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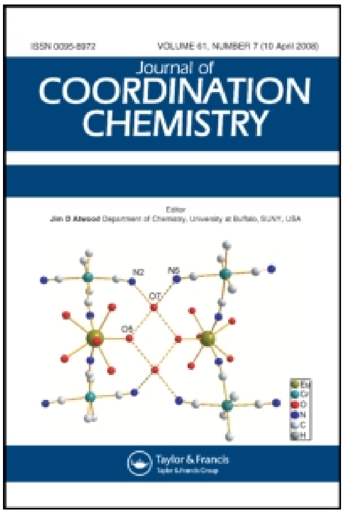

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SYNTHESIS AND CHARACTERIZATION OF OCTAMETHYLCYCLOTETRAPHOSPHAZENETRICARBONYLMOLYBDENUM

F. A. COTTON,† G. A. RUSHOLME and ALAN SHAVER

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The compound $[(CH_3PN)_4]Mo(CO)_3$ has been isolated. The stoichiometry is verified by analytical, spectroscopic and X-ray crystallographic data. The compound is highly insoluble and even with great effort only crystals of poor quality were obtainable. An X-ray structure determination was carried out within the limitations thereby imposed. The structure analysis was carried out in the space group $P2_12_12_1$, with unit cell dimensions of $a = 16.22(1)$ Å, $b = 14.90(1)$ Å, $c = 8.194(7)$ Å and $Z = 4$. The P_4N_4 ring is roughly planar and the molybdenum atom is within bonding distance of five atoms in a chain N–P–N–P–N, but out of bonding range of the remaining P–N–P set. The $Mo(CO)_3$ group has typical dimensions. Due to poor crystal quality and the occurrence of disorder, the structure parameters are too crude to allow a detailed discussion of the ring-to-metal bonding.

INTRODUCTION

Inorganic heteroatom ring systems are conceivable candidates as ligands to transition metal carbonyls. Usually these systems contain donor atoms such as nitrogen that can form localized bonds to transition metal atoms with their lone pair of electrons. But an even more interesting possibility is the bonding of metals to the delocalized π-type bonds that are often present in inorganic ring systems. In cyclophosphazenes, for example, the electrons not used in forming the σ skeleton are considered to be delocalized in some way involving p orbitals on nitrogen and d orbitals on phosphorus.[1] The pπ—dπ bonds of this type do not seem to be greatly influenced by puckering or non-planarity of the ring and exhibit little or no barrier to rotation of the bond. In octamethylcyclotetraphosphazene, $[(CH_3)_2PN]_4$, there is no alternation of bond lengths around the ring.[2] However, tetrafluorotetrasulphurtetranitride, $[FSN]_4$, which might also be expected to possess similar pπ—dπ-type bonds, has a very definite alternation of bond lengths corresponding to single and near double bonds around the ring[3] reminiscent of cyclooctatetraene. Pi bonding of a more usual type involving p orbitals occurs in $[Bu^tNBCl]_4$. This ring exists in a boat conformation with alternating bond lengths.[4]

This diversity in the degrees of delocalization present in inorganic ring systems might lead one to expect many examples of these systems bonded to transition metal carbonyls in analogy to the extensive collection of polyolefin metal complexes. But this is not the case at present. M. F. Hawthorne, it is true, has shown that carboranes have a large and varied transition metal chemistry.[5] However, little has been reported concerning the reactions of other inorganic ring systems. Explosive compounds of the formula $(S_4N_4)(CO)Fe$,[6] $(N_4S_4)(CO)Co_2$[6] and $(N_5S_5)(CO)Mo$[7] appear to be complicated polymers in which the nature of the bonding is unknown. $(S_2N_2H)_2Ni$[8, 9] results from the reaction of S_4N_4 with $NiCl_2$ in methanol and has two -NH-S-N-S-bidentate, non-cyclic ligands.[10] Trotter and coworkers have reported the structures of four complexes containing cyclophosphazene ligands. $[(CH_3)_2PN]_4\cdot H\cdot CuCl_3$[11] contains an eight-membered phosphazene ring with a proton and a $CuCl_3$ group bonded to opposite nitrogen atoms. $\{[(CH_3)_2PN]_4\cdot H\}_2CoCl_4$[12] contains two protonated cyclophosphazene rings and a $CoCl_4^{2-}$ ion. Complexes containing the cation $\{[(CH_3)_2N]_2PN\}_6MCl^+$, where M is Cu[13] and Co[14] have a structure in which the metal resides in the center of the 12-membered ring, bonded to four nitrogen atoms and one chlorine atom in a distorted square pyramidal geometry. These complexes illustrate the ability of the nitrogen atoms in cyclophosphazenes to form localized covalent bonds to transition metal atoms.

The first well-characterized examples of inorganic rings bonded to a metal carbonyl are the compounds $[(RBNR)_3](CO)_3Cr$, where R = CH_3 and

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CH_2CH_3.[15] The physical properties of these borazine complexes are very similar to those of the analogous $[C_6(CH_3)_6](CO)_3Cr$.[16] The X-ray structural determination of the ethyl compound[17] showed that the geometry of the molecular skeleton corresponds to that of $[C_6(CH_3)_6](CO)_3Cr$. The nitrogen atoms are *trans* to the carbonyl groups and are closer to the metal than is the boron atom. Since the difference between the Cr—B and Cr—N bond lengths corresponds to the difference between the covalent radii of boron and nitrogen it is not possible to decide between localized and delocalized bonding models.

We considered the possibility of using octamethylcyclotetraphosphazene, $[(CH_3)_2PN]_4$, as a ligand to a metal carbonyl. Specifically the plan was to make a $Mo(CO)_3$ derivative and to study its spectroscopic and structural properties to see how similar it would be to cyclooctatetraenetricarbonylmolybdenum, $(C_8H_8)(CO)_3Mo$ and whether it would be fluxional. Would the metal bond to the nitrogen lone pairs or the delocalized electrons in the ring? The work of Trotter illustrated the ability of the nitrogens to bond to transition metals by means of their lone pair electrons. It was hoped, however, that the steric limitations imposed by the eight-membered ring might favor a bonding mode involving the delocalized electrons in the ring.

Although the synthesis was successful, the project was beset with problems making it impossible to answer all the above questions conclusively. Not the least of these problems was the synthesis of $[(CH_3)_2PN]_4$ since the previously reported procedures were unsatisfactory.[18] It was necessary to develop an improved synthetic method, which has already been reported.[19]

EXPERIMENTAL

Preparation of Octamethylcyclotetraphosphazetricarbonylmolybdenum.

Method I. All operations were carried out in an atmosphere of pre-purified nitrogen. Tetrahydrofuran was refluxed over sodium and benzophenone and distilled shortly before use. Trisacetonitriletricarbonylmolybdenum, $(CH_3CN)_3(CO)_3Mo$,[20] (0.415 g) was dissolved in 20 ml of THF. This solution (17.5 ml, 0.0012 moles of $(CH_3CN)_3(CO)_3Mo$) was transferred by means of a syringe to a 50 ml pressure equalizing dropping funnel attached to a 50 ml three-necked round-bottom flask fitted with a nitrogen inlet and stopper. The solution was slowly added dropwise to a solution of 0.363 gm (0.0012 moles) of $[(CH_3)_2PN]_4$ in 10 ml of THF at 0°C. Almost immediately a yellow precipitate formed. After the addition was completed the suspension was stirred for one hour at room temperature. The supernatant liquid was removed by means of a syringe and the precipitate was washed with a little pentane and pumped on at room temperature. It decomposed at about 240°C. in nitrogen.

Anal. Calcd. for $C_{11}H_{24}MoN_4O_3P_4$: C, 27·50; H, 5·00; N, 11·67. Found: C, 27·70; H, 5·10; N, 11·44. Analysis was performed by Scandinavian Micro-analytical Laboratory, P.O. Box 25, Herley, Denmark.

The complex is insoluble in common solvents and its pmr spectrum could not be measured. Its infrared spectrum in Nujol is reported in Table I.

Method II. Method I yields $[(CH_3)_2PN]_4(CO)_3Mo$ as a very fine powder. Crystals may be obtained in the following way. The phosphazene, $[(CH_3)_2PN]_4$, (0.148 g) was dissolved in about 10 ml of THF in a tube 20 cm by 1.7 cm fitted with a sidearm-stopcock and stoppered with an inlet valve. The solution was freeze-thaw degassed and frozen again using a liquid nitrogen bath. The $(CH_3CN)_3(CO)_3Mo$(0.180 g) was dissolved in 5.0 ml of THF and the solution was transferred by means of a syringe into the tube and frozen above the ligand solution. The tube was left in the liquid nitrogen bath and allowed to warm as the coolant evaporated. This took about 48 hr. Crystals of $[(CH_3)_2PN]_4(CO)_3Mo$ as identified by their infrared spectrum formed on the wall of the tube. The supernatant liquid was removed with a syringe and the crystals were washed and dried as before.

X-ray Structural Investigation

Flat plate-like crystals of $[(CH_3)_2PN]_4(CO)_3Mo$ obtained from the above preparation were small and rather poor in quality. After considerable screening a crystal was selected and sealed under nitrogen in a capillary. Precession photographs (0k*l*, 1k*l*, h0*l*, h1*l*) indicated orthorhombic symmetry and the systematic absences implied the space group $P2_12_12_1$. A period of 6 months passed before the work was continued, and in that time the original crystal had visibly darkened and crumbled. A new crystal bounded by the 100, $\bar{1}00$, 010, $0\bar{1}0$, 001 and $00\bar{1}$ faces and measuring 0.20 × 0.11 × 0.05 mm was sealed in a capillary under nitrogen and aligned on a General Electric XRD-5 manual diffractometer so that the c* axis was coincident with ϕ. Accurate cell constants were determined by careful centering of 19 strong reflections. Least squares refinement gave the following cell dimensions: $a = 16.22 \pm 0.01$ A, $b = 14.90 \pm 0.01$ A and $c = 8.194 \pm 0.007$ A. The observed density of 1.58 ± 0.07 g/cm^3 obtained by the flotation method agrees with the value of 1.65 g/cm^3, calculated for $Z = 4$. Data were taken on a manually operated diffractometer with Cu Kα radiation out to a limit of $2\theta = 110°$. A total of 1498 reflections were observed using the criteria $I/\sigma(I) > 0$ where $\sigma(I) = [TC + (BT/PT)^2 \times BC]^{1/2}$. $I = TC\text{–}BC$ where TC = total counts, BT = background counting time, PT = peak counting time and BC = background counts.

SOLUTION AND REFINEMENT

The data were reduced and corrected for decomposition and absorption using programs written by Dr. B. G. DeBoer. A Patterson function was computed using 591 reflections ($I/\sigma I > 3$) and solved for the molybdenum atom position in the space group $P2_12_12_1$. Least-squares refinement of the molybdenum position followed by an electron density difference map located the atoms in the eight-membered ring. At this point an unequivocal identification of phosphorus and nitrogen atoms on the basis of electron density could not be made. Both possible arrangements of phosphorus and nitrogen atoms were refined separately. In one arrangment the isotropic temperature factors for the phosphorus atoms became very large while those of the nitrogen atoms became very small. This was taken to indicate that this arrangment was the reverse of the true one. This was verified when in subsequent difference maps, using the other arrangement methyl groups were located next to the atoms identified as phosphorus. Using only data with $I/\sigma(I) > 3$ all atoms were eventually located by means of a series of difference maps and refined isotropically except for the molybdenum atom which was assigned an anisotropic temperature factor. The refinement converged at the rather high discrepency indices of

$R_1 = \Sigma \mid \mid F_0 \mid - \mid F_c \mid \mid / \Sigma \mid F_0 \mid = 0.12$ and

$R_2 = \Sigma w \mid |F_0| - |F_c| \mid^2 / \Sigma w \mid |F_0|^2 = 0.14$,

where equal (unit) weights were used in calculating R_2. A new difference map revealed the problem. A weak set of ghost peaks for the methyl groups and the carbonyl groups appeared in the positions which would result from rotation of the molecule by $2\pi/8$ about an axis passing through the center of the ring and the molybdenum atom. A zero layer Weissenberg picture revealed new very weak spots that indicated that the 16 Ångstrom axis was really 32 Ångstroms long. These spots were not observed when the compound was originally characterized. It is possible that during the data collection the crystal began to disorder or decompose in such a way that molecules formerly related by a 2_1 axis became unrelated due to rotation. Continuing to consider these molecules to be related would superimpose their structures and result in the ghost peaks. Such a process of disordering or decomposition might not be readily detected by monitoring the intensity of the standards. The weak intensity of the ghost peaks and the weakness of the new spots would suggest that such a process was no more than 20% complete. A number of disordered models were used in attempts to fit the data better but without success. The implication of this problem on the validity of the determined structure is discussed later.

DISCUSSION

The method of synthesis, analytical results, infrared spectra and X-ray results are consistent with the formulation of the compound as $[(CH_3)_2PN]_4(CO)_3Mo$. Comparing the infrared spectrum of the complex to that of the ligand (Table I) shows there are large differences, suggesting that the ligand has been changed a great deal. The infrared spectrum in the carbonyl region is typical of a $M(CO)_3$ unit. It is interesting to compare this spectrum to that obtained for $(CH_3C)_8(CO)_3W$ and $(NH_2CH_2CH_2NHCH_2CH_2NH_2)(CO)_3Mo$ which consist of bands at 1987, 1930 and 1903 cm^{-1} (cyclohexane)[21] and 1887 and 1737 cm^{-1} (Nujol mull),[22] respectively. The cyclophosphazene complex has bands at 1900, 1775 and 1745 cm^{-1} (Nujol mull) similar in frequency to those of $(NH_2CH_2CH_2NHCH_2CH_2NH_2)(CO)_3Mo$. This suggests that the cyclophosphazene ligand has an electronic effect on the $Mo(CO)_3$ group analogous to that of three nitrogen ligands. One might conclude from this that the phosphazene ligand exhibits little or no π-acidity in this complex.

The infrared spectrum of the complex is very similar, except for a missing band at 2000 cm^{-1}, to

TABLE I

Infrared Absorption Data[a] (cm^{-1})

$(CH_3)_8P_4N_4$ (in CCl_4 solution):	2980(m), 2910(w), 1410(w), 1300(s), 1220(s, b), 990(m), 920(s), 870(s), 640(s)
$(CH_3)_4P_4N_4 \cdot n$HCl (in 1,3-hexachlorobutadiene mull):	2970(m), 2900(m), 2810(s, b), 2560(s, b), 1320(s), 1278(s)
$(CH_3)_8P_4N_4 \cdot n$HCl (in Nujol mull):	1010(s), 975(m), 940(s), 900(m), 870(m), 790(m), 765(m), 725(w)
$[(CH_3)_8P_4N_4](CO)_3Mo$ (in Nujol mull):	1900(s), 1775(s), 1745(s), 1305(m), 1215(m), 1155(s), 1140(w), 1070(w), 973(w), 950(w), 918(m), 875(m)

[a] s, strong; m, medium; w, weak; b, broad.

that reported for a compound formulated as $[(CH_3)_2PN]_4(CO)_4Mo$.[23] It is probable that the band reported at 2000 cm^{-1} was due to residual $Mo(CO)_6$ which was one of the starting materials. We have previously noted[19] that $[(CH_3)_2PN]_4$ forms a $Mo(CO)_3$ derivative and Paddock has recently[24] renounced the tetracarbonyl in favor of the tricarbonyl formulation. This matter thus seems conclusively settled.

A diagrammatic sketch of the structure of $[(CH)_3)_2PN]_4(CO)_3Mo$ is given in Fig. 1. Atomic positional and thermal parameters are given in Table II. The relevant interatomic distances and angles are given in Tables III and IV, respectively. At this stage of the refinement the disorder problems make it difficult to examine with confidence interesting bond distances and angles. In fact close inspection of the values for some of these distances strongly suggests that they are inaccurate. Despite this, Fig. 1 does seem to be essentially reliable in respect to at least the gross structural features. The gross geometry bears some resemblance to that found in $(C_8H_8)(CO)_3Mo$.[25] The cyclophosphazene ring has been flattened considerably from the saddle conformation which the free ligand assumes[2] (nitrogen atoms on alternate sides of a plane formed by the

TABLE II

Atomic Parameters[a]

Atom	x	y	z	B
N1	0.137(3)	0.783(3)	0.385(6)	2(1)
P1	0.155(1)	0.687(2)	0.370(3)	4.1(6)
N2	0.125(2)	0.630(2)	0.263(3)	−2.1(5)
P2	0.080(1)	0.621(2)	0.062(3)	3.4(4)
N3	0.057(2)	0.692(3)	−0.044(5)	−0.7(8)
P3	0.077(2)	0.801(3)	−0.044(5)	9(1)
N4	0.062(3)	0.850(4)	0.135(7)	3(1)
P4	0.111(3)	0.861(3)	0.280(0)	12(2)
C11	0.162(7)	0.630(8)	0.554(14)	10(3)
C12	0.257(6)	0.692(6)	0.279(11)	8(3)
C21	−0.004(4)	0.552(5)	0.043(8)	5(2)
C22	0.161(4)	0.544(5)	0.006(9)	4(2)
C31	−0.050(6)	0.805(7)	−0.117(4)	10(4)
C32	0.125(5)	0.879(6)	−0.192(11)	7(2)
C41	0.104(5)	0.980(7)	0.393(11)	7(2)
C42	0.228(5)	0.900(6)	0.197(9)	6(2)
C_1	−0.115(3)	0.729(6)	0.234(8)	5(2)
O_1	−0.183(3)	0.716(3)	0.183(6)	7(1)
C_2	−0.053(9)	0.693(10)	0.528(20)	13(5)
O_2	−0.070(4)	0.642(5)	0.632(11)	11(2)
C_3	−0.074(6)	0.827(8)	0.450(12)	7(2)
O_3	−0.119(5)	0.911(6)	0.488(10)	11(2)
Mo	−0.0140(3)	0.745(1)	0.3411(6)	β_{11} 0.0021(1) β_{22} 0.0083(5) β_{33} 0.0072(6) β_{12} 0.0013(5) β_{13} 0.0010(4) β_{23} 0.0018(12)

[a] Estimated standard deviations occurring in the last significant figure are given in parentheses.

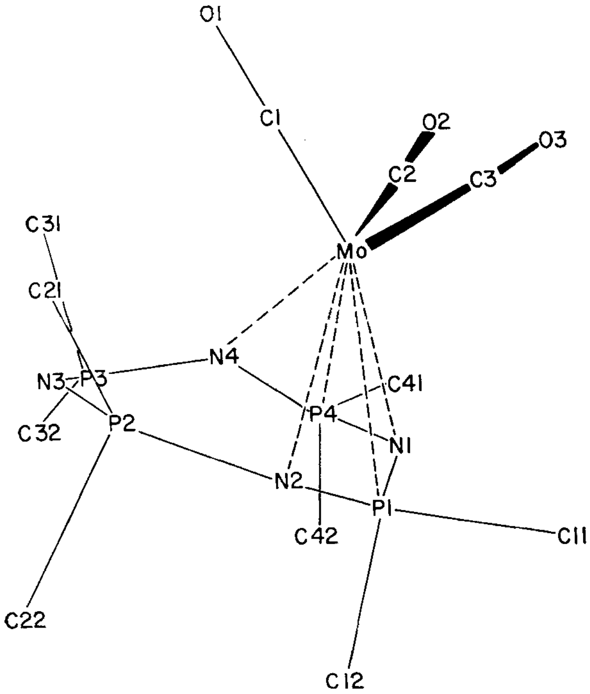

FIGURE 1 A diagrammatic representation of the structure of $[(CH_3)_2PN]_4(CO)_3Mo$.

four phosphorus atoms). The molybdenum atom seems to interact with five of the eight ring atoms. The near planarity of the ring raises the interesting question of how the ring binds to the metal atom. One might expect a much more buckled ring if the metal were bound to the lone pair electrons of N4, N1 and N2 in a manner analogous to the bonding in $\{[(CH_3)_2N]_2PN\}_6MCl$.[13,14] The extremely long metal-to-ligand distances are not easily explained. The average Mo–N distance in $(NH_2CH_2CH_2NHCH_2CH_2NH_2)(CO)_3Mo$ is 2.33 ± 0.01 A[26] while the Mo–P distance is of the order of 2.5 A in the structures of $[(C_6H_6)_2PCH_2CH_2NHCH_2CH_2P(C_6H_5)_2](CO)_4Mo$,[27] $[(C_6H_5)_2PC_6H_4CH = CHCH_3]$-$(CO)_4Mo$[28] and $[(C_2H_5)_5P_5](CO)_4Mo$.[29]

The three nitrogen atoms, N1, N2 and N4, together with the three carbonyl carbon atoms define a very distorted octahedron about the molybdenum atom. However, at the present, regrettably low, level of accuracy, this does not necessarily support the idea of localized Mo–N bonds, although it is not inconsistent with it.

Detailed analysis of the structure must await a better structure determination, which, in turn, will require renewed and perhaps innovative efforts to grow good crystals. At present, we are not in a position to conduct such work.

TABLE III

Intramolecular Distances[a]

Mo–N1	2.55(5)	P1–C11	1.74(14)
Mo–P1	2.88(3)	P1–C12	1.83(13)
Mo–N2	2.91(3)	P2–C21	1.71(9)
Mo–P2	3.31(2)	P2–C22	1.80(9)
Mo–N3	3.45(4)	P3–C31	1.85(15)
Mo–P3	>3.5	P3–C32	2.14(13)
Mo–N4	2.61(5)	P4–C41	2.01(14)
Mo–P4	2.72(5)	P4–C42	2.09(13)
Mo–C1	1.88(8)		
Mo–C2	1.82(15)	C1–O1	1.2(2)
Mo–C3	1.80(11)	C2–O2	1.2(2)
N1–P1	1.47(7)	C3–O3	1.5(2)
P1–N2	1.31(5)		
N2–P2	1.81(5)		
P2–N3	1.41(6)		
N3–P3	1.66(8)		
P3–N4	1.66(9)		
N4–P4	1.45(10)		
P4–N1	1.50(10)		

[a] Estimated standard deviations occurring in the last significant figure are given in parentheses.

TABLE IV

Intramolecular Angles[a]

N1–P1–N2	128
P1–N2–P2	143
N2–P2–N3	128
P2–N3–P3	133
N3–P3–N4	114
P3–N4–P4	134
N4–P4–N1	123
P4–N1–P1	139
C11–P1–C12	108
C21–P2–C22	100
C31–P3–C32	102
C41–P4–C42	87
Mo–C1–O1	172
Mo–C2–O2	164
Mo–C3–O3	161
C1–Mo–C2	92
C1–Mo–C3	81
C2–Mo–C3	72
C1–Mo–N1	160
C2–Mo–N4	163
C3–Mo–N2	158

[a] The bond angles have esds of 4–8°, but in view of probable systematic errors in addition, these are not worth quoting individually.

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