(6) W. H. Baddley, *Inorg. Chim. Acta, Rev.*, **2**, 7 (1968).
(7) G. L. McClure and W. H. Baddley, *J. Organometal. Chem.*, **25**, 261 (1970).
(8) G. L. McClure and W. H. Baddley, *J. Organometal. Chem.*, **27**, 155 (1971).
(9) W. Beck, W. Hieber, and G. Neumair, *Z. Anorg. Allg. Chem.*, **344**, 285 (1966).
(10) J. S. Ricci, J. A. Ibers, M. S. Fraser, and W. H. Baddley, *J. Amer. Chem. Soc.*, **92**, 3489 (1970).
(11) M. Lenarda and W. H. Baddley, *J. Organometal. Chem.*, **39**, 217 (1972).
(12) R. B. King and M. S. Saran, *J. Amer. Chem. Soc.*, **95**, 1811 (1973).
(13) R. B. King and M. S. Saran, *J. Amer. Chem. Soc.*, **95**, 1817 (1973).
(14) W. Beck, K. Schorpp, C. Oetker, R. Schlodder, and H. S. Smedal, *Chem. Ber.*, **106**, 2144 (1973).
(15) R. E. Christopher and L. M. Venanzi, *Inorg. Chim. Acta*, **7**, 219 (1973).
(16) W. Beck, R. Schlodder, and K. H. Lechler, *J. Organometal. Chem.*, **54**, 303 (1973).
(17) S. R. Su and A. Wojcicki, *Inorg. Chim. Acta*, **8**, 55 (1974).
(18) M. Lenarda, R. Ros, M. Graziani, and U. Belluco, *J. Organometal. Chem.*, **65**, 407 (1974).
(19) M. Green, S. Heathcock, and D. C. Wood, *J. Chem. Soc., Dalton Trans.*, 1564 (1973).
(20) S. R. Su and A. Wojcicki, *J. Organometal. Chem.*, **31**, C34 (1971).
(21) J. S. Ricci and J. A. Ibers, *J. Amer. Chem. Soc.*, **93**, 2391 (1971).
(22) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).
(23) J. P. Bibler and A. Wojcicki, *J. Amer. Chem. Soc.*, **88**, 4862 (1966).
(24) R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **2**, 15 (1964).
(25) J. J. Alexander and A. Wojcicki, *Inorg. Chim. Acta*, **5**, 655 (1971).
(26) P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, **5**, 1177 (1966).
(27) S. R. Su and A. Wojcicki, *J. Organometal. Chem.*, **27**, 231 (1971).
(28) M. Graziani and A. Wojcicki, *Inorg. Chim. Acta*, **4**, 347 (1970).
(29) R. B. King and A. Fronzaglia, *J. Amer. Chem. Soc.*, **88**, 709 (1966).
(30) K. W. Barnett and P. M. Treichel, *Inorg. Chem.*, **6**, 294 (1967).
(31) R. B. King and K. H. Pannell, *Inorg. Chem.*, **7**, 2356 (1968).
(32) R. D. Closson, J. Kozikowski, and T. H. Coffield, *J. Org. Chem.*, **22**, 598 (1957).
(33) C. S. Kraihanzel and P. K. Maples, *J. Amer. Chem. Soc.*, **87**, 5267 (1965).
(34) T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).
(35) M. A. Jennings and A. Wojcicki, *Inorg. Chim. Acta*, **3**, 335 (1969).
(36) M. A. Jennings, Ph.D. Thesis, The Ohio State University, 1969.
(37) A. Davison, J. A. McCleverty, and G. Wilkinson, *J. Chem. Soc.*, 1133 (1963).
(38) S. E. Jacobson and A. Wojcicki, *J. Amer. Chem. Soc.*, **95**, 6962 (1973).
(39) J. J. Bloomfield, *J. Org. Chem.*, **26**, 4112 (1961).
(40) J. K. Williams, D. W. Wiley, and B. C. McKusick, *J. Org. Chem.*, **25**, 1279 (1960).
(41) T. H. Martini and J. A. Kampmeier, *Angew. Chem., Int. Ed. Engl.*, **9**, 236 (1970).
(42) E. Campaigne and W. L. Roelfs, *J. Org. Chem.*, **30**, 396 (1965).
(43) S. Trofimenko, *J. Org. Chem.*, **28**, 217 (1963).
(44) W. Beck, R. E. Nitzschmann, and H. S. Smedal, *J. Organometal. Chem.*, **8**, 547 (1967).
(45) T. E. Sloan and A. Wojcicki, *Inorg. Chem.*, **7**, 1268 (1968).
(a) **Note Added in Proof.** The structure of **6** has been now confirmed by X-ray crystallography; see M. R. Churchill and S. W.-Y. Chang, following paper.
(46) Infrared and nmr spectroscopic criteria which may be used to distinguish cis and trans complexes of general type η^5-$C_5H_5Mo(CO)_2(L)X$ are given, *inter alia*, in J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, **92**, 5852 (1970), and in K. W. Barnett and D. W. Slocum, *J. Organometal. Chem.*, **44**, 1 (1972).
(47) J. P. Bibler and A. Wojcicki, *Inorg. Chem.*, **5**, 889 (1966).
(48) W. H. Baddley and L. M. Venanzi, *Inorg. Chem.*, **5**, 33 (1966).
(49) W. H. Baddley, *J. Amer. Chem. Soc.*, **90**, 3705 (1968).
(50) W. H. Baddley, *J. Amer. Chem. Soc.*, **88**, 4545 (1966).
(51) M. Graziani, J. P. Bibler, R. M. Montesano, and A. Wojcicki, *J. Organometal. Chem.*, **16**, 507 (1969).
(52) J. A. Hanna and A. Wojcicki, *Inorg. Chim. Acta*, **9**, 55 (1974).
(53) C. Fontaine, K. N. V. Duong, C. Merienne, A. Gaudemer, and C. Giannotti, *J. Organometal. Chem.*, **38**, 167 (1972).
(54) F. R. Jensen and R. C. Kiskis, *J. Organometal. Chem.*, **49**, C46 (1973).
(a) **Note Added in Proof.** In the study reported herein no attempt was made at examining the reaction mixtures by esr spectroscopy. However, after this paper was accepted for publication we have learned that reactions of TCNE with each of η^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$, $Mn(CO)_5CH_2C_6H_5$ ($[M]CH_2C_6H_5$), and $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ ($[M]_2$) yield initially the corresponding metal–iminotricyanoallyl radicals, $[M]\text{-}N{=}C{=}C(CN)\dot{C}(CN)_2$; see P. J. Krusic, H. Stoklosa, L. E. Manzer, and P. Meakin, *J. Amer. Chem. Soc.*, submitted for publication. We thank Dr. P. J. Krusic for communicating these results to us prior to publication.
(55) M. F. Farona and A. Wojcicki, *Inorg. Chem.*, **4**, 1402 (1965).
(56) Y. Yamamoto and H. Yamazaki, *Inorg. Chem.*, **11**, 211 (1972).

Contribution from the Department of Chemistry,
University of Illinois at Chicago Circle, Chicago, Illinois 60680

Crystal and Molecular Structure of Dicarbonyl(η^5-cyclopentadienyl)triphenylphosphine(1-η-1,1,2,2-tetracyanopropyl)molybdenum, the Product of Insertion of Tetracyanoethylene into a Molybdenum–Methyl Linkage

MELVYN ROWEN CHURCHILL* and SHIRLEY W.-Y. CHANG

Received July 18, 1974 AIC40489J

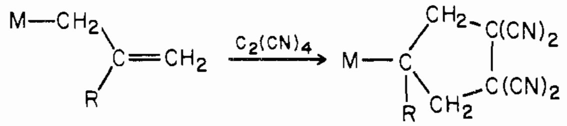
Dicarbonyl-η^5-cyclopentadienyltriphenylphosphine(1-η-1,1,2,2-tetracyanopropyl)molybdenum, $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)[C(CN)_2C(CN)_2CH_3]$, formed by the reaction of $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)(CH_3)$ with tetracyanoethylene, has been subjected to a full three-dimensional X-ray structural analysis. The complex crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ [C_i^1; No. 2] with $a = 8.606$ (1) Å, $b = 12.158$ (2) Å, $c = 13.987$ (2) Å, $\alpha = 85.60$ (2)°, $\beta = 75.95$ (1)°, $\gamma = 88.37$ (1)°, and $V = 1415.4$ Å^3. The observed density of 1.468 (5) g cm^{-3} is consistent with that of 1.460 g cm^{-3} calculated for mol wt 622.48 and $Z = 2$. X-Ray diffraction data complete to $2\theta = 47.5°$ (Mo Kα radiation) were collected with a Picker FACS-1 diffractometer and the structure was solved by means of Patterson, Fourier, and least-squares refinement techniques. All atoms, including hydrogens, have been located and their thermal and positional parameters refined. The resulting discrepancy indices are $R_F = 3.98\%$ and $R_{wF} = 4.76\%$ for the 4346 independent reflections (none rejected). The molybdenum atom has a coordination environment resembling a "four-legged piano stool." The Mo–C(π-C_5H_5) distances range from 2.300 (3) to 2.359 (3) Å, the Mo–P bond length is 2.518 (1) Å, and the Mo–CO bonds are 1.973 (3) and 1.996 (3) Å in length. The Mo–$[C(CN)_2C(CN)_2CH_3]$ σ-bond distance of 2.414 (4) Å is compared with Mo–C distances in molybdenum alkyls, perfluoroalkyls, acyls, and aryls. Within the tetracyanopropyl group, one 2-cyano group and the methyl group are disordered.

Introduction

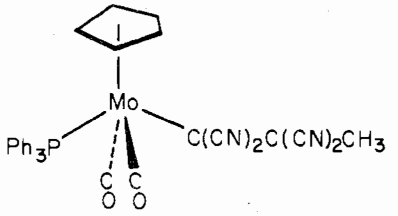
We have, for some time, been interested in so-called "insertion reactions."[1] Following some studies on the products of the insertion of sulfur dioxide into metal–carbon[2-4] and metal–metal[5,6] bonds, we have turned our attention to the products derived from the interaction of tetracyanoethylene with various organo–(transition metal) complexes. We have shown previously that tetracyanoethylene reacts with a σ-allyl *via* a net [3 + 2] cycloaddition reaction[7] (as shown in Scheme I).

We now report the results of a single-crystal X-ray diffraction study on $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)[C(CN)_2C$-

Scheme I



$(CN)_2CH_3]$, I, formed by the reaction of tetracyanoethylene and $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)(CH_3)$.[8] In addition to providing an unambiguous assignment of the molecular structure of $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)[C(CN)_2C(CN)_2CH_3]$, the present study also provides an opportunity for the structural characterization of a hitherto uninvestigated type of metal–carbon linkage, *i.e.*, a metal–polycyanoalkyl linkage. As discussed below, the substitution of a polycyanoalkyl group for an alkyl group causes *a slight increase* in the metal–carbon σ-bond length. This result is in marked contrast to the significant (*i.e.*, *ca.* 0.1 Å) *decrease* in metal–carbon distance found on substituting a *perfluoro*alkyl for an alkyl group in $(\pi\text{-}C_5H_5)Mo(CO)_3R$ derivatives.[9,10]



I

Collection of the Diffraction Data

Yellow crystals of $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)[C(CN)_2C(CN)_2CH_3]$ were provided by Professor Wojcicki of The Ohio State University. The crystal selected for the X-ray diffraction study was a small elongated plate with well-developed (011) and $(0\bar{1}\bar{1})$ faces, 0.10 mm apart and bounded by {001}, 0.18 mm apart, and {100}, 0.30 mm apart.

Preliminary $(0\text{–}2)kl$ Weissenberg photographs, an a axis rotation photograph, $h(0\text{–}2)l$ and $hk(0\text{–}2)$ precession photographs, and b and c cone axis photographs yielded approximate unit-cell dimensions, revealed only $C_i(\bar{1})$ Laue symmetry, and showed no systematic absences. The triclinic space groups $P1$ [C_1^1; No. 1] or $P\bar{1}$ [C_i^1; No. 2] are therefore indicated.

The crystal was transferred to a Picker FACS-1 automated diffractometer, was centered as accurately as possible, and was aligned so as to place a^* precisely coincident with the instrumental ϕ axis. The apparatus and experimental procedure have been described at length previously.[11] Details specific to the present analysis are given below.

Using "high-resolution conditions," the 2θ, ω, and χ settings of the resolved Mo Kα_1 peaks (λ 0.709300 Å)[12] of 12 high-angle (2θ = 38–50°) reflections, which were well-dispersed in reciprocal space, were determined automatically.[13] These values were used in a least-squares refinement of cell and orientation parameters. The resulting cell parameters and their estimated standard deviations[14-16] (at 23.0°) are a = 8.6057 (9) Å, b = 12.1581 (15) Å, c = 13.9868 (19) Å, cos α = 0.0768 (2), cos β = 0.2428 (2), and cos γ = 0.0284 (2). The derived angles are α = 85.60 (2)°, β = 75.95 (1)°, and γ = 88.37 (1)°.[17] The unit-cell volume is 1415.4 Å^3. The measured density (1.468 (5) g cm^{-3}, by neutral buoyancy) is consistent with the value of 1.460 g cm^{-3} calculated for mol wt 622.48 and Z = 2.

Intensity data for reflections in the hemisphere defined by $\pm h,\pm k,+l$ and $2\theta \leq 47.5°$ were collected by executing a coupled θ(crystal)–2θ(counter) scan from 0.6° in 2θ below the Mo Kα_1 peak to 0.6° in 2θ above the Mo Kα_2 peak, the scan rate being 1.0°/min. Stationary-background counts, each of 40-sec duration, were recorded at the two extremes of the scan. The takeoff angle was 3.0° and the diffracted beam was filtered through a niobium β filter (47% transmission of Mo Kα radiation) mounted just in front of the detector aperture (4 mm × 4 mm, 330 mm from the crystal).

The stability of the entire assembly (*i.e.*, X-ray beam, crystal, electronics) was monitored by measuring three reflections (in approximately mutually orthogonal directions in reciprocal space) after each batch of 48 reflections. These reflections decreased steadily in intensity throughout the experiment to about 80% of their initial value. [The surface of the crystal became black, due to decomposition.] Application of an isotropic linear-decay correction to the entire data set led to the root-mean-square fluctuations of the standard reflections from their average values being reduced to 1.00, 0.56, and 0.82%.

The intensity of a reflection, I, and its esd, $\sigma(I)$, were calculated as detailed previously,[11] using an "ignorance factor"[16a,18] p of 0.04. Any negative I was reset to zero.[19]

A total of 4346 symmetry-independent reflections were measured. None was rejected on the basis of being "not significantly above background." We note here that 520 (*i.e.*, *ca.* 12%) of these data had $I < 3\sigma(I)$.

No corrections were made for absorption since θ–2θ scans of the axial 300 reflection at χ = 90° and at 10° intervals from ϕ = 0° to ϕ = 350° showed a variation of less than 2.5% from the mean [μ(Mo Kα) = 5.52 cm^{-1} and μR_{av} = 0.078].

Unscaled structure factor amplitudes, F, and their standard deviations, $\sigma(F)$, were calculated from the expressions $F = (I/Lp)^{1/2}$, $\sigma(F) = (\sigma(I)/Lp)^{1/2}$ for $\sigma(I) \geq I$, and $\sigma(F) = [F - [F^2 - (\sigma(I)/Lp)]^{1/2}]$ for $\sigma(I) < I$. Here Lp, the Lorentz–polarization correction, is given by $(1 + \cos^2 2\theta)/(2 \sin 2\theta)$.

Solution and Refinement of the Structure

All calculations were carried out on the IBM 370/158 computer at the Computer Center of the University of Illinois at Chicago Circle. The following programs were used during the course of the structural analysis: FORDAP, Fourier synthesis, by A. Zalkin; LSHF, structure factor calculation and least-squares refinement, by B. G. DeBoer; STAN1, distances and angles, with esd's, by B. G. DeBoer; PLOD, least-squares planes by B. G. DeBoer; ORTEP, thermal ellipsoid drawings, by C. K. Johnson.

Scattering factors for neutral Mo, P, O, N, and C were taken from the compilation of Cromer and Waber;[20] both the real and the imaginary components of anomalous dispersion were included for all nonhydrogen atoms, using the values of Cromer and Liberman.[21] The Stewart, Davidson, and Simpson scattering factors were used for neutral hydrogen.[22] The function minimized during the least-squares refinement process was $\Sigma w\|F_o| - |F_c\|^2$ where $w(hkl) = \sigma^{-2}[F(hkl)]$.

Discrepancy indices used below are

$$R_F = \frac{\Sigma\|F_o| - |F_c\|}{\Sigma|F_o|} \times 100\ (\%)$$

and

$$R_{wF} = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w|F_o|^2}\right]^{1/2} \times 100\ (\%)$$

The space group was indicated to be the centrosymmetric $P\bar{1}$, rather than as the noncentrosymmetric $P1$, by means of intensity statistics.[23] The positions of the molybdenum and phosphorus atoms were quickly and unambiguously obtained from a three-dimensional Patterson map. A Fourier synthesis, phased by these two atoms (R_F = 59.8%) revealed the locations of all nonhydrogen atoms except one nitrogen atom of a cyanide group. Refinement of positional and isotropic thermal parameters (with the "missing" nitrogen located in the most probable position) led to convergence with R_F = 9.8% and R_{wF} = 12.7%. Refinement was continued, now using anisotropic thermal parameters for the 40 nonhydrogen atoms, and led to convergence with R_F = 5.66% and R_{wF} = 7.78%. A difference-Fourier synthesis at this stage showed an unexpected feature of height ~2 e Å^{-3} about 1 Å from the methyl group of the $C(CN)_2C(CN)_2CH_3$ ligand. A survey of thermal parameters of atoms within this ligand suggested disorder of one cyanide group [C(7)–N(7)] and the methyl group [defined by C(3)]. Accordingly, the nitrogen atom was partitioned between its old position N(7) and a new position, N(7'), corresponding to the anomalous feature in the difference-Fourier synthesis. The system C(2)–C(3)–N(7') was approximately linear. Refinement was continued using coupled occupancy factors of x and $(1 - x)$, respectively, for N(7) and N(7'); convergence was reached with R_F = 5.02% and R_{wF} = 6.57%. Another difference-Fourier synthesis now led to the location of all hydrogen atoms, with peak heights of 0.71–0.32 e Å^{-3} for those of unit occupancy, *ca.* 0.35 e Å^{-3} for hydrogens associated with the C(3) methyl group (occupancy ~65%, based upon an occupancy of ~35% for N(7')), and *ca.* 0.20 e Å^{-3} for the hydrogens of the C(7) methyl group (occupancy ~35%).

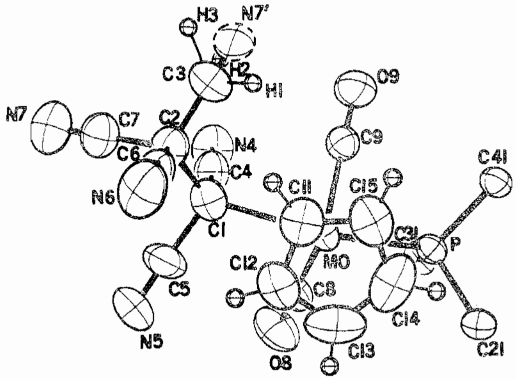


Figure 1. View of the $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)[C(CN)_2C(CN)_2CH_3]$ molecule, showing the disorder within the tetracyanopropyl ligand. [Note that phenyl rings of the PPh_3 group have been omitted.]

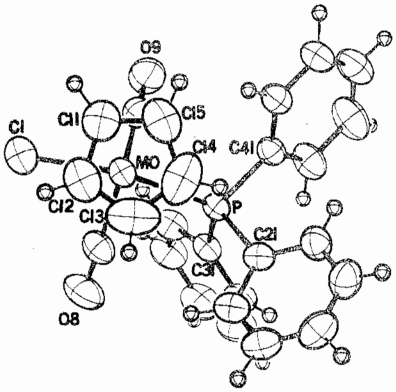


Figure 2. The $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)[C(CN)_2C(CN)_2CH_3]$ molecule, showing the triphenylphosphine ligand. Only atom C(1) of the tetracyanopropyl group is shown.

In the final phase, all positional parameters, anisotropic thermal parameters for nonhydrogen atoms, isotropic thermal parameters for hydrogen atoms, coupled occupancy factors [x for N(7), H(1), H(2), H(3) and $(1 - x)$ for N(7'), H(1'), H(2'), H(3')], and the scale factor were refined. Parameters for H(1'), H(2'), H(3') were not well behaved. These atoms were therefore fixed into positions staggered with respect to the geometry about C(2). The resulting discrepancy indices are R_F = 3.98% and R_{wF} = 4.76%. The maximum shifts during the last cycle of refinement[24] were $(\Delta/\sigma)_{max}$ = 0.05 for a nonhydrogen parameter and $(\Delta/\sigma)_{max}$ = 0.24 for a hydrogen parameter. The final value for x was 0.688 (13).

The "goodness of fit," defined by $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 1.47 (where the number of observations (m) is 4346 and the total number of parameters refined (n) is 463; the ratio m:n is 9.39:1). The function $\sum w(|F_o| - |F_c|)^2$ showed no significant dependence either upon ((sin θ)/λ) or upon $|F_o|$, thereby indicating a correctly chosen weighting scheme. The correctness of the determined structure was confirmed by means of a final difference-Fourier synthesis on which the most prominent features were peaks of 0.98 e Å^{-3} (at 0.45, 0.60, 0.28), 0.81 e Å^{-3} (at 0.33, 0.50, 0.34), 0.74 e Å^{-3} (at 0.18, 0.44, 0.28), 0.63 e Å^{-3} (at 0.51, 0.40, 0.72), 0.58 e Å^{-3} (at 0.21, 0.40, 0.30), and 0.48 e Å^{-3} (at 0.12, 0.18, 0.16); all other peaks were below 0.40 e Å^{-3} in height.

A table of observed and calculated structure factor amplitudes may be obtained.[25] Final positional parameters, with their esd's, are given in Table I; anisotropic thermal parameters (and root-mean-square amplitudes of vibration of atoms along the principal axes of their vibration ellipsoids) are listed in Table II.

The Molecular Structure

Interatomic distances and angles are collected in Tables III and IV, respectively. Least-squares planes are given in Table V. The molecular stereochemistry and labeling of atoms is shown in Figures 1 and 2.

The central molybdenum atom may be regarded as in a formal oxidation state of +II; it has a d^4 outer electron configuration and achieves the expected "noble gas" con-

Table I. Final Positional Parameters, with Esd's[a-d]

Atom	x	y	z	B, Å^2
Mo	0.191986 (27)	0.401270 (19)	0.230614 (18)	2.77
P	0.139756 (82)	0.201735 (58)	0.214191 (52)	2.66
O(8)	0.51565 (29)	0.32386 (22)	0.09427 (21)	5.95
O(9)	0.14592 (33)	0.29402 (21)	0.44642 (18)	5.35
N(4)	0.55761 (35)	0.35533 (26)	0.35758 (26)	5.33
N(5)	0.57766 (52)	0.59615 (35)	0.11730 (28)	7.91
N(6)	0.22347 (54)	0.77104 (28)	0.28767 (34)	7.81
N(7)	0.62275 (70)	0.66574 (52)	0.37976 (53)	7.14
N(7')	0.16494 (130)	0.53543 (105)	0.50960 (83)	6.02
C(1)	0.39250 (40)	0.50471 (27)	0.27871 (28)	4.45
C(2)	0.35560 (44)	0.59564 (29)	0.35336 (29)	4.76
C(3)	0.24493 (49)	0.55095 (34)	0.45069 (30)	5.09
C(4)	0.48561 (38)	0.41932 (29)	0.32193 (28)	4.28
C(5)	0.49803 (46)	0.55899 (34)	0.18779 (27)	5.24
C(6)	0.28352 (54)	0.69494 (29)	0.31218 (33)	5.63
C(7)	0.51244 (51)	0.63708 (33)	0.36987 (34)	5.28
C(8)	0.39894 (38)	0.34891 (26)	0.14693 (25)	3.96
C(9)	0.16703 (36)	0.33276 (24)	0.36592 (23)	3.43
C(11)	0.03215 (43)	0.55991 (29)	0.24453 (32)	4.91
C(12)	0.14092 (46)	0.56620 (31)	0.15124 (31)	5.04
C(13)	0.10347 (54)	0.48199 (42)	0.09675 (30)	6.24
C(14)	−0.02711 (56)	0.42545 (35)	0.15884 (40)	6.37
C(15)	−0.06957 (43)	0.47425 (33)	0.24842 (35)	5.36
C(21)	0.06803 (34)	0.18086 (23)	0.10435 (21)	3.11
C(22)	0.15909 (40)	0.21981 (27)	0.01154 (24)	3.87
C(23)	0.10048 (46)	0.21390 (29)	−0.07174 (25)	4.37
C(24)	−0.04665 (51)	0.16931 (31)	−0.06432 (28)	4.90
C(25)	−0.13941 (49)	0.13134 (33)	0.02712 (29)	5.02
C(26)	−0.08131 (40)	0.13626 (29)	0.11083 (26)	4.17
C(31)	0.31392 (32)	0.10879 (23)	0.20338 (21)	3.04
C(32)	0.34349 (39)	0.02869 (26)	0.13532 (25)	4.04
C(33)	0.46677 (45)	−0.04775 (31)	0.13460 (30)	5.07
C(34)	0.56024 (44)	−0.04336 (32)	0.20255 (31)	5.31
C(35)	0.53086 (42)	0.03595 (32)	0.26990 (29)	4.86
C(36)	0.40970 (37)	0.11287 (28)	0.26996 (24)	3.85
C(41)	−0.00755 (33)	0.12792 (23)	0.31412 (20)	3.09
C(42)	0.00590 (42)	0.01523 (27)	0.33338 (27)	4.45
C(43)	−0.10693 (49)	−0.03932 (34)	0.40893 (32)	5.82
C(44)	−0.23103 (45)	0.01659 (36)	0.46512 (28)	5.25
C(45)	−0.24763 (46)	0.12927 (35)	0.44521 (28)	5.29
C(46)	−0.13559 (39)	0.18374 (29)	0.36996 (25)	4.20
H(1)	0.1348 (49)	0.5327 (33)	0.4485 (32)	3.7 (8)
H(2)	0.2910 (49)	0.4836 (35)	0.4856 (31)	4.0 (9)
H(3)	0.2302 (106)	0.5863 (74)	0.5296 (68)	8.5 (19)
H(1')	0.490	0.693	0.416	5.5
H(2')	0.577	0.667	0.309	5.5
H(3')	0.568	0.578	0.395	5.5
H(11)	0.0289 (56)	0.6104 (40)	0.3013 (35)	8.8 (12)
H(12)	0.2243 (57)	0.6112 (38)	0.1321 (34)	8.4 (11)
H(13)	0.1495 (74)	0.4826 (55)	0.0355 (48)	13.3 (15)
H(14)	−0.0796 (62)	0.3673 (44)	0.1481 (38)	9.6 (12)
H(15)	−0.1468 (65)	0.4598 (45)	0.3120 (41)	10.5 (13)
H(22)	0.2612 (64)	0.2540 (42)	0.0128 (39)	9.8 (12)
H(23)	0.1743 (52)	0.2446 (36)	−0.1330 (36)	8.0 (11)
H(24)	−0.0856 (53)	0.1567 (37)	−0.1204 (34)	8.0 (12)
H(25)	−0.2419 (69)	0.1100 (46)	0.0231 (43)	11.0 (13)
H(26)	−0.1385 (54)	0.1054 (40)	0.1780 (35)	8.8 (11)
H(32)	0.2651 (46)	0.0259 (31)	0.0844 (28)	6.6 (9)
H(33)	0.4781 (47)	−0.1022 (33)	0.0819 (30)	6.8 (9)
H(34)	0.6567 (49)	−0.0932 (32)	0.2039 (30)	7.1 (10)
H(35)	0.5885 (54)	0.0439 (38)	0.3195 (34)	8.1 (11)
H(36)	0.4071 (48)	0.1700 (33)	0.3216 (30)	7.0 (9)
H(42)	0.1032 (54)	−0.0224 (38)	0.2939 (36)	9.0 (14)
H(43)	−0.0781 (55)	−0.1144 (40)	0.4264 (35)	8.8 (12)
H(44)	−0.2945 (52)	−0.0357 (36)	0.5232 (33)	8.0 (10)
H(45)	−0.3385 (54)	0.1689 (38)	0.4980 (34)	8.5 (12)
H(46)	−0.1453 (58)	0.2661 (43)	0.3581 (37)	9.2 (13)

[a] Estimated standard deviations are right-adjusted to the last digit of the preceding number and are those derived from the inverse of the final least-squares matrix. [b] For nonhydrogen atoms the "equivalent isotropic temperature factors" are listed. For anisotropic thermal parameters, see Table II. [c] Occupancy factors are 0.688 (13) for N(7), H(1), H(2), H(3) and 0.312 (−13) for N(7'), H(1'), H(2'), H(3'). [d] C(3) and C(7) are, in fact "composite atoms." C(3) represents ~69% C(methyl) and ~31% C(cyanide), while C(7) represents ~69% C(cyanide) and ~31% C(methyl). However, the difference in the centroids of the superposed part-atoms is no greater than *ca.* 0.1 Å (*i.e.*, the difference between normal C–CH$_3$ and C–CN bond lengths).

Table II. Anisotropic Thermal Parameters[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U\rangle$[b]
Mo	2.460 (16)	2.452 (17)	3.291 (18)	0.134 (11)	−0.680 (12)	0.314 (12)	0.164, 0.180, 0.215
P	2.501 (41)	2.650 (42)	2.692 (42)	0.084 (31)	−0.509 (33)	0.185 (33)	0.171, 0.177, 0.201
O(8)	4.19 (16)	5.97 (19)	6.39 (20)	0.43 (13)	1.04 (15)	−0.01 (16)	0.200, 0.271, 0.335
O(9)	6.94 (20)	4.96 (17)	4.18 (17)	−0.70 (14)	−1.54 (14)	0.36 (14)	0.220, 0.255, 0.300
N(4)	4.03 (19)	5.15 (21)	7.16 (25)	0.94 (16)	−2.19 (18)	−0.31 (19)	0.198, 0.268, 0.303
N(5)	8.97 (33)	8.31 (32)	5.62 (26)	−4.56 (27)	−0.22 (24)	1.41 (23)	0.199, 0.308, 0.408
N(6)	10.56 (39)	3.82 (22)	10.14 (38)	0.41 (23)	−4.87 (32)	0.22 (23)	0.215, 0.308, 0.395
N(7)	6.31 (37)	7.21 (36)	8.55 (48)	−1.05 (26)	−2.74 (29)	−1.18 (30)	0.247, 0.315, 0.334
N(7′)	4.57 (59)	8.37 (78)	4.41 (66)	−1.22 (51)	1.10 (51)	−2.80 (54)	0.178, 0.253, 0.364
C(1)	3.96 (21)	3.89 (21)	5.43 (25)	0.00 (16)	−1.25 (18)	0.43 (18)	0.212, 0.224, 0.271
C(2)	5.04 (18)	4.08 (16)	5.41 (19)	0.01 (13)	−1.81 (15)	−0.21 (14)	0.227, 0.239, 0.269
C(3)	4.53 (20)	5.25 (21)	4.89 (21)	0.12 (16)	−0.21 (19)	0.38 (17)	0.222, 0.247, 0.288
C(4)	3.14 (19)	4.37 (22)	5.46 (25)	0.05 (17)	−1.32 (18)	−0.36 (19)	0.195, 0.235, 0.263
C(5)	5.23 (25)	6.18 (28)	3.63 (22)	−0.73 (21)	−0.02 (19)	0.71 (20)	0.194, 0.278, 0.290
C(6)	7.63 (32)	3.12 (22)	7.16 (32)	0.25 (21)	−3.84 (27)	−0.32 (21)	0.198, 0.244, 0.339
C(7)	5.48 (23)	4.45 (19)	6.13 (25)	−0.24 (17)	−1.76 (21)	−0.52 (18)	0.234, 0.259, 0.281
C(8)	3.72 (20)	3.55 (19)	4.23 (21)	−0.06 (15)	−0.57 (17)	0.79 (16)	0.189, 0.217, 0.260
C(9)	3.79 (19)	3.02 (18)	3.54 (20)	−0.07 (14)	−1.02 (15)	−0.14 (15)	0.195, 0.209, 0.220
C(11)	4.32 (23)	3.88 (22)	6.80 (30)	1.59 (18)	−2.07 (21)	−0.41 (20)	0.171, 0.265, 0.295
C(12)	4.71 (24)	3.89 (22)	6.50 (30)	0.50 (18)	−2.03 (22)	1.73 (21)	0.170, 0.251, 0.315
C(13)	6.25 (31)	8.14 (38)	4.28 (25)	3.73 (29)	−1.97 (23)	0.59 (25)	0.164, 0.253, 0.382
C(14)	6.49 (32)	4.41 (25)	10.16 (44)	2.20 (23)	−5.85 (32)	−1.06 (27)	0.155, 0.256, 0.390
C(15)	3.28 (21)	5.35 (26)	7.50 (33)	1.07 (19)	−1.89 (21)	0.79 (24)	0.171, 0.265, 0.323
C(21)	3.39 (17)	2.97 (17)	2.89 (17)	0.50 (13)	−0.68 (13)	−0.03 (13)	0.179, 0.193, 0.222
C(22)	4.15 (20)	3.77 (19)	3.41 (19)	0.83 (16)	−0.61 (16)	0.07 (15)	0.196, 0.207, 0.257
C(23)	5.73 (25)	4.12 (21)	3.26 (19)	1.17 (18)	−1.27 (18)	−0.05 (16)	0.192, 0.218, 0.286
C(24)	6.81 (29)	4.39 (23)	4.20 (23)	0.57 (20)	−2.74 (21)	−0.35 (18)	0.198, 0.235, 0.303
C(25)	5.54 (25)	5.12 (25)	4.93 (25)	−0.93 (20)	−2.27 (20)	−0.08 (20)	0.216, 0.246, 0.288
C(26)	3.85 (20)	4.68 (22)	4.07 (21)	−0.63 (17)	−1.12 (16)	−0.09 (17)	0.210, 0.225, 0.252
C(31)	2.65 (16)	2.88 (16)	3.29 (17)	0.07 (12)	−0.31 (13)	0.30 (14)	0.177, 0.183, 0.225
C(32)	4.07 (20)	3.41 (19)	4.09 (20)	0.58 (15)	−0.04 (16)	−0.21 (16)	0.204, 0.249, 0.299
C(33)	5.13 (25)	4.33 (23)	5.17 (25)	1.28 (19)	−0.27 (20)	−0.32 (19)	0.195, 0.253, 0.315
C(34)	4.10 (23)	4.90 (25)	6.28 (29)	1.41 (19)	−0.37 (22)	0.33 (22)	0.208, 0.241, 0.289
C(35)	3.80 (21)	5.47 (26)	5.09 (25)	0.70 (18)	−0.98 (18)	0.49 (21)	0.192, 0.215, 0.251
C(36)	3.36 (18)	4.06 (20)	3.95 (20)	0.60 (15)	−0.75 (15)	0.22 (16)	0.182, 0.229, 0.288
C(41)	3.16 (17)	3.21 (17)	2.78 (16)	−0.19 (13)	−0.64 (13)	0.26 (13)	0.178, 0.201, 0.212
C(42)	4.19 (21)	3.53 (20)	5.08 (23)	−0.03 (16)	−0.58 (18)	1.31 (17)	0.182, 0.229, 0.288
C(43)	5.40 (27)	4.85 (25)	6.46 (30)	−0.67 (21)	−0.86 (23)	2.58 (23)	0.185, 0.267, 0.340
C(44)	4.37 (24)	6.74 (31)	4.16 (23)	−0.82 (21)	−0.47 (19)	1.13 (21)	0.202, 0.251, 0.310
C(45)	4.65 (24)	6.58 (30)	4.02 (23)	−1.56 (21)	0.43 (18)	−0.63 (21)	0.195, 0.252, 0.315
C(46)	3.69 (20)	4.19 (21)	4.24 (21)	−0.46 (16)	0.08 (16)	−0.51 (17)	0.197, 0.226, 0.264

[a] These anisotropic thermal parameters are analogous to the usual form of the isotropic thermal parameters and have units of Å^2. They enter the expression for the structure factor in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.
[b] These values correspond to the root-mean-square amplitudes of vibration (in Å) of the atom along the three principal axes (minor, median, major, respectively) of its vibration ellipsoid. For relative orientations, see the figures.

figuration by the donation of six electrons from a π-cyclopentadienyl anion, two electrons from each of the two carbonyl ligands, two electrons from the triphenylphosphine ligand, and two electrons from the tetracyanopropyl ligand. The overall coordination geometry about the molybdenum(II) atom is, perhaps, most graphically described as "resembling a four-legged piano stool." Angles between the monodentate ligands show considerable variation, with large "trans angles" [P–Mo–C(1) = 136.84 (8)° and C(8)–Mo–C(9) = 108.41 (13)°] and smaller "cis angles" [P–Mo–C(8) = 76.70 (9)°, P–Mo–C(9) = 76.31 (9)°, C(1)–Mo–C(8) = 75.93 (13)°, and C(1)–Mo–C(9) = 81.50 (12)°]. As might be expected, this pattern of angles is very similar to that found in (π-C_5H_5)Mo(CO)$_2$(PPh$_3$)(COCH$_3$)[26] [P–Mo–C(acyl) = 132.7 (4)°, OC–Mo–CO = 107.9 (5)°, P–Mo–CO = 78.3 (3) and 79.8 (4)°, C(acyl)–Mo–CO = 73.2 (5) and 74.2 (5)°] and in such related species as (π-C_5H_5)Mo(CO)$_3$(C_2H_5),[27] (π-C_5H_5)Mo(CO)$_3$(C_3F_7),[10] (π-C_5H_5)Mo(CO)$_3$(CH$_2$CO$_2$H),[28] [(azulene)Mo(CO)$_3$CH$_3$]$_2$,[29] (π-C_5H_5)W(CO)$_3$(σ-C_6H_5),[30] [(π-C_5H_5)Mo(CO)$_3$]$_2$,[31,32] [(π-C_5H_5)W(CO)$_3$]$_2$,[31] [(π-C_5H_5)Cr(CO)$_3$]$_2$,[33] (π-C_5H_5)W(CO)$_3$(AuPPh$_3$),[34] (π-C_5H_5)Mo(CO)$_3$–Mo(CO)$_2$(CNMe)(π-C_5H_5),[35] [(π-C_5H_5)Mo(CO)$_3$]$_3$Tl,[36] [(π-C_5H_5)Mo(CO)$_3$][(π-C_5H_5)Fe(CO)$_2$]$_2$SnCl,[37] [(π-C_5H_5)Mo(CO)$_3$S][Re$_2$Mo(π-C_5H_5)(CO)$_8$](S),[38] (π-C_5H_5)Mo(CO)$_3$Cl,[39] and (π-C_5H_5)Mo(CO)$_2$($\ddot{\text{N}}$HNC(CO$_2$Et)$\ddot{\text{C}}$OH.[40]

Angles from "c.o.g." (the centroid of the π-cyclopentadienyl ligand) to the monodentate ligands show considerably less variation, with c.o.g.–Mo–P = 111.51°, c.o.g.–Mo–C(1) = 111.42°, c.o.g.–Mo–C(8) = 124.20°, and c.o.g.–Mo–C(9) = 127.34°. The overall rotational conformation of the molecule is such that the triphenylphosphine–metal linkage passes essentially below C(14) [P···C(13) = 3.706 (5), P···C(14) = 3.171 (4), P···C(15) = 3.733 (4) Å], C(1) lies beneath the C(11)–C(12) bond [C(1)···C(11) = 3.294 (5), C(1)···C(12) = 3.163 (5) Å], and the carbonyl ligands lie asymmetrically below the C(12)–C(13) and C(11)–C(15) bonds [C(8)···C(12) = 3.397 (5), C(8)···C(13) = 3.168 (5) Å; C(9)···C(11) = 3.451 (5), C(9)···C(15) = 3.286 (5) Å]. The immediate coordination environment of the molybdenum(II) atom thus approximates to $C_s(m)$ symmetry.

Individual molybdenum–carbon distances for the π-cyclopentadienyl ligand vary significantly, from Mo–C(12) = 2.300 (3) to Mo–C(15) = 2.359 (3) Å [difference = 0.059 Å or ~18σ].[41] We note here that this seems to be a general phenomenon for this type of complex: Mo–C distances from 2.310 (13) to 2.376 (14) Å were found in (π-C_5H_5)Mo(CO)$_2$(PPh$_3$)(COCH$_3$),[26] while the range in [(azulene)Mo(CO)$_3$CH$_3$]$_2$[29] is from 2.286 (10) to 2.439 (9) Å.

Nevertheless, the five carbon atoms of the π-cyclopentadienyl ligand are coplanar within the limits of experimental error, the root-mean-square deviations from the

Table III. Interatomic Distances (in Å) with Estimated Standard Deviations[a]

Atoms	Dist	Atoms	Dist
(a) Distances from the Molybdenum Atom			
Mo–C(1)	2.414 (4)	Mo–P	2.5175 (8)
Mo···C(2)	3.536 (4)		
Mo–C(8)	1.996 (3)	Mo···O(8)	3.135 (2)
Mo–C(9)	1.973 (3)	Mo···O(9)	3.132 (2)
Mo–c.o.g[b]	2.007		
Mo–C(11)	2.330 (3)	Mo···H(11)	2.99 (5)
Mo–C(12)	2.300 (3)	Mo···H(12)	2.79 (5)
Mo–C(13)	2.327 (4)	Mo···H(13)	2.93 (7)
Mo–C(14)	2.343 (4)	Mo···H(14)	2.90 (5)
Mo–C(15)	2.359 (3)	Mo···H(15)	2.95 (5)
(b) Distances within $C(CN)_2C(CN)_2CH_3$ Ligand			
C(1)–C(2)	1.552 (5)	C(1)···C(7)[c]	2.516 (5)
C(1)···C(3)[c]	2.530 (5)	C(1)···N(4)	2.616 (4)
C(1)–C(4)	1.475 (5)	C(1)···N(5)	2.615 (5)
C(1)–C(5)	1.491 (5)	C(2)···N(7′)	2.467 (11)
C(2)–C(3)[c]	1.530 (5)	C(2)···N(6)	2.599 (5)
C(2)–C(6)	1.483 (5)	C(2)···N(7)	2.592 (7)
C(2)–C(7)[c]	1.529 (6)	C(5)–N(5)	1.126 (5)
C(3)–N(7′)[c]	0.947 (10)	C(6)–N(6)	1.118 (5)
C(4)–N(4)	1.141 (4)	C(7)–N(7)[c]	1.064 (6)
(c) Distances within Carbonyl Ligands			
C(8)–O(8)	1.141 (4)	C(9)–O(9)	1.161 (4)
(d) Distances within π-C_5H_5 Ligand			
C(11)–C(12)	1.407 (6)	C(11)–H(11)	1.03 (5)
C(12)–C(13)	1.411 (6)	C(12)–H(12)	0.89 (5)
C(13)–C(14)	1.403 (7)	C(13)–H(13)	0.85 (6)
C(14)–C(15)	1.391 (6)	C(14)–H(14)	0.89 (5)
C(15)–C(11)	1.369 (5)	C(15)–H(15)	0.98 (5)
(e) Distances within PPh_3 Ligand			
C(21)–C(22)	1.399 (4)	C(21)–P	1.826 (3)
C(22)–C(23)	1.384 (5)	C(22)–H(22)	0.99 (5)
C(23)–C(24)	1.369 (5)	C(23)–H(23)	0.99 (5)
C(24)–C(25)	1.386 (5)	C(24)–H(24)	0.95 (5)
C(25)–C(26)	1.386 (5)	C(25)–H(25)	0.94 (6)
C(26)–C(21)	1.389 (4)	C(26)–H(26)	1.00 (5)
C(31)–C(32)	1.389 (4)	C(31)–P	1.835 (3)
C(32)–C(33)	1.389 (5)	C(32)–H(32)	1.09 (4)
C(33)–C(34)	1.391 (6)	C(33)–H(33)	1.01 (4)
C(34)–C(35)	1.375 (6)	C(34)–H(34)	1.02 (4)
C(35)–C(36)	1.381 (5)	C(35)–H(35)	0.96 (5)
C(36)–C(31)	1.390 (5)	C(36)–H(36)	1.04 (4)
C(41)–C(42)	1.383 (4)	C(41)–P	1.838 (3)
C(42)–C(43)	1.389 (5)	C(42)–H(42)	1.00 (4)
C(43)–C(44)	1.361 (6)	C(43)–H(43)	0.97 (5)
C(44)–C(45)	1.387 (6)	C(44)–H(44)	1.04 (4)
C(45)–C(46)	1.383 (5)	C(45)–H(45)	1.07 (4)
C(46)–C(41)	1.380 (4)	C(46)–H(46)	1.01 (5)
(f) Carbon–Hydrogen Distances within Methyl Groups			
C(3)–H(1)	0.99 (4)	C(3)–H(3)	1.19 (9)
C(3)–H(2)	1.04 (4)		
(g) Contacts within Coordination Sphere (to 4.0 Å)			
P···C(13)	3.706 (5)	C(8)···C(12)	3.397 (5)
P···C(14)	3.171 (4)	C(8)···C(13)	3.168 (5)
P···C(15)	3.733 (4)	C(8)···C(14)	3.724 (5)
C(1)···C(11)	3.294 (5)	C(9)···C(14)	3.767 (5)
C(1)···C(12)	3.163 (5)	C(9)···C(15)	3.286 (5)
C(1)···C(13)	3.995 (6)	C(9)···C(11)	3.451 (5)

[a] Esd's, shown in parentheses, are right-adjusted to the last digit of the preceding number. They are calculated from the full positional correlation matrix using the FORTRAN IV program STAN1 by B. G. DeBoer. Contributions from errors in the unit cell parameters are included. No distances have been corrected for possible librational effects. [b] c.o.g. is the centroid of the π-cyclopentadienyl ligand. [c] Unreliable, due to disorder.

least-squares plane being only 0.002 Å (see Table V). The molybdenum atom lies +2.006 Å from this plane, while deviations of hydrogen atom range from +0.07 to −0.13 Å (σ = 0.06 Å).

Carbon–carbon distances within the π-cyclopentadienyl ligand range from C(15)–C(11) = 1.369 (5) to C(12)–C(13) = 1.411 (6) Å, the mean value being 1.396 ± 0.020 Å.[42] This is contracted from the true C–C(π-cyclopentadienyl) distance of ~1.43 Å as a result of libration of the five-membered ring about its molybdenum–c.o.g. axis. (See relative orientations of the atomic vibration ellipsoids in Figure 1.)

Carbon–hydrogen distances within the π-cyclopentadienyl ligand range from 0.85 (6) to 1.03 (5) Å, with an average value of 0.93 ± 0.07 Å,[42] which is less than the accepted internuclear distance of 1.08 Å, but is consistent with other X-ray-determined C–H distances.[43] Angles within the π-cyclopentadienyl system are as expected, with C–C–C angles ranging from 106.28 (37) to 108.95 (40)° [mean 108.00°] and H–C–C angles ranging from 115.0 (33) to 136.4 (34)° [mean 125.9°].

The carbonyl ligands are slightly, but significantly, distorted from linearity, with Mo–C(8)–O(8) = 175.50 (30)° and Mo–C(9)–O(9) = 177.20 (29)°.[44] Molybdenum–carbonyl distances are Mo–C(8) = 1.996 (3) and Mo–C(9) = 1.973 (3) Å [average 1.985 ± 0.016 Å[42]], while carbon–oxygen distances are C(8)–O(8) = 1.141 (4) and C(9)–O(9) = 1.161 (4) Å [average 1.151 ± 0.014 Å[42]].

The Triphenylphosphine Ligand

The molybdenum–phosphorus distance of 2.5175 (8) Å is slightly longer than that of 2.473 (3) Å found[26] in $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)(COCH_3)$ but is still substantially contracted from the predicted single-bond length of ~2.72 Å [based on r(Mo) = 1.62 Å, using half the Mo–Mo distance of 3.235 (1) Å in $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$[31] and r(P) = 1.10 Å[45]]. This suggests significant π character in the metal–phosphorus bond, presumably through dπ–dπ back-donation.

Phosphorus–carbon distances are 1.826 (3), 1.835 (3), and 1.838 (3) Å, giving an average value of 1.833 ± 0.006 Å.[42] As is generally observed for metal complexes of triphenylphosphine,[46] angles about the phosphorus atom show pronounced deviations from perfect T_d symmetry. Thus, Mo–P–C angles are all substantially greater than the ideal tetrahedral angle of 109.47° [Mo–P–C(21) = 112.84 (9)°, Mo–P–C(31) = 115.58 (9)°, Mo–P–C(41) = 118.37 (10)°], while C–P–C angles are all contracted from this value [C(21)–P–C(31) = 103.77 (13)°, C(21)–P–C(41) = 103.27 (13)°, C(31)–P–C(41) = 101.12 (13)°].

The 18 independent carbon–carbon distances range from 1.361 (6) to 1.399 (4) Å, averaging 1.384 ± 0.009 Å,[42] as compared to the accepted C–C(aromatic) distance of 1.394 ± 0.005 Å.[47] C–C–C angles within the phenyl rings range from 118.64 (30) to 121.16 (34)°, averaging 120.00°. The internal angles at the P-bonded carbons are all less than 120°, individual values being C(26)–C(21)–C(22) = 118.64 (30)°, C(36)–C(31)–C(32) = 119.61 (28)°, and C(46)–C(41)–C(42) = 118.81 (28)°. This pattern of small angles at the P-bonded carbons has been noted previously in $(PPh_3CuBr)_4$,[48] $(PPh_3CuCl)_4$,[49] $(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)Br$,[50] and $(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)_2$[51] and is probably a general phenomenon.[52]

Carbon–hydrogen distances within the triphenylphosphine ligand vary from 0.94 (6) to 1.09 (4) Å, the average of the 15 independent values being 1.01 ± 0.04 Å,[42] as opposed to the expected value of ~0.95 Å.[43] H–C–C angles within the phenyl rings range from 110.1 (24) to 130.0 (25)°, the mean value being 119.8°.

Each of the phenyl rings is planar, rms deviations from planarity being 0.004 Å for C(21)–C(26), 0.006 Å for C(31)–C(36), and 0.007 Å for C(41)–C(46). Hydrogen atoms are (within the limits of experimental error) coplanar with the carbocyclic rings, the greatest deviations being (in order) 0.16 Å for H(43), 0.14 Å for H(45), 0.12 Å for H(44), 0.10 Å for

Table IV. Interatomic Angles (in deg) with Estimated Standard Deviations[a]

Atoms	Angle	Atoms	Angle
(a) Angles around Molybdenum Atom			
P-Mo-C(1)	136.84 (8)	c.o.g.-Mo-P[b]	111.51
P-Mo-C(8)	76.70 (9)	c.o.g.-Mo-C(1)	111.42
P-Mo-C(9)	76.31 (9)	c.o.g.-Mo-C(8)	124.20
C(1)-Mo-C(8)	75.93 (13)	c.o.g.-Mo-C(9)	127.34
C(1)-Mo-C(9)	81.50 (12)		
C(8)-Mo-C(9)	108.41 (13)		
(b) Angles around Phosphorus Atom			
Mo-P-C(21)	112.84 (9)	C(21)-P-C(31)	103.77 (13)
Mo-P-C(31)	115.58 (9)	C(21)-P-C(41)	103.27 (13)
Mo-P-C(41)	118.37 (10)	C(31)-P-C(41)	101.12 (13)
(c) Angles within $C(CN)_2C(CN)_2CH_3$ Ligand			
Mo-C(1)-C(2)	124.66 (23)	C(1)-C(2)-C(3)	110.29 (30)
Mo-C(1)-C(4)	103.81 (21)	C(1)-C(2)-C(6)	111.27 (33)
Mo-C(1)-C(5)	108.36 (25)	C(1)-C(2)-C(7)	109.49 (30)
C(2)-C(1)-C(4)	105.50 (31)	C(3)-C(2)-C(6)	110.48 (34)
C(2)-C(1)-C(5)	104.79 (29)	C(3)-C(2)-C(7)	111.14 (34)
C(4)-C(1)-C(5)	109.11 (31)	C(6)-C(2)-C(7)	104.02 (31)
C(1)-C(4)-N(4)	177.91 (44)	C(2)-C(6)-N(6)	175.14 (56)
C(1)-C(5)-N(5)	177.20 (51)	C(2)-C(7)-N(7)	178.79 (51)
		C(2)-C(3)-N(7′)	169.23 (98)
(d) Angles within Carbonyl Groups			
Mo-C(8)-O(8)	175.50 (30)	Mo-C(9)-O(9)	177.20 (29)
(e) C-C-C Angles within π-C_5H_5 Ligand			
C(15)-C(11)-C(12)	108.31 (39)	C(13)-C(14)-C(15)	108.95 (40)
C(11)-C(12)-C(13)	108.01 (37)	C(14)-C(15)-C(11)	108.46 (41)
C(12)-C(13)-C(14)	106.28 (37)		
(f) H-C-C Angles within π-C_5H_5 Ligand			
H(11)-C(11)-C(15)	125.2 (27)	H(13)-C(13)-C(14)	134.6 (48)
H(11)-C(11)-C(12)	126.5 (27)	H(14)-C(14)-C(13)	129.9 (35)
H(12)-C(12)-C(11)	125.8 (31)	H(14)-C(14)-C(15)	121.2 (35)
H(12)-C(12)-C(13)	125.9 (31)	H(15)-C(15)-C(14)	136.4 (34)
H(13)-C(13)-C(12)	118.2 (47)	H(15)-C(15)-C(11)	115.0 (33)
(g) C-C-C Angles within PPh_3 Ligand			
C(26)-C(21)-C(22)	118.64 (30)	C(36)-C(31)-C(32)	119.61 (28)
C(21)-C(22)-C(23)	120.29 (33)	C(31)-C(32)-C(33)	120.22 (35)
C(22)-C(23)-C(24)	120.44 (34)	C(32)-C(33)-C(34)	119.43 (36)
C(23)-C(24)-C(25)	120.13 (34)	C(33)-C(34)-C(35)	120.30 (34)
C(24)-C(25)-C(26)	119.83 (36)	C(34)-C(35)-C(36)	120.40 (38)
C(25)-C(26)-C(21)	120.65 (33)	C(35)-C(36)-C(31)	120.04 (33)
C(46)-C(41)-C(42)	118.81 (28)	C(43)-C(44)-C(45)	119.63 (34)
C(41)-C(42)-C(43)	119.90 (34)	C(44)-C(45)-C(46)	119.47 (36)
C(42)-C(43)-C(44)	120.99 (37)	C(45)-C(46)-C(41)	121.16 (34)
(h) (Substituent)-C-C Angles within PPh_3 Ligand			
P-C(21)-C(26)	121.85 (23)	P-C(31)-C(36)	119.13 (23)
P-C(21)-C(22)	119.25 (24)	P-C(31)-C(32)	121.04 (24)
H(22)-C(22)-C(21)	114.4 (31)	H(32)-C(32)-C(31)	118.5 (20)
H(22)-C(22)-C(23)	125.2 (31)	H(32)-C(32)-C(33)	121.3 (20)
H(23)-C(23)-C(22)	113.3 (27)	H(33)-C(33)-C(32)	113.8 (24)
H(23)-C(23)-C(24)	126.3 (27)	H(33)-C(33)-C(34)	126.8 (24)
H(24)-C(24)-C(23)	122.7 (28)	H(34)-C(34)-C(33)	124.1 (24)
H(24)-C(24)-C(25)	117.0 (28)	H(34)-C(34)-C(35)	115.5 (24)
H(25)-C(25)-C(24)	111.7 (36)	H(35)-C(35)-C(34)	125.4 (28)
H(25)-C(25)-C(26)	128.3 (37)	H(35)-C(35)-C(36)	114.2 (28)
H(26)-C(26)-C(25)	123.8 (27)	H(36)-C(36)-C(35)	111.4 (23)
H(26)-C(26)-C(21)	115.5 (27)	H(36)-C(36)-C(31)	128.6 (23)
P-C(41)-C(46)	120.51 (23)	H(44)-C(44)-C(43)	110.1 (24)
P-C(41)-C(42)	120.67 (23)	H(44)-C(44)-C(45)	130.0 (25)
H(42)-C(42)-C(41)	117.0 (27)	H(45)-C(45)-C(44)	115.1 (25)
H(42)-C(42)-C(43)	123.0 (28)	H(45)-C(45)-C(46)	124.8 (26)
H(43)-C(43)-C(42)	114.7 (28)	H(46)-C(46)-C(45)	119.0 (29)
H(43)-C(43)-C(44)	123.1 (28)	H(46)-C(46)-C(41)	119.7 (29)
(i) Angles within Methyl Groups			
C(2)-C(3)-H(1)	116.5 (26)	H(1)-C(2)-H(2)	107.6 (33)
C(2)-C(3)-H(2)	114.5 (23)	H(1)-C(2)-H(3)	104.4 (47)
C(2)-C(3)-H(3)	126.3 (46)	H(2)-C(2)-H(3)	81.6 (46)

[a] See footnote *a* to Table III. [b] See footnote *b* to Table III.

Table V. Least-Squares Planes and Deviations of Atoms from Those Planes[a,b]

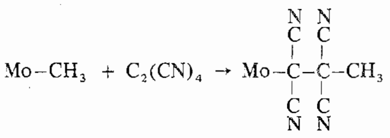
Atom	Dev, Å	Atom	Dev, Å
Plane I: $0.73415X - 0.57696Y + 0.35797Z = -2.0910$			
C(11)*	−0.000	H(11)	0.01
C(12)*	0.002	H(12)	0.07
C(13)*	−0.003	H(13)	−0.13
C(14)*	0.003	H(14)	0.02
C(15)*	−0.002	H(15)	0.05
		Mo	2.006
C(1)	2.841	P	2.973
C(8)	3.091	O(8)	3.634
C(9)	3.239	O(9)	3.919
Plane II: $-0.39904X + 0.90689Y + 0.13533Z = 1.9288$			
C(21)*	−0.001	P	0.160
C(22)*	0.001	H(22)	0.05
C(23)*	0.002	H(23)	0.01
C(24)*	−0.006	H(24)	−0.10
C(25)*	0.007	H(25)	0.09
C(26)*	−0.003	H(26)	−0.06
Plane III: $0.49105X + 0.58133Y - 0.64879Z = 0.8226$			
C(31)*	−0.006	P	−0.180
C(32)*	−0.000	H(32)	−0.03
C(33)*	0.003	H(33)	0.01
C(34)*	0.000	H(34)	0.06
C(35)*	−0.006	H(35)	−0.02
C(36)*	0.009	H(36)	0.06
Plane IV: $0.72768X + 0.23167Y + 0.64561Z = 3.8961$			
C(41)*	0.009	P	0.004
C(42)*	−0.004	H(42)	0.05
C(43)*	−0.006	H(43)	0.16
C(44)*	0.010	H(44)	0.12
C(45)*	−0.005	H(45)	0.14
C(46)*	−0.004	H(46)	0.03

Dihedral Angles

Planes	Value, deg	Planes	Value, deg
I-II	140.15	II-III	75.91
I-III	101.95	II-IV	89.59
I-IV	129.17	III-IV	85.81

[a] Equations for planes are in Cartesian coordinates such that $X = xa \sin\gamma + [zc(\cos\beta - \cos\alpha\cos\gamma)/\sin\gamma]$, $Y = yb + xa\cos\gamma + zc\cos\alpha$, and $Z = zc[(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)/\sin^2\gamma]^{1/2}$. This corresponds to defining the mutually orthogonal directions as $(b \times c^*)$, b, and c^*. [b] Planes are derived using unit weights for atoms marked with an asterisk and zero weight for all other atoms.

Scheme II



$$\mathrm{Mo{-}CH_3} + \mathrm{C_2(CN)_4} \rightarrow \mathrm{Mo{-}C(CN)_2{-}C(CN)_2{-}CH_3}$$

H(24), and 0.09 Å for H(25) [$\sigma \approx 0.05$ Å]. The phosphorus atom is essentially coplanar with the phenyl ring defined by C(41) through C(46) [deviation 0.004 Å] but is displaced significantly from the planes of the other two phenyl groups—by 0.160 Å from the C(21)–C(26) plane and by 0.180 Å from the C(31)–C(36) plane.

The Tetracyanopropyl Ligand

The present crystallographic study confirms that tetracyanoethylene "inserts" into a molybdenum–methyl linkage, as indicated in Scheme II.

However, as clearly shown in Figure 1, the resulting 1,-1,2,2-tetracyanopropyl ligand is subject to disorder in the crystalline state. Thus, one 2-cyano substituent and the methyl group are disordered such that in ~69% of the molecules the cyano substituent is defined by C(7)–N(7) and the methyl group by C(3), H(1), H(2), and H(3); in the remaining ~31% of the molecules in the crystal, the cyano group is defined by C(3)–N(7′) and the methyl group by C(7), H(1′), H(2′), and H(3′). The most serious consequence of this is that the refined position of C(3) represents a "composite atom" comprised of ~69% C(CN) and ~31% C(CH_3); the same argument, *mutatis mutandis*, applies to C(7). Since C(sp^3)–CH_3 and C(sp^3)–CN bond lengths differ by ~0.1 Å, it follows that all distances and angles involving atoms C(3) and C(7) should be taken *cum grano salis*. We restrict our discussion, therefore, to the initial Mo–C$(CN)_2$–C fragment of the tetracyanopropyl ligand. [Other distances and angles are, however, provided in Tables III and IV.]

Table VI. Molybdenum–Carbon σ-Bond Lengths (in Å)

Complex	Bond	Length	Ref
$(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)\cdot[C(CN)_2C(CN)_2CH_3]$	$Mo{-}C(CN)_2{-}C(CN)_2CH_3$	2.414 (4)	This work
$(\pi\text{-}C_5H_5)Mo(CO)_3(C_2H_5)$	$Mo{-}C_2H_5$	2.397 (19)	27b
$[(azulene)Mo(CO)_3(CH_3)]_2$	$Mo{-}CH_3$	2.383 (10)	29
$(\pi\text{-}C_5H_5)Mo(CO)_3(CH_2CO_2H)$	$Mo{-}CH_2CO_2H$[a]	2.370 (22)	28
$(\pi\text{-}C_5H_5)Mo(CO)_3C_3F_7$	$Mo{-}C_3F_7$	2.288 (9)	10
$(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)\cdot(COCH_3)$	$Mo{-}COCH_3$	2.264 (14)	26
$(\pi\text{-}C_7H_7)Mo(CO)_2(C_6F_5)$	$Mo{-}C_6F_5$	2.244 (9)	*b*
$(C_5H_5)_3Mo(NO)$[c]	$Mo{-}(\sigma\text{-}C_5H_5)$[c]	2.291 (3)	*d*

[a] See footnote 53. [b] M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 1110 (1969). [c] The overall stereochemistry about molybdenum and oxidation state in this molecule are markedly different from others in this table. The low Mo–C(sp^3) bond length thus provides no inconsistency with the other data. [d] J. L. Calderon, F. A. Cotton, and P. Legzdins, *J. Amer. Chem. Soc.*, 91, 2528 (1969).

The molybdenum–tetracyanopropyl σ bond, Mo–C(1), is 2.414 (4) Å in length. This may be compared with the reported molybdenum–alkyl distances of 2.383 (10) Å [for Mo–CH_3 in $[(azulene)Mo(CO)_3CH_3]_2$[29]], 2.397 (19) Å [for Mo–C_2H_5 in $(\pi\text{-}C_5H_5)Mo(CO)_3(C_2H_5)$[27b]], and 2.370 (22) Å[53] [for Mo–CH_2CO_2H in $(\pi\text{-}C_5H_5)Mo(CO)_3(CH_2CO_2H)$[28]]; the weighted average of these three values is 2.384 ± 0.008 Å.[54]

It thus appears that a molybdenum–polycyanoalkyl[55] bond is slightly, but significantly, *longer* than a normal molybdenum–alkyl distance. [The difference of 0.030 Å corresponds to 3.3σ.] This result is in contrast to studies on the molybdenum–perfluoroalkyl complex $(\pi\text{-}C_5H_5)Mo(CO)_3(C_3F_7)$,[10] where the Mo–$C_3F_7$ linkage of 2.288 (9) Å is 0.096 Å (*i.e.*, ~9.8σ) *shorter* than the above molybdenum–alkyl distance. Our present result is particularly surprising in view of the fact that both fluoro and cyano substituents act as net electron withdrawers in both aromatic and aliphatic organic systems.

The molybdenum–polycyanoalkyl bond length is compared with related molybdenum–carbon σ-bond lengths in Table VI.

Angles about C(1) show pronounced deviations from T_d symmetry with Mo–C(1)–C(2) = 124.66 (23)°; other angles are Mo–C(1)–C(4) = 103.81 (21)°, Mo–C(1)–C(5) = 108.36 (25)°, C(2)–C(1)–C(4) = 105.50 (31)°, C(2)–C(1)–C(5) = 104.79 (29)°, and C(4)–C(1)–C(5) = 109.11 (31)°. The increase of the Mo–C(α)–C(β) angle from a regular tetrahedral angle of 109.47° seems to be common to all species with a Mo–C(sp^3)–C(sp^3) moiety; thus the Mo–CH_2–CH_3 angle in $(\pi\text{-}C_5H_5)Mo(CO)_3(C_2H_5)$[27b] is 120.9 (11)°, while the Mo–CF_2–C_2F_5 angle in $(\pi\text{-}C_5H_5)Mo(CO)_3(C_3F_7)$[10] is 123.3°. There is thus no correlation between this angle and the observed Mo–C(α) bond length.

Within the tetracyanopropyl ligand, the accurately determined C–CN distances are C(1)–C(4) = 1.475 (5), C(1)–C(5) = 1.491 (5), and C(2)–C(6) = 1.483 (5) Å. The average C–CN distance of 1.483 ± 0.008 Å[42] may be compared with that of 1.473 ± 0.004 Å found in $(\pi\text{-}C_5H_5)Fe(CO)_2[C_4H_7(CN)_4]$,[7] while the C(1)–C(2) distance of 1.552 (5) Å is comparable to the previously determined –C$(CN)_2$–C$(CN)_2$– bond length of 1.602 ± 0.005 Å.[7]

Acknowledgment. We thank Professor A. Wojcicki for providing a sample of the complex and for his continuing interest in these studies. This research was made possible by a generous allocation of time on the IBM 370/158 computer at the Computer Center of the University of Illinois at Chicago Circle and by the financial support of the National Science Foundation through Grant No. GP-42724X (to M. R. C.).

Registry No. I, 52992-52-6.

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 Street, 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 AIC40489J.

References and Notes

(1) The literature on "insertion reactions" has been covered comprehensively by two recent review articles, *viz.*, A. Wojcicki, *Advan. Organometal. Chem.*, **11**, 87 (1973); **12**, 31 (1974).
(2) M. R. Churchill and J. Wormald, *Inorg. Chem.*, **9**, 2430 (1970); M. R. Churchill, J. Wormald, D. A. T. Young, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **91**, 7201 (1969).
(3) M. R. Churchill and J. Wormald, *J. Amer. Chem. Soc.*, **93**, 354 (1971); M. R. Churchill, J. Wormald, D. A. Ross, and A. Wojcicki, *ibid.*, **92**, 1795 (1970).
(4) M. R. Churchill and J. Wormald, *Inorg. Chem.*, **10**, 572 (1971).
(5) M. R. Churchill, B. G. DeBoer, and K. L. Kalra, *Inorg. Chem.*, **12**, 1646 (1973); M. R. Churchill, B. G. DeBoer, K. L. Kalra, P. Reich-Rohrwig, and A. Wojcicki, *J. Chem. Soc., Chem. Commun.*, 981 (1972).
(6) M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, **12**, 1650 (1973).
(7) M. R. Churchill and S. W.-Y. Ni Chang, *J. Amer. Chem. Soc.*, **95**, 5931 (1973).
(8) S. R. Su, J. A. Hanna, and A. Wojcicki, *J. Organometal. Chem.*, **21**, P21 (1970); S. R. Su and A. Wojcicki, preceding paper.
(9) M. R. Churchill, *Perspect. Struct. Chem.*, **3**, 91 (1970); see, especially, Table 8 on p 153.
(10) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **6**, 1213 (1967); M. R. Churchill and J. P. Fennessey, *Chem. Commun.*, 695 (1966).
(11) M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **12**, 525 (1973).
(12) J. A. Bearden, *Rev. Mod. Phys.*, **39**, 78 (1967).
(13) Crystal orientation, centering of reflections, least-squares refinement of cell parameters and orientation parameters, and the θ–2θ scan were all performed using local versions of the programs written originally by Busing and Levy and adapted by the Picker Corp. to the PDP8/I computer which forms part of the FACS-1 system: see W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **22**, 457 (1967).
(14) Here (and elsewhere in this article) the estimated standard deviations (esd's) are given in parentheses and are right-adjusted to the last digit of the preceding number.
(15) As has been pointed out elsewhere (*e.g.*, ref 16a) the cell parameters should be looked upon as "instrumental cell parameters" since they may be affected by systematic errors (*e.g.*, imperfections in the diffractometer *per se*, alignment errors of the diffractometer, and errors in centering the crystal precisely). Similarly, the esd's of the parameters are estimates of precision rather than of absolute accuracy (*cf.* ref 16b).
(16) (a) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967); (b) G. L. Simon and L. F. Dahl, *J. Amer. Chem. Soc.*, **95**, 2164 (1973); see, especially, footnote 28.
(17) The parameters given here define a "type I" or "positive" reduced cell (*i.e.*, all angles acute): see "International Tables for X-Ray Crystallography," Vol. I, 3rd ed, Kynoch Press, Birmingham, England, p 531.
(18) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).
(19) Data reduction was performed using the FORTRAN IV program RDUS, by B. G. DeBoer.
(20) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(21) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(22) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(23) I. L. Karle, K. S. Dragonette, and S. A. Brenner, *Acta Crystallogr.*, **19**, 713 (1965).
(24) The large number of variables led to our refining parameters in blocks. First, parameters for the $(\pi\text{-}C_5H_5)Mo(CO)_2[C(CN)_2C(CN)_2CH_3]$ portion of the molecule were refined; second, parameters for the PPh_3 ligand were refined. This process was repeated. Third (and finally), all positional parameters were refined, while all other parameters were held constant (three cycles). The full positional correlation matrix from the last cycle of refinement was used as an input to STAN1, for calculating esd's on distances and angles. Within the tables of positional and thermal parameters, the esd's are from the last cycle in which that particular parameter was refined.
(25) See paragraph at end of paper regarding supplementary material.
(26) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **7**, 953 (1968).
(27) (a) M. J. Bennett and R. Mason, *Proc. Chem. Soc., London*, 273 (1963); (b) M. J. Bennett, Ph.D. Thesis, Sheffield, England, 1965, pp 38–74.
(28) (a) J. K. P. Ariyaratne, A. M. Bjerrum, M. L. H. Green, M. Ishaq, C. K. Prout, and M. G. Swanick, *J. Chem. Soc. A*, 1309 (1969); (b) M. L. H. Green, J. K. P. Ariyaratne, A. M. Bjerrum, M. Ishaq, and C. K. Prout, *Chem. Commun.*, 430 (1967).
(29) (a) P. H. Bird and M. R. Churchill, *Inorg. Chem.*, **7**, 349 (1968); (b) P. H. Bird and M. R. Churchill, *Chem. Commun.*, 705 (1967).
(30) (a) V. A. Semion and Yu. T. Struchkov, *Zh. Strukt. Khim.*, **9**, 1046 (1968); (b) V. A. Semion, Yu. A. Chapovskii, Yu. T. Struchkov, and A. N. Nesmeyanov, *Chem. Commun.*, 666 (1968).
(31) R. D. Adams, D. M. Collins, and F. A. Cotton, *Inorg. Chem.*, **13**, 1086 (1974).
(32) F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, **27**, 809 (1957).
(33) R. D. Adams, D. M. Collins, and F. A. Cotton, *J. Amer. Chem. Soc.*, **96**, 749 (1974).
(34) J. B. Wilford and H. M. Powell, *J. Chem. Soc. A*, 8 (1969).
(35) R. D. Adams, M. Brice, and F. A. Cotton, *J. Amer. Chem. Soc.*, **95**, 6594 (1973).
(36) J. Rajaram and J. A. Ibers, *Inorg. Chem.*, **12**, 1313 (1973).
(37) J. E. O'Connor and E. R. Corey, *J. Amer. Chem. Soc.*, **89**, 3930 (1967).
(38) P. J. Vergamini, H. Vahrenkamp, and L. F. Dahl, *J. Amer. Chem. Soc.*, **93**, 6326 (1971).
(39) S. Chaiwasi and R. H. Fenn, *Acta Crystallogr., Sect. B*, **24**, 525 (1968).
(40) J. R. Knox and C. K. Prout, *Acta Crystallogr., Sect. B*, **25**, 1952 (1969).
(41) $\sigma(\text{diff}) = (\sigma_1^2 + \sigma_2^2)^{1/2}$.
(42) Esd's for average distances etc. are calculated *via* the "scatter" formula $\sigma(\text{mean}) = [\sum(\chi_i - \bar{\chi})^2/(N-1)]^{1/2}$, where χ_i is the *i*th of N equivalent measurements and $\bar{\chi}$ is the mean value.
(43) M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).
(44) S. F. A. Kettle, *Inorg. Chem.*, **4**, 1661 (1965).
(45) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 246.
(46) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 2970 (1968); see, especially, Table 7, p 2976.
(47) *Chem. Soc., Spec. Publ.*, **No. 18,** S16s (1965).
(48) M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, **13**, 1427 (1974).
(49) M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, **13**, 1065 (1974).
(50) M. R. Churchill, K. L. Kalra, and M. V. Veidis, *Inorg. Chem.*, **12**, 1656 (1973).
(51) M. R. Churchill and M. V. Veidis, *J. Chem. Soc., Dalton Trans.*, 670 (1972).
(52) This might also serve as a warning to those who believe that treatment of phenyl rings as rigid bodies of precise D_{6h} (carbocyclic) symmetry is a truly legitimate procedure.
(53) The distance reported by Prout, *et al.*,[28] is 2.36 ± 0.022 Å. The value of 2.370 Å given here is calculated by us from the positional parameters and cell coordinates given in ref 28, *i.e.*: $x(\text{Mo}) = 0.0806$, $y(\text{Mo}) = 0.1886$; $z(\text{Mo}) = 0.1736$, $x(\text{C}(2)) = -0.1305$; $y(\text{C}(2)) = 0.0601$, $z(\text{C}(2)) = 0.2360$; $a = 6.82$, $b = 13.17$, $c = 12.17$ Å; $\beta = 92.7°$.
(54) The weighted average $(\bar{x})$ is calculated *via* the expression $\bar{x} = \sum(x_i/\sigma_i^2)/\sum(1/\sigma_i^2)$, where x_i is the *i*th value and σ_i is its esd. The esd of the weighted average, $\sigma(\bar{x})$, is given by $\sigma(\bar{x}) = [1/\sum(1/\sigma_i^2)]^{1/2}$.
(55) We here imply that cyanide ligands are attached to the α-carbon atom (*i.e.*, that directly bonded to the molybdenum atom).