1·951 (4) and 1·963 (4) Å with the longest value for the Co—N(3) bond. One of the amine protons bonded to N(3) is 2·48 Å from chloride Cl(2), perhaps contributing to the slightly longer Co—N(3) bond length. None of the other coordinated amine nitrogens interacts with other atoms in the crystal structure. Dien N lengths in Co(en)(dien)Cl^{2+} are 1·944 (7), 1·974 (7) and 1·993 (7) Å, giving an average Co—N length for this structure of 1·968 Å compared with a value of 1·950 Å for Co(bpy)(dien)Cl^{2+}. The opposite pattern appears in the difference in Co—Cl lengths for the two structures. This bond is longer for the bpy structure with a value of 2·263 (2) Å, compared with a value of 2·249 (3) Å for π-Co(en)(dien)Cl^{2+}. Both values are within the range of other Co$^{\rm III}$—Cl lengths, however.

The crystal structure of the complex consists of stacks of complex cations along the crystallographic *c* axis. The stacking interactions are created by the parallel orientation of planar bipyridine ligands of adjacent cations. Separations between atoms of adjacent bipyridine ligands are greater than 4 Å. With the exception of the contact between the H atom of N(3) and Cl(2), there are no interactions between the complex cation and the chloride ions and water molecules of the unit cell. Weak hydrogen bonds appear to exist between the hydrogen of water O(1) and chloride Cl(3) and between water molecules O(2) and O(3).

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Structure of Tetracarbonyl[2-(β-diphenylphosphinoethyl)pyridine]molybdenum(0)

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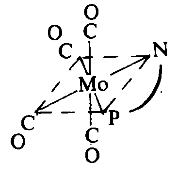
Abstract. [Mo(CO)$_4$(C$_{19}$H$_{18}$NP)], $M_r = 499{\cdot}31$, monoclinic, $P2_1/n$, $a = 12{\cdot}484$ (4), $b = 10{\cdot}300$ (2), $c = 16{\cdot}988$ (4) Å, $\beta = 96{\cdot}66$ (2)°, $V = 2169{\cdot}66$ Å^3, $Z = 4$, $D_x = 1{\cdot}529$ g cm^{-3}; λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 6{\cdot}998$ cm^{-1}, $F(000) = 1008$, $R = 0{\cdot}0433$ for 3133 unique reflections. The environment about the central Mo atom is a distorted octahedron; the two phenyl rings are planar, with a dihedral angle between them of 76·54°. The pyridine ring is not perfectly planar, but has two atoms out of plane.

Introduction. Mo(CO)$_6$ reacts with 2-(β-diphenylphosphinoethyl)pyridine (np) to form the substitution complex tetracarbonyl{2-(β-diphenylphosphinoethyl)pyridine}molybdenum(0) (Knebel & Angelici, 1973). Since this derivative (I) provides a convenient starting material for the synthesis of other np complexes of molybdenum, an unequivocal molecular structure provided by X-ray crystallographic data will be most beneficial to subsequent studies.



(I)

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Experimental. Prismatic colorless crystal, 0·07 × 0·15 × 0·40 mm; Syntex $P2_1$ diffractometer; data collected using ω scan, $2\theta_{\max} = 50°$; graphite-monochromated radiation; lattice parameters from least-squares refinement of 15 reflections ($12{\cdot}73° \leq 2\theta \leq 24{\cdot}80°$); angles measured by a centering routine associated with the diffractometer; systematic absences ($h0l$: $h + l =$ odd, $0k0$: $k =$ odd) consistent with space group $P2_1/n$; three standard reflections monitored every 100 reflections showed no deterioration in intensities; 4195 unique reflections, 3133 observed [$I > 2\sigma(I)$], h: −14 to 14, k: 0 to 12, l: 0 to 20; variable scan 3·91–29·3° min^{-1}; Lorentz and polarization corrections applied; no absorption corrections; scattering factors from *International Tables for X-ray Crystallography* (1974) with correction for real and imaginary parts of anomalous dispersion; structure solved by Patterson methods; refinement: full-matrix least squares (*SHELX76*; Sheldrick, 1976); function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = 1{\cdot}3539/\sigma^2(F_o)$; $\sigma(F_o)$ from counting statistics; H atoms from difference Fourier synthesis and refined isotropically; non-H atoms anisotropic; 343 parameters refined; final $R = 0{\cdot}0433$, $wR = 0{\cdot}0324$, $S = 1{\cdot}3949$; $(\Delta/\sigma)_{\max} = 0{\cdot}22$; $(\Delta/\sigma)_{\text{ave}} = 0{\cdot}022$. The maximum and minimum peaks in the final difference map are 0·5407 and −0·4099 e Å^{-3}, respectively.

Discussion. Table 1 lists the atomic coordinates for all atoms except hydrogen.† Fig. 1 is a *PLUTO* drawing (Motherwell & Clegg, 1978) of the molecule (arbitrary atom size) which includes the atomic numbering scheme. Bond angles and bond lengths are given in Table 2. Fig. 2 is a crystal packing diagram.

The local environment about the Mo atom in the complex Mo(CO)$_4$(np) is a distorted octahedron. The Mo—C bonds to the two CO groups *trans* to the P and *trans* to the N atom [1·998 (4) and 1·953 (4) Å, respectively] are considerably shorter than those to the CO groups in Mo(CO)$_6$ (2·08 Å) (Arnesen & Seip, 1966); and the Mo—C bonds to the mutually *trans* CO groups [2·034 (5) and 2·033 (5) Å] are slightly shorter than the Mo—C bond lengths (2·08 Å) in the hexacarbonyl. This Mo—C bond shortening is consistent with the weaker π acidity of the np ligand compared with the carbonyl group. In the substituted derivative Mo(CO)$_4$(np), electronic charge is directed from the molybdenum atom to the remaining carbonyls through $d\pi$–$p\pi^*$ orbital overlap. As expected, the Mo—C bonds *trans* to the np ligand are strengthened to a greater extent than those *cis*.

Table 1. *Positional and equivalent isotropic temperature factors of non-hydrogen atoms*

	x	y	z	U_{eq}(Å^2)
Mo	0·26689 (3)	0·16747 (3)	0·14853 (2)	0·0358 (1)
P	0·19146 (8)	0·2664 (1)	0·01872 (6)	0·0408 (3)
N	0·1089 (2)	0·2291 (3)	0·1999 (2)	0·039 (1)
O(1)	0·1663 (3)	−0·1108 (3)	0·1065 (2)	0·073 (1)
O(2)	0·3780 (2)	0·4383 (3)	0·1945 (2)	0·063 (1)
O(3)	0·3855 (3)	0·0618 (3)	0·3091 (2)	0·067 (1)
O(4)	0·4802 (2)	0·0908 (3)	0·0820 (2)	0·077 (1)
C(1)	0·2010 (3)	−0·0096 (4)	0·1211 (2)	0·047 (1)
C(2)	0·3351 (3)	0·3426 (4)	0·1783 (2)	0·043 (1)
C(3)	0·3377 (3)	0·0983 (4)	0·2515 (3)	0·046 (1)
C(4)	0·4001 (3)	0·1195 (4)	0·1059 (3)	0·048 (1)
C(5)	0·1197 (3)	0·2530 (4)	0·2786 (3)	0·048 (2)
C(6)	0·0396 (4)	0·3025 (4)	0·3184 (3)	0·054 (2)
C(7)	−0·0579 (4)	0·3299 (5)	0·2767 (3)	0·065 (2)
C(8)	−0·0724 (3)	0·3046 (4)	0·1972 (3)	0·059 (2)
C(9)	0·0116 (3)	0·2528 (4)	0·1592 (2)	0·043 (1)
C(10)	−0·0070 (4)	0·2231 (5)	0·0720 (3)	0·050 (2)
C(11)	0·0513 (3)	0·3189 (5)	0·0222 (3)	0·053 (2)
C(12)	0·2602 (3)	0·4111 (4)	−0·0121 (2)	0·040 (1)
C(13)	0·2393 (4)	0·5341 (5)	0·0149 (3)	0·055 (2)
C(14)	0·2984 (5)	0·6408 (5)	−0·0057 (3)	0·068 (2)
C(15)	0·3789 (5)	0·6251 (6)	−0·0521 (3)	0·074 (2)
C(16)	0·4018 (4)	0·5037 (7)	−0·0783 (3)	0·072 (2)
C(17)	0·3430 (4)	0·3983 (5)	−0·0587 (3)	0·056 (2)
C(18)	0·1836 (3)	0·1666 (4)	−0·0716 (2)	0·047 (1)
C(19)	0·1291 (4)	0·2110 (6)	−0·1426 (3)	0·071 (2)
C(20)	0·1263 (5)	0·1358 (8)	−0·2102 (3)	0·086 (3)
C(21)	0·1771 (5)	0·0183 (7)	−0·2083 (4)	0·080 (3)
C(22)	0·2315 (5)	−0·0267 (5)	−0·1401 (3)	0·070 (2)
C(23)	0·2353 (4)	0·0485 (4)	−0·0712 (3)	0·054 (2)

Note: Standard deviations of the last digit are in parentheses. $U_{\text{eq}} = \frac{1}{3}$ (trace of orthogonalized U_{ij} tensors).

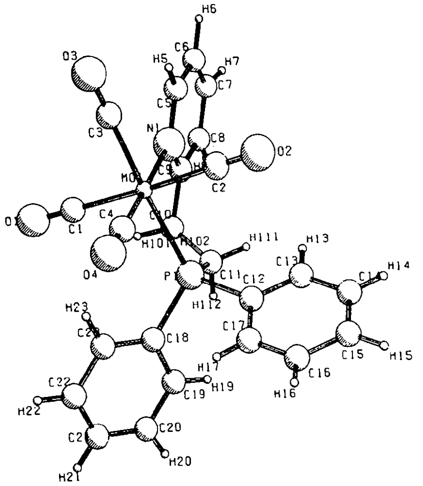

Fig. 1. *PLUTO* drawing (Motherwell & Clegg, 1978) of Mo(CO)$_4$(np), with the atomic numbering scheme.

In contrast to the contracted X—Mo—X chelate bond angle of 76·62 (7)° in Mo(CO)$_4$(nn) (nn = phenanthroline) (Bruins Slot, Murrall & Welch, 1985) and 80·2 (1)° in Mo(CO)$_4$(pp) [pp = 1,2-bis(diphenylphosphino)ethane] (Bernal, Reisner, Dobson & Dobson, 1986), the N—Mo—P angle in Mo(CO)$_4$(np) is 88·4 (1)° – much closer to the ideal octahedral geometry. These differences are primarily a result of increased strain in the five-membered chelate ring in the

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† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44770 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and bond angles* (°) *for non-hydrogen atoms* (*standard deviations are in parentheses*)

Mo—P	2·511 (1)	N—Mo—P	88·4 (1)
Mo—N	2·335 (3)	C(1)—Mo—P	93·6 (1)
Mo—C(1)	2·033 (5)	C(1)—Mo—N	89·6 (1)
Mo—C(2)	2·034 (5)	C(2)—Mo—P	87·8 (1)
Mo—C(3)	1·998 (4)	C(2)—Mo—N	90·8 (1)
Mo—C(4)	1·953 (4)	C(1)—Mo—C(2)	178·6 (2)
		C(3)—Mo—P	175·2 (1)
		C(3)—Mo—N	94·4 (1)
		C(3)—Mo—C(1)	90·4 (2)
		C(3)—Mo—C(2)	88·2 (2)
		C(4)—Mo—P	91·5 (1)
		C(4)—Mo—N	178·8 (1)
		C(4)—Mo—C(1)	91·6 (2)
		C(4)—Mo—C(2)	88·1 (2)
		C(4)—Mo—C(3)	85·7 (2)
P—C(11)	1·839 (4)	C(11)—P—Mo	110·7 (1)
P—C(12)	1·827 (4)	C(12)—P—Mo	116·2 (1)
P—C(18)	1·841 (4)	C(18)—P—Mo	118·9 (1)
		C(12)—P—C(11)	104·4 (2)
		C(18)—P—C(11)	103·4 (2)
		C(18)—P—C(12)	101·4 (2)
N—C(5)	1·350 (5)	C(5)—N—Mo	115·4 (3)
N—C(9)	1·349 (4)	C(9)—N—Mo	127·3 (3)
		C(9)—N—C(5)	117·1 (3)
C(1)—O(1)	1·145 (5)	O(1)—C(1)—Mo	178·3 (4)
C(2)—O(2)	1·140 (4)	O(2)—C(2)—Mo	176·7 (3)
C(3)—O(3)	1·148 (4)	O(3)—C(3)—Mo	174·9 (4)
C(4)—O(4)	1·159 (4)	O(4)—C(4)—Mo	178·7 (4)
C(5)—C(6)	1·370 (5)	C(6)—C(5)—N	124·2 (4)
C(6)—C(7)	1·365 (6)	C(7)—C(6)—C(5)	118·6 (4)
C(7)—C(8)	1·366 (6)	C(8)—C(7)—C(6)	118·9 (4)
C(8)—C(9)	1·400 (5)	C(9)—C(8)—C(7)	120·5 (4)
C(9)—C(10)	1·503 (6)	C(10)—C(9)—N	119·8 (4)
		C(10)—C(9)—C(8)	119·5 (4)
C(10)—C(11)	1·538 (6)	C(10)—C(11)—P	110·0 (3)
		C(11)—C(10)—C(9)	112·5 (4)
C(12)—C(13)	1·383 (6)	C(13)—C(12)—P	122·6 (3)
C(12)—C(17)	1·380 (6)	C(17)—C(12)—P	119·7 (3)
		C(17)—C(12)—C(13)	117·5 (4)
C(13)—C(14)	1·391 (6)	C(14)—C(13)—C(12)	120·9 (5)
C(14)—C(15)	1·356 (7)	C(15)—C(14)—C(13)	120·2 (5)
C(15)—C(16)	1·368 (7)	C(16)—C(15)—C(14)	119·6 (5)
C(16)—C(17)	1·372 (7)	C(17)—C(16)—C(15)	120·4 (5)
		C(16)—C(17)—C(12)	121·4 (5)
C(18)—C(19)	1·391 (6)	C(19)—C(18)—P	120·8 (4)
C(18)—C(23)	1·377 (6)	C(23)—C(18)—P	120·6 (3)
		C(23)—C(18)—C(19)	118·5 (4)
C(19)—C(20)	1·382 (7)	C(20)—C(19)—C(18)	120·0 (6)
C(20)—C(21)	1·366 (8)	C(21)—C(20)—C(19)	120·6 (6)
C(21)—C(22)	1·356 (8)	C(22)—C(21)—C(20)	120·5 (6)
C(22)—C(23)	1·399 (6)	C(23)—C(22)—C(21)	119·4 (6)
		C(22)—C(23)—C(18)	120·9 (5)

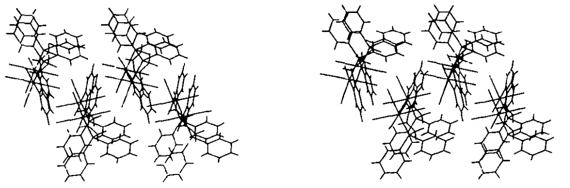

Fig. 2. Crystal packing diagram of $Mo(CO)_4(np)$ (view down the *a* axis).

nn and pp complexes that is much less prevalent in the six-membered np derivative.

The Mo—C bond *trans* to the pyridine N atom has a bond length of 1·953 (4) Å, quite comparable to the *trans* Mo—C bond [1·958 (3) Å] in the $Mo(CO)_4(nn)$ complex (Bruins Slot, Murrall & Welch, 1985). Also, the Mo—C bond *trans* to the P atom has a bond length of 1·998 (4) Å, again quite comparable to the Mo—C bonds [1·974 (8) and 1·999 (8) Å] *trans* to the P atoms in the complex $Mo(CO)_4(pp)$ (Bernal, Reisner, Dobson & Dobson, 1986).

The mutually *trans* Mo—C bonds in $Mo(CO)_4(np)$ [2·034 (5) and 2·033 (5) Å] are slightly shorter than those in the hexacarbonyl (2·08 Å) and very similar to those in the nn [2·024 (3) and 2·026 (3) Å] and in the pp complex [2·053 (9) and 2·030 (9) Å].

The C—O bond lengths in the np derivative are also affected by the presence of the less strongly π-acidic np ligand. While differences among the four CO bond lengths are small [C—O bond lengths *trans* to np are 1·148 (4) and 1·159 (4) Å and those *cis* to the ligand are 1·145 (5) and 1·140 (4) Å], the trend is typical of that observed in other substituted metal carbonyls. Similar variations in C—O bond lengths are present in the nn derivative and the pp complex. Typical of transition-metal carbonyl derivatives (Carter, McPhail & Sim, 1966), the four Mo—C—O units in $Mo(CO)_4(np)$ are nonlinear, ranging from 174·9 (4) to 178·7 (4)°. Also, the three principal axes in $Mo(CO)_4(np)$ differ only slightly from linearity [C(1)—Mo—C(2) = 178·6 (2), C(3)—Mo—P = 175·2 (1) and C(4)—Mo—N = 178·8 (1)°].

The Mo—N bond length of 2·335 (3) Å in $Mo(CO)_4(np)$ is longer than the Mo—N bond lengths [2·2434 (21) Å] found in the nn complex. However, the Mo—P bond length of 2·511 (1) Å is quite comparable to the Mo—P bonds observed in the pp complex [2·500 (2) and 2·495 (2) Å]. The Mo—P bond length is considerably shorter than the sum of the single-bond radii (1·61 Å for the Mo^0 atom, and 1·10 Å for the P atom) (Pauling, 1960) indicative of extensive $d\pi$–$d\pi$ backbonding from the metal to the phosphorus.

A larger deviation from the ideal *cis* bond angle of 90° is observed in $Mo(CO)_4(nn)$ than in the np complex; the N—Mo—C(3) bond angle in $Mo(CO)_4(np)$ is 94·4 (1)°, while the similar bond angle in the nn complex is 96·60 (10)°. Further, the N—Mo—C(4) angle in $Mo(CO)_4(np)$ is 178·8 (1)°, while the similar bond angle in the nn complex is 170·20 (10)°.

Whereas the P—Mo—C(4) bond angle of 91·5 (1)° in $Mo(CO)_4(np)$ deviates only slightly from the ideal angle of 90°, more severe distortions of the P—Mo—C (*trans* to the other P) bond angles [93·1 (2) and 96·4 (3)°] are observed in the pp complex. Those distortions have been attributed to ligand–metal ring strain with some interaction with the phenyl ring. In the np complex, steric factors probably account for the small deviation from octahedral geometry.

In the $Mo(CO)_4(np)$ structure, the mutually *trans* carbonyl groups are skewed, with C(1) being pushed away from the phosphorus atom [P—Mo—C(1) = 93·6 (1)°] and C(2) being moved slightly towards the phosphorus atom [P—Mo—C(2) = 87·8 (1)°]. This skewing of the z axis is evident in the pp but not in the nn complex, where both *trans* CO groups are pushed away from the ligating atoms.

The P—C(sp^3) distance of 1·839 (4) Å can be compared with values of 1·85 (Doedens, Robinson & Ibers, 1967), 1·865 (Churchill & O'Brien, 1970), 1·88 (Cheung, Lai & Mok, 1971) and 1·846 (7) and 1·844 (8) Å (Bernal, Reisner, Dobson & Dobson, 1986). The average of 1·834 (6) Å for the two P—C(sp^2) distances is in good agreement with other reported values of 1·827 (Churchill & O'Brien, 1970), 1·83 (Cheung, Lai & Lam, 1970; Doedens, Robinson & Ibers, 1967), 1·828 (Daly, 1964), 1·81 (La Placa & Ibers, 1965) and 1·838 Å (Bernal, Reisner, Dobson & Dobson, 1986). The mean C—C bond length and C—C—C bond angle for the two phenyl groups are 1·377 (7) Å and 118·3 (5)°, respectively.

Least-squares planes were calculated for each of the three rings. The two phenyl rings (rings 1 and 2) are essentially planar, while the pyridine ring (ring 3) has two out-of-plane atoms [N and C(9)]. For ring 1 [C(18)—C(23)], the maximum and minimum deviations are 0·0051 and −0·0064 Å; the maximum and minimum deviations for ring 2 [C(12)—C(17)] are 0·0060 and −0·0066 Å. The dihedral angle between these two rings is 76·54 (7)°. The maximum deviation from planarity for ring 3 is 0·127 and the minimum is −0·0105 Å. The dihedral angle between rings 1 and 3 is 42·27 (7)° and that between rings 2 and 3 is 84·41 (6)°.

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Tris(3-ethylpyridinium) Decavanadate Monohydrate

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Abstract. $[C_7H_{10}N]_3[V_{10}H_3O_{28}].H_2O$, $M_r = 1302{\cdot}8$, monoclinic, $P2_1/n$, $a = 7{\cdot}294$ (2), $b = 23{\cdot}083$ (7), $c = 24{\cdot}403$ (3) Å, $\beta = 96{\cdot}92$ (1)°, $V = 4079$ (1) Å^3, $Z = 4$, $D_m = 2{\cdot}1$ (1) (by flotation in $Br_3CH—CCl_4$), $D_x = 2{\cdot}12$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}77$ mm^{-1}, $F(000) = 2576$, room temperature, $R = 0{\cdot}042$ for 2242 observed reflections. The molecule is very similar to other triply protonated decavanadates recently described. The three protons link the decavanadate anion in layers parallel to (100), and these layers are held together by hydrogen bonding through the water molecule.

Introduction. The structures of several decavanadates have previously been described, for example $K_2Zn_2V_{10}O_{28}.16H_2O$ (Evans, 1966), $Ca_3V_{10}O_{28}.17H_2O$

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