

- Ghosh, P. P., Ganagi, M. S. and Ashok, A., 'Simulator users manual', ANURAG Report ANU/PACE/90/02, Hyderabad, 1990.
- Fox, G. C., Johnson, M. A., Lyzenga, G. A., Otto, S. W., Salman, J. K. and Walker, D. W., *Solving Problems on Concurrent Processors*, Prentice-Hall International, New York, 1988, vol. I.
- Weissbein, D. A., Mangus, J. F. and George, M. W., in *Hypercube Concurrent Computers and Applications* (ed. Fox, G. E.), ACM Inc., Pasadena, USA, 1988, vol. II, p. 1127.
- Intel Scientific Computers, CFD, June 1989 (technical literature distributed by Intel Corporation, Santa Clara, USA).

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RESEARCH COMMUNICATIONS

Novel coordination behaviour of *gem*-bis(pyrazolyl) cyclotriphosphazenes as tridentate NNN-donor ligands: The crystal structure of $[\text{Mo}(\text{CO})_3 \{ \text{N}_3\text{P}_3\text{Ph}_4(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_2 \}]$

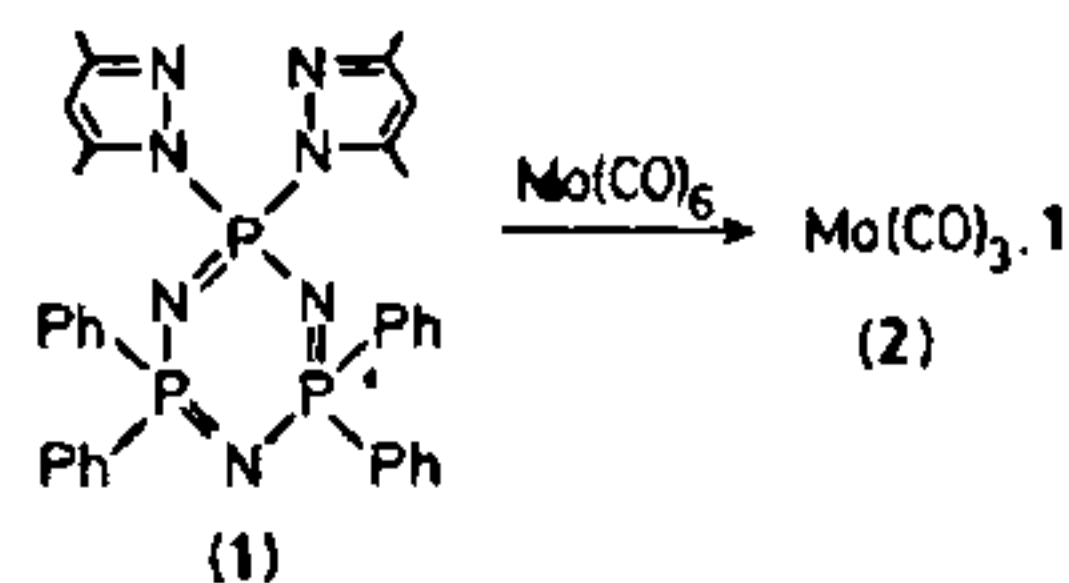
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Reactions of group 6 metal carbonyls with bis(pyrazolyl) phosphazenes yield metal tricarbonyl complexes, $[\text{M}(\text{CO})_3 \cdot \text{L}]$ [$\text{L} = \text{N}_3\text{P}_3\text{Ph}_4(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_2$ (1) or $\text{N}_3\text{P}_3(\text{MeNCH}_2\text{CH}_2\text{O})_2(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_2$ (4)]. The structure of the complex $[\text{Mo}(\text{CO})_3 \cdot 1]$, determined by single-crystal X-ray analysis, shows that the (pyrazolyl) phosphazene acts as a tridentate ligand; the two pyridinic pyrazolyl nitrogen atoms and a phosphazene ring nitrogen atom are coordinated to the metal. A similar structure is proposed for the complexes $[\text{M}(\text{CO})_3 \cdot 4]$ ($\text{M} = \text{Mo}$ or W) on the basis of their spectroscopic data.

CURRENT interest in cyclophosphazenes is mainly focused on their organometallic chemistry^{1,2}. Zerovalent metal complexes of cyclotriphosphazenes are sparse and have not been structurally characterized^{1,3}. In this communication, we report the synthesis and structural study of the molybdenum tricarbonyl complex 2 of 2,2,4,4-tetraphenyl-6,6-bis(3,5-dimethyl-1-pyrazolyl) cyclotriphosphazene (1) in which a phosphazene ring nitrogen atom is involved in coordination along with the two pyrazolyl pyridinic nitrogen atoms. We also report the synthesis and spectroscopic studies of a new bis(pyrazolyl) cyclotriphosphazene, viz. 2,2,4,4-bis(*N*-methylethanolamino)-6,6-bis(3,5-dimethyl-1-pyrazolyl) cyclotriphosphazene (4) and its metal tricarbonyl complexes, $[\text{M}(\text{CO})_3 \cdot 4]$ ($\text{M} = \text{Mo}$ (5a) or W (5b)). Complexes 2 and 5 are the first examples of structurally well-characterized systems in which a cyclotriphosphazene acts as a tridentate ligand. Pd(II) and Pt(II)

complexes of pyrazolylphosphazenes are known but in these complexes there is no involvement of phosphazene ring nitrogen atom in coordination⁴.



Compound 2 was prepared by heating⁴ the ligand 1 (0.5 g) and molybdenum hexacarbonyl (0.2 g) (molar ratio 1:1) in 40 ml acetonitrile under reflux in an atmosphere of dry N_2 for 6 h. The product was precipitated as yellow crystals, which was washed with acetonitrile and dried under vacuum (yield: 76%). Single crystals were obtained by carrying out the reaction under appropriate dilute conditions and cooling the reaction mixture to 0°C . Compound 2 is not soluble in common organic solvents. Elemental analyses and infrared spectrum showed it to be a metal tricarbonyl derivative, $[\text{Mo}(\text{CO})_3 \cdot 1]$. The structure of the complex was determined by single-crystal X-ray diffraction and a view of the molecule is shown in Figure 1. In addition to the pyridyl nitrogen atoms of the pyrazolyl groups, a nitrogen atom of the phosphazene ring is involved in coordination to the metal.

The geometry around the metal atom is distorted octahedral with short M–C bonds on one face and longer M–N bonds on the opposite face. The metalocycle is in a boat form and the heads of the boat (P1 and Mo) are bridged by a phosphazene ring nitrogen atom. The phosphazene ring is distinctly non-planar; the phosphorus atom (P3) and the adjacent nitrogen atom (N2) project upward (by 0.17 \AA) from the plane formed by the other phosphazene ring atoms (N3, P1, N1, P2). The phosphorus-nitrogen bond distances are in the range $1.557(2)$ – $1.637(2) \text{ \AA}$ with a mean value 1.600 \AA . The phosphazene ring nitrogen–metal bond is longer ($2.394(2) \text{ \AA}$) than the pyrazolyl nitrogen–metal

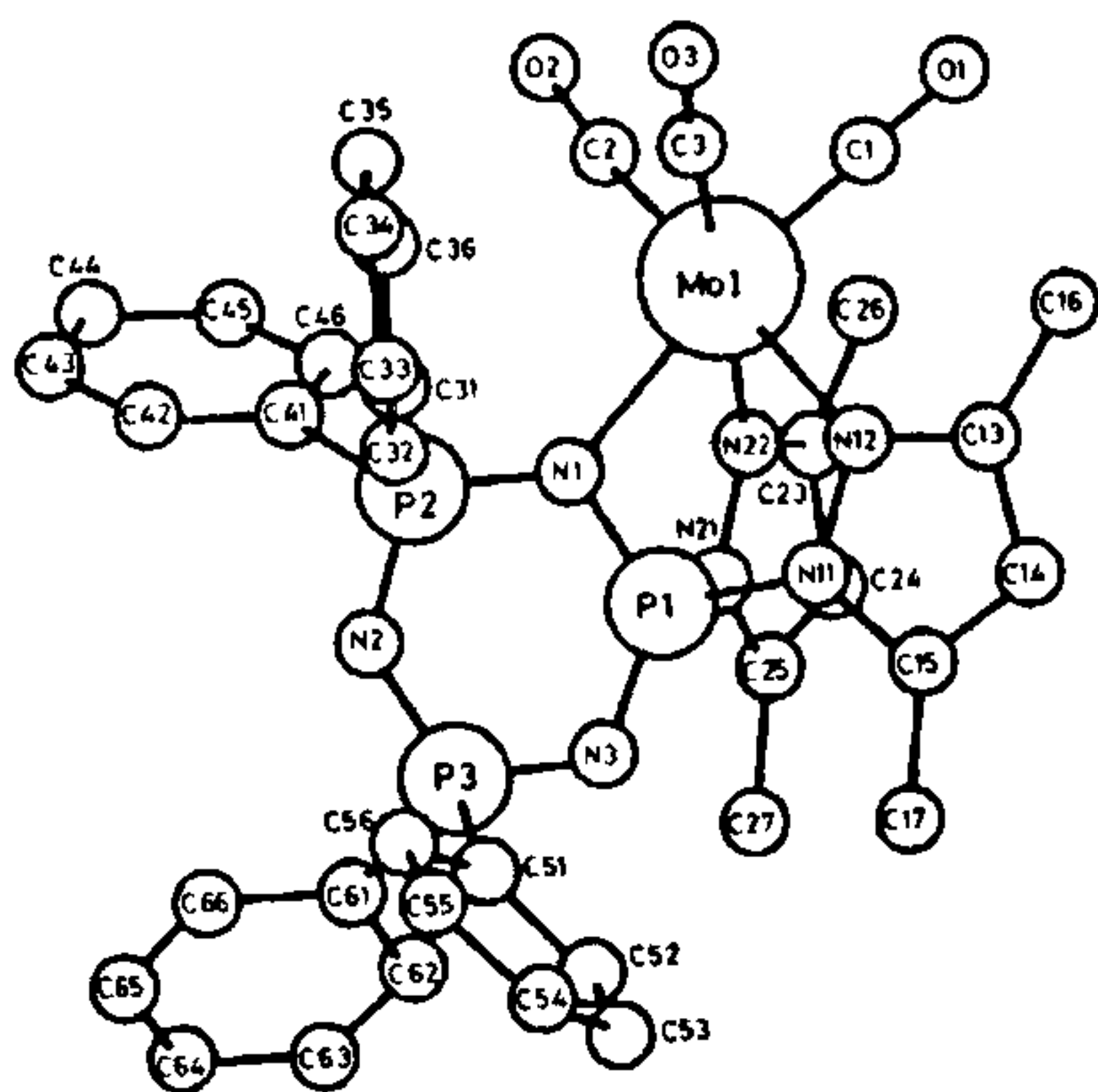
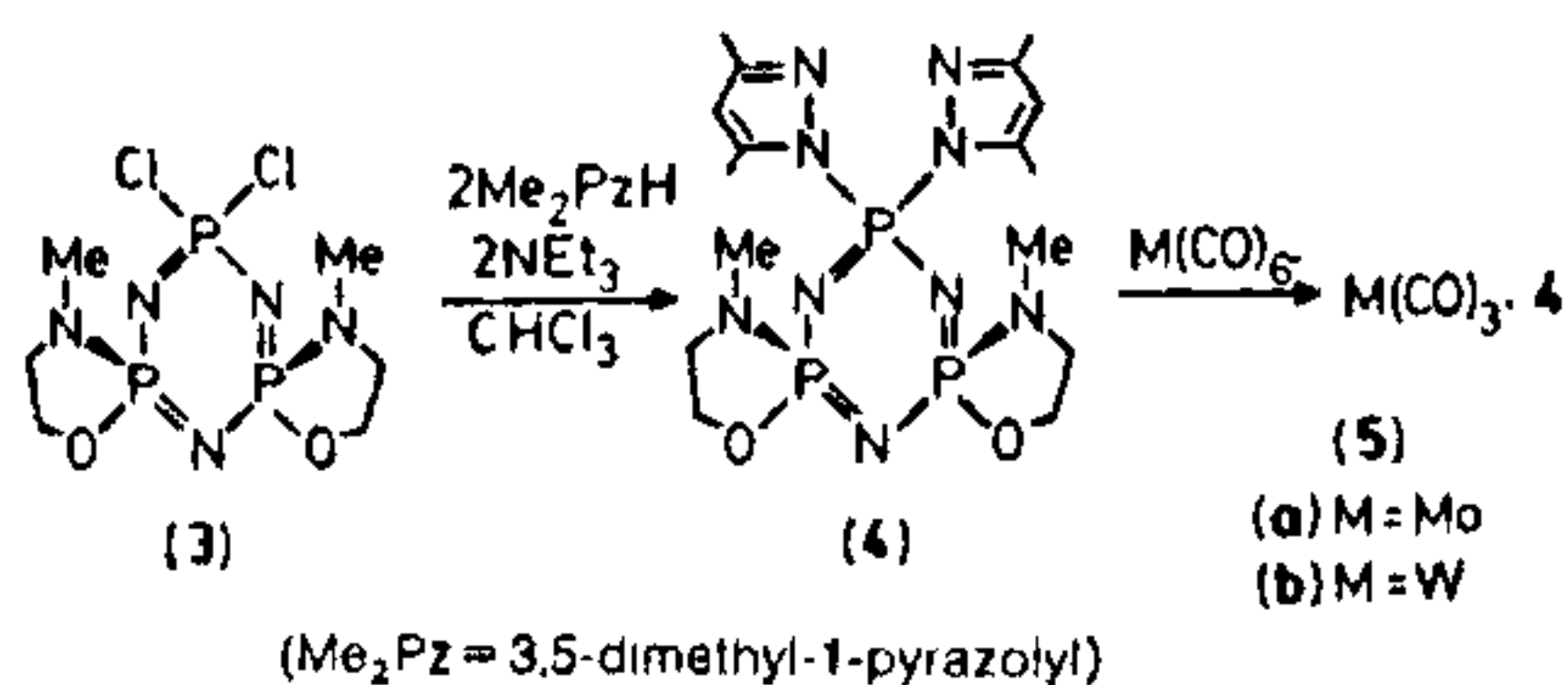


Figure 1. PLUTO diagram of compound 2. Selected bond lengths (Å) and bond angles (°) are as follows: Mo-Cl=1.910(3); Mo-C2=1.934(3); Mo-C3=1.939(3); Mo-N1=2.394(2); Mo-N12=2.299(2); Mo-N22=2.311(2); P1-N1=1.593(2); N1-P2=1.637(2); P2-N2=1.598(3); N2-P3=1.588(3); P3-N3=1.626(2); N3-P1=1.557(2); Cl-Mo-C2=82.6(1); Cl-Mo-C3=82.4(1); C2-Mo-C3=84.4(1); N1-Mo-N12=73.8(1); N1-Mo-N22=73.4(1); N12-Mo-N22=79.5(1); phosphazene ring angles at P1=122.4(1), P2=114.4(1), P3=115.9(1), N1=120.1(1), N2=126.3(2), N3=120.1(1). Crystal data for 2: Triclinic, P $\bar{1}$; $a=10.764(4)$, $b=11.591(2)$, $c=15.113(2)$ Å; $\alpha=100.98(2)^\circ$, $\beta=89.52(4)^\circ$, $\gamma=78.26(4)^\circ$; $V=1810$ Å³; $Z=2$; $T=291$ K; $\lambda(\text{MoK}\alpha)=0.71069$ Å; 8057 observed reflections ($F > 6\sigma(F)$) ($1 < \theta < 30$); Solved by the Patterson heavy atom technique and refined by difference Fourier syntheses using SHELEX76; The final $R=0.0398$; $R_w=0.0477$. Further details of the structure can be had from the authors.

bonds (2.299(2), 2.311(2) Å). As a consequence, the metal-carbon bond opposite to the phosphazene ring nitrogen atom is shorter (1.910(3) Å) than the other metal-carbon bonds (1.934(3), 1.939(3) Å).

Since compound 2 is insoluble in common organic solvents, we have attempted to modify the ligand to overcome this problem. We have prepared bis(*N*-methylethanolamino) bis(3,5-dimethyl-1-pyrazolyl) cyclotriphosphazene 4 from the structurally characterized dichloro bis(*N*-methylethanolamino) cyclotriphosphazene (3)⁵. Treatment of this ligand with $M(\text{CO})_6$ ($M=\text{Mo}$ or W) yields soluble metal tricarbonyl complexes, $[M(\text{CO})_3 \cdot 4]$ (5). They are assigned a structure similar to 2 on the basis of IR, ¹H and ³¹P NMR data. The ³¹P NMR spectrum of 4 showed an A_2X pattern



($\delta_A=31.2$, $\delta_X=6.1$ ppm; $J_{AX}=68.0$ Hz); the spectrum of 5a showed an ABX pattern ($\delta_A=30.6$, $\delta_B=27.3$, $\delta_X=-3.3$ ppm; $J_{AX}=66.1$, $J_{BX}=60.8$, $J_{AB}=50.5$ Hz). Single-crystal X-ray structure determination of compound 5b is in progress.

1. Allcock, H. R., Desorcie, J. L. and Riding, G. H., *Polyhedron*, 1986, 6, 119.
2. Allcock, H. R., Manners, I., Mang, M. N. and Parvez, M., *Inorg. Chem.*, 1990, 29, 522.
3. Srivatsava, S. C., Shrimal, A. K. and Pandey, R. V., *Trans. Met. Chem.*, 1987, 12, 421.
4. Gallicano, K. D. and Paddock, N. L., *Can. J. Chem.*, 1982, 60, 521.
5. Chandrasekhar, V., Krishnamurthy, S. S., Manohar, H., Vasudeva Murthy, R., Shaw, R. A. and Woods, M., *J. Chem. Soc., Dalton Trans.*, 1984, 621.

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A new fossil pollen record—*Transdanubiapollenites* Kedves & Pardutz from the Neyveli lignite deposit, South India

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Well-preserved fossil pollen of *Transdanubiapollenites* Kedves & Pardutz, previously reported from the Eocene of Hungary, has been recovered for the first time from the Miocene sediments of South India. The present record is significant as it extends the stratigraphic range of *Transdanubiapollenites*. I propose new species, *T. indicus*.

THE form genus *Transdanubiapollenites* was proposed by Kedves & Pardutz¹ for pollen characterized by three narrow colpi, retipilate exine and ornamented lumina, and described under *Transdanubiapollenites magnus*. Pollen grains recovered by me from lignite core samples of Mine III, Neyveli Lignite Field, South India² (Figure 1) are distinct in having thicker exine, shorter colpi; lumina of varying size and shape (usually polygonal), and muri thickened at the joints. I have given the specific epithet *indicus* after the name of the country. The genus differs from *Retitrescolpites* Sah, in having ectonexine comprised of free bacula/spines and ornamented lumina³.