effects,[40-41] or some combination of both of these. The short interligand distances between dicyanovinylidene and cyclopentadienyl atoms result in a distance of 3.23 Å between the midpoint of the dicyanovinylidene C(1)-C(2) double bond and the midpoint of the cyclopentadienyl C(31)-C(35) aromatic bond. This distance is shorter than the value of 3.45 Å estimated[42] from the sum of the radii for these types of bonds [*r*(aromatic bond) = 1.85 Å, *r*(C=C) = 1.6 Å]. This overlapping of dicyanovinylidene and cyclopentadienyl π orbitals is symmetry allowed and is presumed to be an attractive

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(32) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **7**, 953 (1968).

(33) H. J. Plastas, J. M. Stewart, and S. O. Grim, *Inorg. Chem.*, **12**, 265 (1973).

(34) J. D. Verkade, *Coord. Chem. Rev.*, **9**, 1 (1972).

(35) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2953 (1970).

(36) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 314 (1965).

(37) S. F. A. Kettle, *Inorg. Chem.*, **4**, 1661 (1965).

(38) M. Herberhold and C. R. Jablonski, *Inorg. Chim. Acta*, **7**, 241 (1973).

(39) J. D. Kennedy, W. McFarlane, and D. S. Rycroft, *Inorg. Chem.*, **12**, 2742 (1973).

(40) T. A. George and C. D. Turnipseed, *Inorg. Chem.*, **12**, 394 (1973).

(41) N. D. Epiotis, *J. Amer. Chem. Soc.*, **95**, 3087 (1973).

(42) G. Briegleb, *Fortschr. Chem. Forsch.*, **1**, 642 (1950).

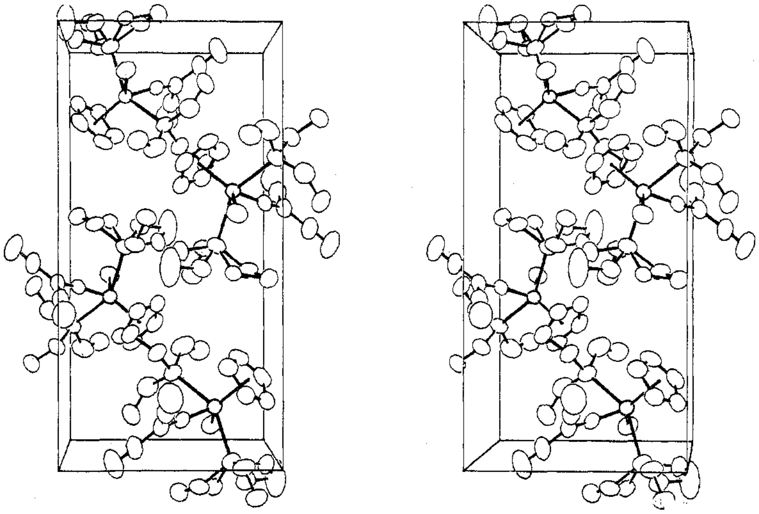

Figure 3. Stereoscopic packing diagram of $MoCl(C_5H_5)[C{=}C(CN)_2][P(OCH_3)_3]_2$. The view is approximately down *z*. Hydrogen atoms have been omitted for clarity. The 50% probability vibrational ellipsoids are shown.

interaction. For similar square-pyramidal complexes of the type $Mo(CO)_n(\pi\text{-}C_5H_5)L_{4-n}$, in the projection of the molecule onto the plane of the cyclopentadienyl ring, the best π-acceptor ligand (CO) usually passes directly over a cyclopentadienyl ring aromatic bond as does the dicyanovinylidene ligand and this ligand can show a significant bending of the metal-ligand linkage.[22-25,28,32,43,44] A tilting of the π-cyclopentadienyl ring is also a general feature of this class of compounds.[28] However it is difficult to determine from the way the structural results are presented in the literature whether the carbonyl ligand consistently bends toward the cyclopentadienyl ring, which in turn tilts toward the carbonyl ligand, as obtains here.

The results of the present crystal structure are consistent with a "through-space" ligand-ligand attractive interaction as well as an asymmetric metal-ligand π-back-bonding interaction. Both of these effects could be important. Clearly there is a need for further theoretical work to clarify the electronic nature of these structural results.

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Registry No. $MoCl(\pi\text{-}C_5H_5)[C{=}C(CN)_2][P(OCH_3)_3]_2$, 50545-80-7.

Supplementary Material Available. A listing of 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, 24× 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 $4.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1667.

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(43) R. H. Fenn and J. H. Cross, *J. Chem. Soc. A*, 3312 (1971).

(44) A. Mawby and J. E. Pringle, *J. Inorg. Nucl. Chem.*, 34, 525 (1972).