Dimolybdenum Compounds with Crosswise-Bridging Acetonitrile Molecules

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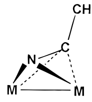
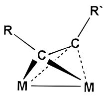
Several years ago we reported an efficient method for the preparation of the $[Mo_2(CH_3CN)_{8(10)}]^{4+}$ cation as its BF_4^- salt.[1] We were interested in this cation as a possible synthon for making other dimolybdenum compounds and have found that it enters into a number of interesting—but not always predictable—reactions. We report two such reactions and their products here. Both products contain the crosswise-bridging μ,η^2-acetonitrile molecule, **I**. Only one prior example of this structural element is known to us, namely the one in $W_2Cl_4(\mu\text{-dppm})_2(\mu,\eta^2\text{-}CH_3CN)$, reported earlier by J. Eglin and coworkers.[2] We have found two more examples, and with a different metal (Mo). We think this is significant because it shows that the previous case is not an isolated curiosity and that the capacity of acetonitrile (and presumably other nitriles) to bond in this and other ways besides simple $CH_3CN{\rightarrow}M$ end-on bonding is more important than previously believed.



I



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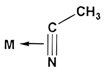
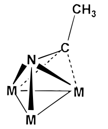


III



IV

The reaction of $[Mo_2(CH_3CN)_8](BF_4)_4$ with bis(diphenylphosphino)amine (dppa) in acetonitrile follows the course shown in eq 1. A color change from deep blue to dark green took place within minutes, but nevertheless the reaction mixture was stirred for 12 h at room temperature. The clear solution was then layered with a mixture of hexanes and diethyl ether. After a few days dark green crystals had formed. The crystalline yield is ca. 60% based on $[Mo_2(CH_3CN)_8](BF_4)_4$. When exposed to air at room temperature, these crystals lose crystallinity due to loss of solvent. This substance, compound **1**, was shown by X-ray crystallography to have the composition $[Mo_2(\mu,\eta^2\text{-}CH_3CN)(\mu\text{-dppa})(\mu\text{-}NC(CH_3)P(C_6H_5)_2NP(C_6H_5)_2)(CH_3CN)_5](BF_4)_3{\cdot}CH_3OH_{0.5}{\cdot}(CH_3CN)_3$.[3] This formulation of compound **1** is strongly supported by physical measurements.[3]

$$[Mo_2(NCCH_3)_8](BF_4)_4 \xrightarrow[-\,H^+,\ -\,BF_4^-]{RT,\ 12h;\quad +\,NCCH_3,\ +\,2\ dppa} [Mo_2(\mu,\eta^2\text{-}NCCH_3)(\mu\text{-}NC(CH_3)P(Ph_2)NP(Ph_2)(dppa)(CH_3CN)_5](BF_4)_3 \qquad (1)$$

The solvents of crystallization (MeOH, non-coordinated MeCN) can be removed from the crystals by oil pump vacuum. This was shown by elemental analysis of the remaining green powder.

When the reaction is carried out in the presence of traces of water, a second product crystallizes, compound **2**. The crystalline yield was up to 18%, based on $[Mo_2(CH_3CN)_8](BF_4)_4$. Higher yields of **2** can be obtained if a stoichiometric amount of water (with respect to $[Mo_2(CH_3CN)_8](BF_4)_2)$ is added to the reaction mixture at the outset. Compound **1** cannot be isolated under these circumstances. The composition of **2**, from an X-ray structure determination, is $[Mo_2(\mu,\eta^2\text{-}CH_3CN)(\mu\text{-}O)(\mu\text{-dppa})_2(CH_3CN)_4](BF_4)_2{\cdot}(CH_3CN){\cdot}(hexanes)_{0.5}$,[3] and again the solvents of crystallization are removed in oil pump vacuum.[3]

The structure of the core region of **1** is shown in Figure 1. There are two remarkable features of this structure. First, it contains a μ,η^2-CH_3CN ligand in a crosswise relationship to the metal−metal bond. This will be discussed further below. Second, there is an unusual chelating ligand, which also bridges the two molybdenum atoms with one nitrogen atom. This ligand has arisen by the linking of a deprotonated dppa molecule and one acetonitrile molecule, as shown in eq 2. Since molecule **1** has no unpaired electrons (as indicated by the molar susceptibility and the easily accessible NMR spectra) but an odd number of counterions, it must be assumed that a negatively charged ligand is present. The lack of a ^{1}H-NMR signal for the H attached to N(4) and the short N(4)−P(3) bond distance indicate a double bond between the two latter atoms. Moreover, within the constraints of a six-membered ring, the N(10)−C(101)−

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[1] (a) Cotton, F. A.; Wiesinger, K. J. *Inorg. Chem.* **1991**, *30*, 871. (b) Cotton, F. A.: Eglin, J. L.; Wiesinger, K. J. *Inorg. Chim. Acta* **1992**, *195*, 11. (c) Cotton, F. A.; Wiesinger, K. *J. Inorg. Synth.* **1992**, *29*, 134.

[2] Eglin, J. L.; Hines, E.; Valente, E. J.; Zubkowski, J. D. *Inorg. Chim. Acta* **1995**, *229*, 113.

[3] Compounds **1** and **2** were crystallized by layering solutions of the compounds in acetonitrile/methanol or acetonitrile, respectively, with hexanes and then diethyl ether. Within a week bright dark green (**1**) or bluish green (**2**) crystals formed at room temperature. **1** crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with $a = 15.292(3)$ Å, $b = 15.654(6)$ Å, $c = 18.145(7)$ Å, $\alpha = 75.95(2)°$, $\beta = 75.35(2)°$, $\gamma = 70.42(3)°$. Cell volume = 3899(2) Å^3. The data were collected on an Enraf-Nonius Fast diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å) at −100 °C. All non-hydrogen atoms were anisotropically refined; in calculating Fc values, H atoms of all nonsolvent molecules were included in ideal positions. A common temperature factor was refined for all H atoms. 7663 unique data were collected with $6874 > 4s(I)$, $R_{1(obs)} = 8.0$, $wR_{2(obs)} = 18.4$. We believe that these relatively high values are the result of severe disorder of some of the included solvent molecules and BF_4^- ions. Spectroscopic data: ^{1}H-NMR (200.1 MHz, CD_3CN, 22.2 °C) δ (ppm) = 8.58−8.70 (m, 3H, aromat. H), 8.10−8.17 (m, 3H, aromat. H), 7.54−7.67 (m, 12H, aromat. H), 6.80−7.36 (m, 22H, aromat. H), 4.74 (dd, 1H, $^2J_{P(1,2)-H} = 17$ Hz, N−*H*), 3.85 (d, 3H, $^2J_{P(4)-H} = 29$ Hz, P(4)−C−CH_3), 3.46 (s, 3H, bridging NCCH_3), 1.95 (s, 15H, terminal NCCH_3); $^{31}P\{^1H\}$-NMR(CH_3CN, 22 °C, 81 Hz) δ (ppm) = 81.5 (d, $^2J_{P(2)-P(1)} = 53$ Hz, P(2)), 80.6 (dd, $^2J_{P(1)-P(2)} = 53$ Hz, $^2J_{P(1)-P(3)} = 34$ Hz, P(1)) 52.3 (t, $^2J_{P(3)-P(1)} = 34$ Hz, $^2J_{P(3)-P(4)} = 33$ Hz, P(3)), 21.4 (d, $^2J_{P(4)-P(3)} = 33$ Hz, P(4)); IR (KBr) ν (cm^{-1}) = 3055 w, 2963 m, 2313 w, 2280 m, 1636 m, 1481 m, 1436 m, 1261 s, 1084 vs, 803 s, 742 m, 696 s, 531 m, 505 m; UV−vis (acetonitrile) ν (nm) = 715 b; +FAB/DIP-MS (Nitrobenzyl alcohol (NBA)) *m/z* = 1170 ($[M - 2\,CH_3CN]^+$, Mo-98, rel. int. 4%), 1129 ($[M - 3CH_3CN]^+$, 4%), 1104 ($[M - C_2H_6 - CH_3CN - C_6H_5]^+$, 5%), 1088 ($[M - 4CH_3CN]^+$, 8%), 1082 ($[M - C_{12}H_{10} - CH_4]^+$, 13%), 1047 ($[M - 5CH_3CN]^+$, 4%), 1041 $[M - (C_6H_5)_2P - CN]^+$, 3%), 1026 $[M - (C_6H_5)_2P - CH_3CN]^+$, 12%), 980 ($[M - 6CH_3CN - CN]^+$, 14%), 537 ($[(C_6H_5)_2PN(C_6H_5)_2P(C_6H_5)_2]^+$, 20%), 468 ($[(CH_3)CN{-}(C_6H_5)_2PN(H)_2(C_6H_5)_2{-}NC(CH_3)]^+$, 20%), 427 ($[(C_6H_5)_2PN(H)_2P(C_6H_5)_2{-}C(CH_3)N]^+$, 28%), 386 $[(C_6H_5)_2PN(H_2)P(C_6H_5)_2]^+$, 100%); $\chi_{mol} = 7 \times 10^{-5}$ cm^3 mol^{-1} (298 K); Elemental analysis for $Mo_2C_{62}H_{62}N_9P_4B_3F_{12}$ (1509.40 g/mol) calcd C, 49.34; H, 4.14; N, 8.35; found C, 49.21; H, 4.41; N, 8.09. **2** crystallizes in the orthorhombic space group *Cmcm* (No. 63), with $a = 13.804(1)$ Å, $b = 22.629(2)$ Å, $c = 24.862(2)$ Å; volume = 7766(1) Å^3. The data were collected on a CAD4 diffractometer (Mo Kα radiation; $\lambda = 0.71073$ Å) at room temperature with the crystal mounted in a capillary. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms on the ligands were placed in calculated positions. Peaks representing interstitial hexane molecules were refined as partially occupied carbon sites, but since they represent a mixture of several isomers no single molecular model for the solvent molecule is implied. The presence of hexanes in the crystals was confirmed by ^{1}H-NMR spectroscopy. 3652 unique data were collected with $2766 > 2s(I)$, $R_{1(obs)} = 4.7$, $wR_{2(obs)} = 12.6$. Spectroscopic data: ^{1}H-NMR (200.1 MHz, CD_3CN, 22.2 °C) δ (ppm) = 7.33−8.17 (m, 40H, aromat. H), 5.53 (b, 1H, N−*H*), 5.15 (b, 1H, N−*H*), 3.43 (s, 3H, bridging $NCCH_3$), 1.95 (s, 12H, terminal NCCH_3); $^{31}P\{^1H\}$-NMR (CH_3CN, 22.2 °C, 81 MHz), AA′BB′ system, multiplets centered at δ (ppm) = 74.6, 67.0; IR (KBr) ν (cm^{-1}) = 3052 w, 2963 m, 2315 m, 2286 s, 1684 m, 1633 m, 1572 w, 1482 m, 1435 s, 1262 s, 1054 vs, 802 st, 752 m, 705 s, 504 m, 521 m; UV−vis (acetonitrile) ν (nm) = 725 b; $\chi_{mol} = 3 \times 10^{-5}$ cm^3 mol^{-1} (298 K); Elemental analysis for $Mo_2C_{58}H_{57}N_7P_4OB_2F_8$ (1357.50 g/mol) Calcd C, 51.29; H, 4.20; N, 7.22; found C, 51.08; H, 4.47; N, 6.93. $[Mo_2(m,h^2\text{-}CH_3CN)(m\text{-}O)(m\text{-dppma})_2(CH_3CN)_4](BF_4)_2$: $^{31}P\{^1H\}$-NMR (81 MHz, CH_3CN) AA′BB′ system, multiplets centered at δ (ppm) = 96.2 and 86.4; ^{1}H-NMR (200.1 MHz, CD_3CN, 22.2 °C) δ (ppm) = 7.35−8.22 (m, 40H, aromat. H), 4.40 (dd, 3H, $^2J_{P-H} = 15$ Hz, 45 Hz, N-CH_3), 3.43 (d, 3H, $^2J_{P-H} = 10$ Hz, N−CH_3), 3.37 (s, 3H, bridging NCCH_3), 1.95 (s, 12H, terminal NCCH_3); IR (KBr) ν (cm^{-1}) = 3052 w, 2962 m, 2315 m, 2285 m, 1685 m, 1572 w, 1482 m, 1300 m, 1262 m, 1053 vs, 875 s, 803 m, 751 m, 701 s, 640 m, 614 w, 505 m, 525 m; UV−vis (CH_3CN) ν (nm) = 723 b; $\chi_{mol} = 4 \times 10^{-5}$ cm^3 mol^{-1} (298 K); Elemental analysis for $Mo_2C_{60}H_{61}N_7OP_4B_2F_8$ (1385.55 g/mol) calcd C, 52.01; H, 4.44; N, 7.08; found C, 51.82; H, 4.54; N, 6.97. Crystal yield: ca. 54%.

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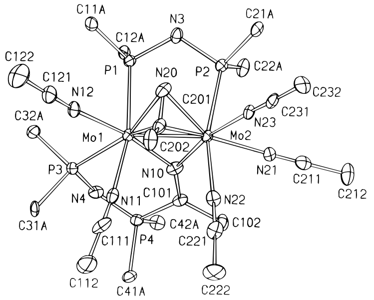


Figure 1. ORTEP representation of the core atoms in $[Mo_2(\mu,\eta^2\text{-}NCCH_3)(\mu\text{-dppa})(m\text{-}NC(CH_3)P(C_6H_5)_2NP(C_6H_5)_2)(NCCH_3)_5](BF_4)_3$ (**1**). Thermal ellipsoids for Mo, P, N, C are shown at 50% probability. Selected bond distances (in Å) and angles (in deg) are as follows: Mo(1)−Mo(2) 2.493(15), Mo(1)−N(10) 2.068(8), Mo(1)−N(20) 2.169(8), Mo(1)−N(11) 2.156(9), Mo(1)−N(12) 2.19(1), Mo(1)−P(1) 2.579(3), Mo(1)−P(3) 2.630(3), Mo(2)−N(10) 2.045(8), Mo(2)−C(201) 2.09(1), Mo(1)−C(201) 2.13(1), Mo(2)−N(20) 2.14(1), Mo(2)−N(22) 2.16(1), Mo(2)−N(23) 2.19(1), Mo(2)−N(21) 2.22(1), Mo(2)−P(2) 2.524(3), P(4)−C(101) 1.83(1), N(20)−C(201)−C(202) 134.6(10), N(10)−C(101)−C(102) 123.3(9), Mo(2)−N(10)−Mo(1) 74.6(3), Mo(2)−N(20)−Mo(1) 70.7(2), Mo(2)−C(201)−Mo(1) 72.4(3).

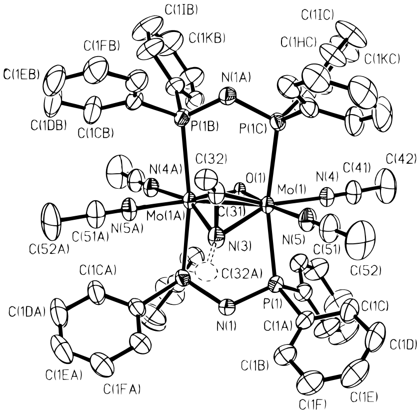
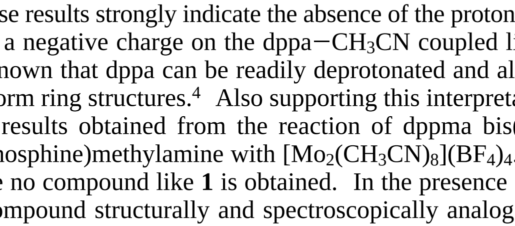


Figure 2. ORTEP representation of $[Mo_2(\mu\text{-}NCCH_3)(\mu\text{-}O)(\mu\text{-dppa})_2(NCCH_3)_4](BF_4)_2$ (**2**). The disorder of the bridging acetonitrile is shown by dashed lines. Thermal ellipsoids are shown at 40% probability. Selected bond angles (in deg) and distances (in Å) are as follows: Mo(1)−Mo(1) 2.4174(8), Mo(1)−N(3) = Mo(1)−C(31) 2.115(4), Mo(1)−O(1) 2.082(3), Mo(1)−N(5) 2.117(5), Mo(1)−P(1) 2.560(1), P(1)−N(1) 1.683(2), Mo(1)−O(1)−Mo(1) 71.0(1), Mo(1)−N(3)−Mo(1) = Mo(1)−C(31)−Mo(1) 69.7(2).

P(4)−N(4) atoms are nearly coplanar (mean deviation 0.03 Å). These results strongly indicate the absence of the proton on N(4) and a negative charge on the dppa−CH_3CN coupled ligand. It is known that dppa can be readily deprotonated and also tends to form ring structures.[4] Also supporting this interpretation are the results obtained from the reaction of dppma bis(diphenylphosphine)methylamine with $[Mo_2(CH_3CN)_8](BF_4)_4$. In this case no compound like **1** is obtained. In the presence of water a compound structurally and spectroscopically analogous to **2** is formed.[3] However, we have not been able to find any previous report of the nucleophilic attack of phosphine on a nitrile carbon atom. As mentioned, this attack does not occur when water molecules are introduced, probably because water is able to reprotonate deprotonated dppa.[4]



(2)

The structure of **2** is shown in Figure 2. Here, again, there is a μ,η^2-CH_3CN ligand. The rest of the molecule is made up of conventional ligands, namely two μ-dppa molecules, four CH_3CN ligands coordinated in the usual end-on way, and a bridging O^{2-} anion. The formulation of the bridging oxygen as O^{2-} (not as OH^- or H_2O) is supported by the number of counterions (2 BF_4^-), the absence of O−H ^{1}H-NMR signals, the short Mo−O(1) bond distances (2.082(3) Å), the acute Mo−O(1)−Mo angle (71.0(1)°), and the molar susceptibility of the compound (OH^- as the bridging ligand would demand an unpaired electron in the Mo_2 core).

Table 1. Comparison of Selected Bond Distances (Å) and Angles (deg) of **1**, **2**, and $W_2Cl_4(m\text{-dppm})_2(\mu,\eta^2\text{-}CH_3CN)_3$ (**3**)

	1	**2**	**3**
N−C	1.27(1)	1.34(1)	1.30(1)
C−CH_3	1.49(2)	1.47(1)	1.62(1)
N−C−CH_3	134.6(10)	117.7(5)	116.3(7)
M−N−M	70.7(2)	69.7(2)	72.9(2)
M−C−M	72.4(3)	69.7(2)	72.8(2)

Both molecules **1** and **2** display the geometry of edge-sharing bioctahedra. The Mo−Mo bond can be formally regarded as a double bond. The comparatively short Mo−Mo distances (**1**, 2.493(2) Å; **2**, 2.417(1) Å) are due to the small bridging atoms. No reduction of the Mo_2^{4+} core has taken place. The elongated Mo−Mo bond distances in comparison to the starting material (d(Mo−Mo) = 2.187(1) Å)[1a] is due to the change from a paddle wheel type structure to an edge-sharing bioctahedral structure.[5]

The dimensions of the (μ,η^2-CH_3CN)Mo_2 units in **1** and **2** as well as the corresponding (μ,η^2-CH_3CN)W_2 unit in $W_2Cl_4(\mu\text{-dppm})_2(\mu,\eta^2\text{-}CH_3CN)$ (**3**) are collected for comparison in Table 1). In all cases the bridging acetonitrile ligand is significantly bent. In **2** and **3** it is relatively close to the ideal value for sp^2-hybridized atoms, while the angle in **1** is significantly larger.

It is somewhat surprising that this type of bridging nitrile group, **I**, was not found until recently, since it is essentially similar to the crosswise bridging that has been known for some time with acetylenes, **II**, and phospha-alkynes R−C≡P. For example, in a series of $[CpMo(CO)]_2(RCCR)$ compounds,[6] the C≡C distances were extended to about 1.34 Å and the C≡C-C angles were all close to 134°.

There are reports concerning the occurrence of η^2-RCN ligands in mononuclear compounds, **III**, analogous to η^2-RCCR ligands.[7] Also, there are cases in which RCN molecules are bound through their π-electrons to clusters of three or four metal atoms, **IV**.[8]

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Supporting Information Available: Listing of crystallographic data, bond distances, bond angles, and anisotropic thermal parameters (20 pages). Ordering information is given on any current masthead page.

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