The Crystal and Molecular Structure of *trans*-Bis(dinitrogen)bis[1,2-bis(diphenylphosphino)ethane]molybdenum(0)

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Since the discovery of the dinitrogen-coordinated complex of a transition metal,[1] attention has been drawn to dinitrogen complexes of transition metals in relation to nitrogen fixation in biological systems. Molybdenum-dinitrogen complexes are especially interesting because of the key role of molybdenum in both chemical and biological nitrogen fixation. In previous papers[2] we reported briefly the preparation of molybdenum-dinitrogen complexes of the types $Mo(N_2)(PPh_3)_2 \cdot C_6H_5CH_3$ and *trans*-$Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2$ obtained by the reduction of molybdenum(III) acetylacetonate with trialkylaluminum in the presence of triphenylphosphine or 1,2-bis(diphenylphosphino)-ethane under a nitrogen atmosphere. In this communication we wish to report the crystal and molecular structure of the latter molybdenum-dinitrogen complex, *trans*-bis(dinitrogen)bis[1,2-bis(diphenylphosphino)-ethane]molybdenum(0), determined by three-dimensional X-ray analysis.

Orange crystals suitable for X-ray analysis were obtained by recrystallization of the complex from toluene/*n*-hexane. The specimen was sealed off in a thin-walled Pyrex capillary in a nitrogen atmosphere. Crystals are triclinic, space group $P\bar{1}$ with one molecule in a unit cell of dimensions, $a=10.64$, $b=12.63$, $c=10.51$Å, $\alpha=92.47$, $\beta=118.91$, and $\gamma=71.20°$. Intensity measurements were carried out on the four-circle diffractometer using monochromatized Mo$K\alpha$ radiation. A total of 3253 reflections were recorded in the range of $2\theta \leq 55°$. Lorentz and polarization corrections were made, absorption correction being neglected. The positions of molybdenum atom and two phosphorus atoms were determined from three-dimensional Patterson map. All other light atoms except hydrogen atoms then revealed their positions on three-dimensional electron density map calculated on the basis of molybdenum and phosphorus contributions. Structure was refined by block-diagonal least-squares with isotropic temperature factors, to an R factor of 0.148.

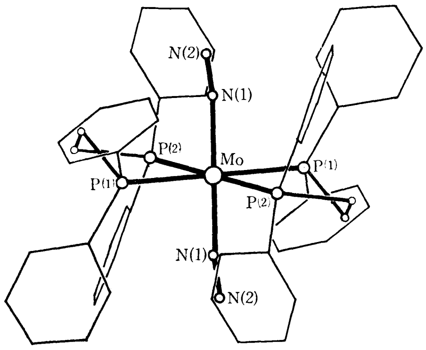

Table 1. Bond lengths and angles

Bond length		Bond angle	
Mo–P(1)	2.50 Å (0.004)	P(1)–Mo–P(2)	80.9°(0.1)
Mo–P(2)	2.45 (0.005)	N(1)–Mo–P(1)	87.3 (0.4)
Mo–N(1)	2.01 (0.012)	N(1)–Mo–P(2)	84.3 (0.5)
N(1)–N(2)	1.10 (0.02)	N(2)–N(1)–Mo	171.8 (1.1)

Values in parentheses indicate standard deviation.

Molybdenum atom occupies the center of symmetry, and four phosphorus atoms and *trans* two nitrogen molecules form a distorted octahedron. The end view along the *b* axis is shown above. The bond lengths and angles at this stage are summarized in Table 1. There is no significant elongation of the N–N bond upon coordination, as in the case of ruthenium- and cobalt-dinitrogen complexes.[3] The Mo–N bond length of 2.01 Å is not significantly shorter than a metal-nitrogen (M–N) single bond distance (1.95—2.15 Å). It is of great interest that the Mo–N–N entity is slightly bent in contrast to the M–N–N entities of ruthenium- and cobalt-dinitrogen complexes which are almost linear.[3]

Calculations were carried out at the Computer Center, the University of Tokyo, with programs of UNICS.

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