

Dimolybdenum Complexes with a Potentially Tetradentate PNNP Ligand, 2,7-Bis(diphenylphosphino)-1,8-naphthyridine (dpnapy)

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Reaction of *cis*-[Mo₂(O₂CCH₃)₂(CH₃CN)₆](BF₄)₂ with a potentially tetradentate PNNP ligand, 2,7-bis(diphenylphosphino)-1,8-naphthyridine (dpnapy), in a 1:2 molar ratio afforded a mixture of isomeric dimolybdenum complexes, *cis*-[Mo₂(O₂CCH₃)₂(dpnapy-*N,P*)₂](BF₄)₂ (**1**) and *trans*-[Mo₂(O₂CCH₃)₂(dpnapy-*N,N'*)₂](BF₄)₂ (**2**) in 63 and 5% yields, respectively, which were characterized by X-ray crystallography.

Metal-metal bonded di- and trinuclear complexes have been of general interest in connection with minimal models for the surface of heterogeneous catalysts.^{1,2} In particular, linearly-ordered, small-size clusters have potential importance in catalytic reactions as well as in material chemistry. We have systematically studied di-, tri- and polynuclear complexes of palladium and platinum with isocyanide and diphosphine ligands by the use of chemical and electrochemical procedures.³⁻¹² Recently, a tridentate phosphine, bis(diphenylphosphinomethyl)phenylphosphine (dpmp), has been used in platinum and palladium chemistry to construct the metal-metal bonded linear trinuclear aggregates [Pt₂M(μ-dpmp)₂(XylNC)₂](PF₆)₂ (M = Pt, Pd) and [Pt₂MCl(μ-dpmp)₂(XylNC)₂](PF₆)₂ (M = Rh, Ir).¹³⁻¹⁷ The quadruply bonded dimolybdenum(II) complexes *trans*-[Mo₂(μ-dpmp)₂(O₂CR)₂](BF₄)₂ (R = CH₃, Bu^t, Ph) were also prepared and were readily transformed into the ligand-oxidized complexes *trans*-[Mo₂(μ-dpmp-O)₂(O₂CR)₂](BF₄)₂ [dpmp-O = Ph₂PCH₂P(Ph)CH₂PPh₂(=O)].¹⁸ In this report, a potentially tetradentate PNNP ligand, 2,7-bis(diphenylphosphino)-1,8-naphthyridine (dpnapy), was reacted with *cis*-[Mo₂(O₂CCH₃)₂(CH₃CN)₆](BF₄)₂ to afford two isomeric dimolybdenum(II) complexes, *cis*-[Mo₂(O₂CCH₃)₂(dpnapy-*N,P*)₂](BF₄)₂ (**1**) and *trans*-[Mo₂(O₂CCH₃)₂(dpnapy-*N,N'*)₂](BF₄)₂ (**2**). The dpnapy ligand, originally prepared by Ziessel,¹⁹ involves four PNNP donor atoms suitably arranged for bonding to a linear arrangement of metals. However, structurally characterized transition metal complexes with dpnapy are limited to two examples, [Au₂K(μ-dpnapy)₃]³⁺ and [Ag₃(μ-dpnapy)₃]³⁺.²⁰ The rigid hetero-donor system of dpnapy is expected to show various coordination modes in small-size cluster cores.

To a dichloromethane solution containing *cis*-[Mo₂(O₂CMe)₂(MeCN)₆](BF₄)₂ was added 2 equiv. of dpnapy, and the solution was stirred at room temperature for 12 h. The resultant green solution was concentrated to dryness, and the residue was crystallized from an acetone/toluene mixed solvent to afford block-shaped, dark green crystals of *cis*-[Mo₂(O₂CCH₃)₂(dpnapy-*N,P*)₂](BF₄)₂ · 0.5C₇H₈ (1 · 0.5C₇H₈) in 63% yield. The mother liquor was concentrated to dryness and the residue was crystallized from an acetone/benzene mixed solvent to give a mixture of dark green microcrystals of **1** (not purified) and light green crystals of *trans*-[Mo₂(O₂CCH₃)₂(dpnapy-*N,N'*)₂](BF₄)₂ · 5C₆H₆ (**2** · 5C₆H₆) in a ratio of 3:1 (deter-

mined by ³¹P{¹H} NMR spectroscopy). The yield of **2** · 5C₆H₆ was estimated to *ca.* 5% on the basis of the ³¹P{¹H} NMR spectrum, although **2** was not isolated as a pure compound. The formula of **2** was determined by X-ray crystallography (*vide infra*). The ³¹P{¹H} NMR spectrum of **1** showed two singlets at δ 5.78 and 39.34 in a 1:1 ratio, and the spectrum of **2** one singlet at δ -6.43, indicating an asymmetrical (**1**) and a symmetrical (**2**) coordination mode of the dpnapy ligand, respectively.

An ORTEP diagram of the complex cation of **1** with the atomic numbering scheme is illustrated in Fig. 2. The

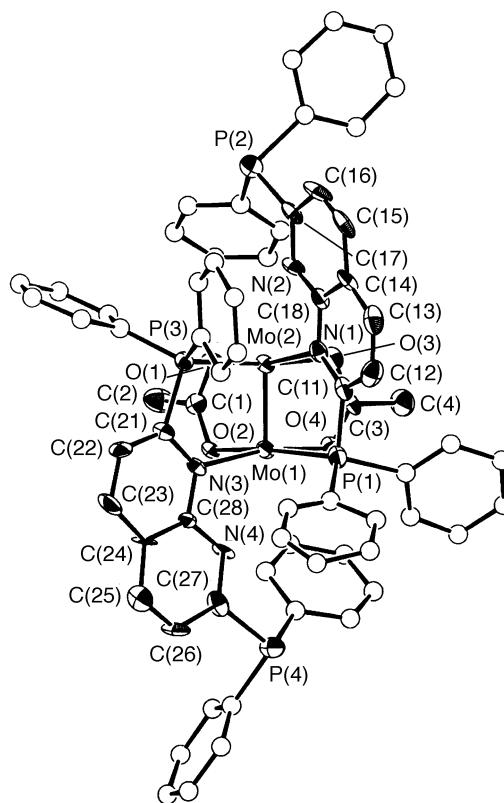


Fig. 2 ORTEP plot of the complex cation of **1** with 50% probability ellipsoids. Carbon atoms of the phenyl groups are drawn by arbitrary circles and hydrogen atoms are omitted for clarity. Crystal data: monoclinic, *P*2₁/*n*, *a* = 14.374(3) Å, *b* = 25.803(7) Å, *c* = 20.942(4) Å, β = 91.51(2)°, *V* = 7765 Å³, *T* = -100 °C, *D*_{calc} = 1.490 g cm⁻³, *R* = 0.059 and *R*_w = 0.068 for 5457 independent reflections with *I* > 2.5σ(*I*)

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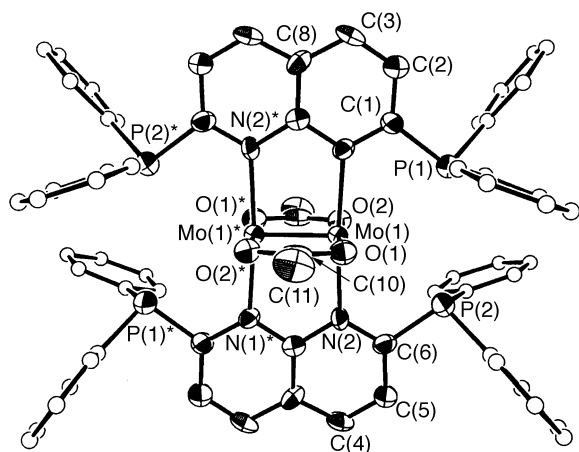


Fig. 3 ORTEP plot of the complex cation of **2** with 50% probability ellipsoids. Carbon atoms of the phenyl groups are drawn by arbitrary circles and hydrogen atoms are omitted for clarity. Crystal data: triclinic, $P\bar{1}$ (No. 2), $a = 13.861(3)$ Å, $b = 14.134(8)$ Å, $c = 12.790(6)$ Å, $\alpha = 109.63(5)^\circ$, $\beta = 99.68(3)^\circ$, $\gamma = 89.94(3)^\circ$, $V = 2322$ Å³, $T = 23^\circ\text{C}$, $D_{\text{calc}} = 1.338$ g cm⁻³, $R = 0.058$ and $R_w = 0.058$ for 3303 independent reflections with $I > 3\sigma(I)$

complex cation of **1** comprises a dimolybdenum centre bridged by two acetate groups and two dpnapy ligands in a *cis* arrangement (Fig. 2). The Mo(1)–Mo(2) distance is 2.119(1) Å, which indicates the presence of a Mo–Mo quadruple bond.²¹ The two dpnapy ligands coordinate through a set of P, N donors and adopt a head-to-tail structure [average Mo–N = 2.192(10) Å and average Mo–P = 2.569(4) Å]. The Mo–Mo–N angles [average 99.5(3)°] are considerably expanded from 90°, which is contrasted with the Mo–Mo–P angles [average 92.94(10)°]. The remaining P and N atoms of dpnapy are outside of the normal bonding sphere of Mo atoms with average Mo...P and Mo...N distances of 4.863(4) and 2.789(10) Å, respectively. The latter value suggests a weak interaction of the N atoms with the axial orbitals of the Mo atoms, which may cause a slight elongation of the Mo–Mo quadruple bond in comparison with that of **2** (*vide infra*). The PNNP array of dpnapy ligands are not parallel to the Mo–Mo vector, the uncoordinated P and N atoms hanging over the axial vacant site of the dimolybdenum unit. This deformation of dpnapy probably prevents the formation of a head-to-head structure.

A perspective view of the complex cation of **2** with the atomic numbering scheme is given in Fig. 3. The complex cation has a crystallographically imposed inversion centre on the middle of the Mo–Mo bond. The two Mo^{II} ions are joined by a metal–metal quadruple bond, which is further supported by two acetate and two dpnapy bridging ligands with a *trans* arrangement. The Mo–Mo bond length of 2.099(2) Å is slightly shorter than that of **1**. The dpnapy ligand bridges the dimolybdenum centre though the two pyridyl nitrogen atoms [average Mo–N = 2.200(11) Å] and the two phosphine units are uncoordinated with an average Mo...P distance of 3.239(4) Å. The lone pairs of the phosphine units are not directed towards the metal. The crystal structure shows that the *trans* arrangement of two dpnapy ligands, bridging *via* two N atoms on a dimetal centre, is much more favored than the *cis* arrangement owing to the steric repulsion between the two uncoordinated phosphine units. The distortion of the dimolybdenum centre from an ideal paddle-wheel structure is significantly smaller than is found in **1**; the average Mo–Mo–N and Mo–Mo–O angles are 92.7(3) and 92.3(3)°, respectively. However, the

interatomic distance between the two uncoordinated P atoms is considerably short at 3.529(4) Å, which is within the sum of the van der Waals radii (*ca.* 3.8 Å). This short contact should destabilize the dimolybdenum structure and might be responsible for its low yield.

Techniques used: ¹H and ³¹P NMR, X-ray crystallography

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Table 1: Crystallographic and experimental data for **1** · 2CH₂Cl₂ · C₇H₈ and **2** · 5C₆H₆

Table 2: Selected bond distances and angles for **1** · 2CH₂Cl₂ · C₇H₈

Table 3: Selected bond distances and angles for **2** · 5C₆H₆

Figure 1: Possible coordination modes of dpnapy for multinuclear cores

Scheme: 1

Appendix: Tables of fractional atomic co-ordinates for non-H and H atoms, anisotropic thermal parameters, bond lengths and angles

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