with three bpy⁻ radical ($S = \frac{1}{2}$) ligands. It is interesting that a comparable magnitude of *intra*molecular antiferromagnetic exchange interaction is present in the two types of complexes.

Supplementary Material Available: Tables VI–X (experimental magnetic susceptibility data) (14 pages). Ordering information is given on any current masthead page.

References and Notes

(1) University of Colorado.
(2) University of Illinois.
(3) Camille and Henry Dreyfus Fellow, 1972–1977; A. P. Sloan Foundation Fellow, 1976–1978.
(4) (a) V. E. Wulf and S. Herzog, *Z. Anorg. Allg. Chem.*, **387**, 81 (1972); (b) I. Hanzaki and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **44**, 2312 (1971).
(5) R. A. Zelonka and M. C. Baird, *J. Am. Chem. Soc.*, **93**, 6066 (1971); Y. Y. Lim and R. S. Drago, *Inorg. Chem.*, **11**, 1334 (1972); N. M. Karayannis, C. M. Paleos, C. M. Mikulaski, L. L. Pytlewski, H. Blum, and M. M. Labes, *Inorg. Chim. Acta*, **7**, 74 (1973); P. F. Richardson and R. W. Kreilick, *J. Am. Chem. Soc.*, **99**, 8183 (1977).
(6) A preliminary report has appeared: R. M. Buchanan, H. H. Downs, W. B. Shorthill, C. G. Pierpont, S. L. Kessel, and D. N. Hendrickson, *J. Am. Chem. Soc.*, **100**, 4318 (1978).
(7) C. G. Pierpont, H. H. Downs, and T. G. Rukavina, *J. Am. Chem. Soc.*, **96**, 5573 (1974).
(8) The preparation of tris(semiquinone) complexes has been very recently reported by the direct reaction of a semiquinone with a metal salt; see A. V. Lobanov, G. A. Abakumov, and G. A. Razulaev, *Proc. Acad. Sci. USSR (Engl. Transl.)*, 441 (1977).
(9) C. Floriani, R. Henzi, and F. Calderazzo, *J. Chem. Soc., Dalton Trans.*, 2640 (1972).

(10) C. G. Pierpont, *Inorg. Chem.*, **16**, 636 (1977). The values of R_F and R_{wF} are defined as

$$R_F = \frac{\Sigma|F_o| - |F_c|}{\Sigma|F_o|}$$

$$R_{wF} = \left(\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w|F_o|^2} \right)^{1/2}$$

The function minimized during refinement was $\Sigma w(|F_o| - |F_c|)^2$ with weights calculated by the equation $w = 4F_o^2/\sigma^2(F_o^2)$.
(11) D. M. Duggan, E. K. Barefield, and D. N. Hendrickson, *Inorg. Chem.*, **12**, 985 (1973).
(12) R. G. Wollmann and D. N. Hendrickson, *Inorg. Chem.*, **16**, 3079 (1977).
(13) C. G. Pierpont and H. H. Downs, *J. Am. Chem. Soc.*, **98**, 4834 (1976).
(14) C. G. Pierpont and H. H. Downs, *Inorg. Chem.*, **16**, 2970 (1977).
(15) K. N. Raymond, S. S. Isied, L. D. Brown, F. R. Froncyek, and J. H. Nibert, *J. Am. Chem. Soc.*, **98**, 1767 (1976).
(16) C. G. Pierpont and H. H. Downs, *Inorg. Chem.*, **14**, 343 (1975).
(17) C. G. Pierpont and R. M. Buchanan, *J. Am. Chem. Soc.*, **97**, 4912 (1975).
(18) J. Iball and C. H. Morgan, *Acta Crystallogr.*, **23**, 239 (1967).
(19) T. A. Hamor and D. J. Watkins, *Chem. Commun.*, 440 (1969).
(20) H. H. Downs, R. M. Buchanan, and C. G. Pierpont, submitted for publication.
(21) N. N. Greenwood and T. C. Gibb, "Mossbauer Spectroscopy", Chapman and Hall, London, 1971, Chapter 6.
(22) See paragraph at end of paper regarding supplementary material.
(23) S. L. Kessel and D. N. Hendrickson, manuscript in preparation.
(24) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Am. Chem. Soc.*, **90**, 4201 (1968); T. G. Edwards and R. Ginter, *Mol. Phys.*, **15**, 367 (1968); O. Kikuchi and K. Someno, *Bull. Chem. Soc. Jpn.*, **40**, 2972 (1967); J. A. Pedersen and J. Spanget-Larsen, *Chem. Phys. Lett.*, **35**, 41 (1975).
(25) L. Pasimeni, M. Brustolon, and C. Corvaja, *Chem. Phys. Lett.*, **30**, 249 (1975), and references cited therein.
(26) B. D. Olafson and W. A. Goddard, *Proc. Natl. Acad. Sci. U.S.A.*, **74**, 1315 (1977).

Reactions of Activated Quadruply Bonded Molybdenum Dimers. Formation of New Rectangular Clusters Containing the Tetrametal Analogue of Cyclobutadiyne

Roger N. McGinnis, Timothy R. Ryan, and R. E. McCarley*

Contribution from the Ames Laboratory-USDOE and Department of Chemistry, Iowa State University, Ames, Iowa 50011. Received May 25, 1978

Abstract: A new quadruply bonded molybdenum dimer, $Mo_2Cl_4(P(C_6H_5)_3)_2(CH_3OH)_2$, has been prepared, characterized by structure analysis, and shown to exhibit unusual reactivity. In benzene solution the new dimer undergoes self-addition across the quadruple bond resulting in formation of a novel tetrameric cluster unit. Structure determination of the triethylphosphine substituted tetramer, $Mo_4Cl_8(PEt_3)_4$, revealed the molecular, rectangular cluster unit with two short Mo–Mo bonds, 2.211 (3) Å, and two long bonds, 2.901 (2) Å. The short Mo–Mo bonds are unsupported by bridging ligands but the long bonds are each bridged by two Cl atoms, and the coordination sphere of each Mo is completed by one Cl and one PEt_3 terminal ligand. The Mo–Mo bond distances, diamagnetism, and number of electrons available for bonding are consistent with assessment of bonding in the rectangle as two triple and two single bonds, the tetrametal analogue of cyclobutadiyne.

Since the structural elucidation of the first compound characterized as having a metal–metal quadruple bond, and the subsequent proliferation of compounds having multiple bond order,[1] the potential reactivity of such compounds toward addition of molecular species across the multiple bond has been of considerable interest. However, until the present time few reactions of this type have actually been demonstrated.[2] We now report the preparation and structure of an unusually reactive quadruply bonded molybdenum dimer and the structural characterization of products resulting from its addition reactions.

It was our belief that reactivity of the quadruple bond could be promoted by preparing derivatives with weakly bonded ligands. Ligand dissociation in solution would then provide species having lower coordination number and less hindered approach of substrate molecules to the region of the metal-metal bond. For this purpose our interest was drawn to the still unreported compound $Mo_2Cl_4(PPh_3)_4$. In our unsuccessful attempts to prepare this derivative we examined the reaction of $(NH_4)_5Mo_2Cl_9\cdot H_2O$ with triphenylphosphine in methanol, an approach known to be successful for preparation of other phosphine derivatives $Mo_2Cl_4(PR_3)_4$.[3] Instead, this reaction, even in the presence of a large excess of triphenylphosphine, has led to the new compound $Mo_2Cl_4(PPh_3)_2(CH_3OH)_2$.[4] Recrystallization of this product from methanol provided well-formed blue crystals of the solvate $Mo_2Cl_4(PPh_3)_2(CH_3OH)_2\cdot nCH_3OH$,[5] which, however, dissociate and crumble upon removal of the solvent. Thus for the structure
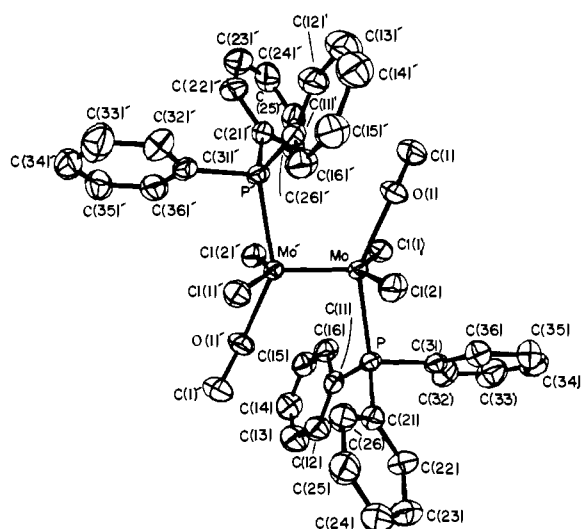
Figure 1. Structure of the $Mo_2Cl_4(P(C_6H_5)_3)_2(CH_3OH)_2$ molecule with numbering scheme for the atoms shown. Atoms are represented by thermal ellipsoids scaled to enclose 50% of the electron density.

Figure 2. Structure of the cluster molecule $Mo_4Cl_8(P(C_2H_5)_3)_4$ with numbering scheme for the atoms shown. Thermal ellipsoids are scaled to enclose 50% of the electron density.

determination crystals of the solvate were loaded into capillaries and sealed with the inclusion of some methanol.

Subsequent solution and refinement of the crystal structure[6] has revealed the discrete molecular species shown in Figure 1. Crystallographically the molecule is located in a site of C_i symmetry, but discounting the phenyl and methyl groups the molecule has idealized C_{2h} symmetry. The geometric disposition of ligands on one metal with respect to those on the other is consistent with that expected for minimizing nonbonded repulsions between ligands opposed to each other in the eclipsed configuration. Surprisingly little is revealed by the structure in regard to the unusual reactivity of the molecule (vide infra). The Mo–Mo distance of 2.143 (1) Å is quite comparable to that in $Mo_2Cl_8^{4-}$, 2.141 ± 0.006 Å (average of several structures);[1] $Mo_2(CH_3)_8^{4-}$, 2.148 (2) Å;[7] $Mo_2(O_2CC_6H_5)_2$-$Br_2(P-n-Bu_3)_2$,[8] 2.091 (3) Å; and $Mo_2Br_6(H_2O)_2^{2-}$, 2.122 (2) Å.[9] Only the Mo–O distance, 2.211 (5) Å, and M–O–C angle, 133.8 (5)°, are somewhat larger than normal values.[10]

Upon dissolution of $Mo_2Cl_4(PPh_3)_2(CH_3OH)_2$ in benzene at 25 °C the bright blue solution initially produced changes color, and within 30-60 min precipitation of a brown, microcrystalline product is essentially complete. Definitive characterization of this product proved difficult because of secondary reaction with liberated methanol. Analyses of product isolated within 1 h of initial reaction, however, indicated the composition $[MoCl_2(PPh_3)]_n$.[11] Subsequent reaction of this brown material with trialkylphosphines in benzene at 25 °C affords the new, brownish yellow, crystalline compounds $Mo_4Cl_8(PR_3)_4$, R = C_2H_5 or C_4H_9. Although structure determinations on these compounds have not resulted in refinements of desired accuracy, notably in the carbon atom parameters, the essential features of the new tetrameric clusters are well defined.[12] As shown in Figure 2 for $Mo_4Cl_8(PEt_3)_4$ the new cluster derivatives have rectangular geometry with effective C_{2h} symmetry. The Mo–Mo distances in the short and long dimensions of the rectangle are 2.211 (3) and 2.901 (2) Å, respectively. Two Cl atoms bridge between the Mo atoms over each of the long edges of the rectangle and each Mo also is bound to one Cl and one P terminal ligand. The existence of Mo–Mo bonding between pairs of metal atoms in the long direction of the rectangle is supported not only by the Mo–Mo distance but also by the acute bridge bond angles Mo–Cl–Mo which average 74.4 (2)°.[13] A comparison of these Mo–Mo bond distances with those found in other structures, combined with the observed diamagnetism and number of metal electrons
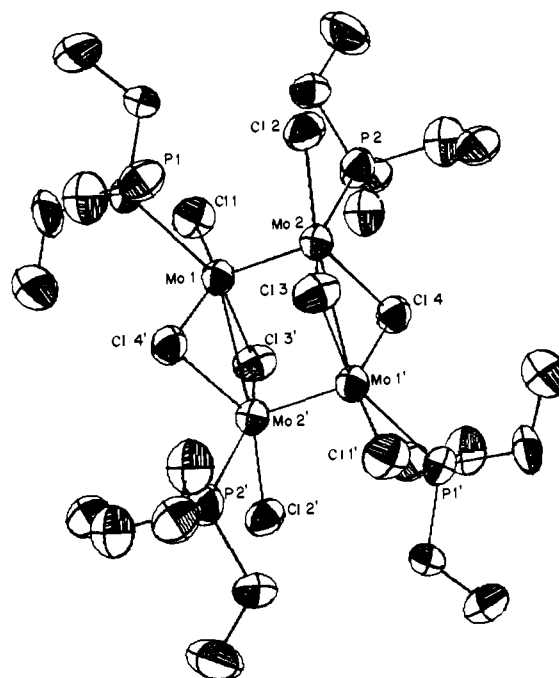
available, shows that the Mo–Mo bonding is best regarded as consisting of single bonds on the long edges,[14] and triple bonds on the short edges[15] of the rectangle. Thus the new clusters may be justifiably regarded as tetrametal analogues of cyclobutadiyne. In the facile reaction leading to the brown triphenylphosphine derivative addition of two quadruply bonded dimers apparently occurs, with elimination of the coordinated methanol ligands. The electron pairs utilized in the dimers for δ bonding are effectively recast for forming the long σ bonds in the tetramer,[20] as represented by the scheme (loss of two methanol ligands understood).
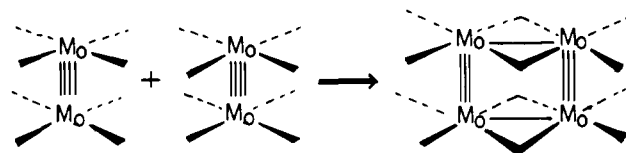
In media containing methanol the reaction of $Mo_2Cl_4(PPh_3)_2(CH_3OH)_2$ follows a different course. If a solution of the dimer (4 g) in methanol (25 mL)–decalin (50 mL)–HCl (0.64 M) is warmed to 70 °C a yellow, microcrystalline precipitate having the composition $[MoCl_2(CH_3OH)]_n$[21] results within 1 h. Although this yellow product is rather insoluble in common solvents, it reacts readily with triethylphosphine in benzene to provide $Mo_4Cl_8(PEt_3)_4$ as confirmed by X-ray powder diffraction and infrared spectra. We thus infer that the correct formulation of the yellow precipitate is $Mo_4Cl_8(CH_3OH)_4$. Evidently both the CH_3OH and PPh_3 ligands of the dimer are very labile and loss of either may occur upon formation of the tetrameric unit depending on the solvent system. A more complete understanding of the path of these reactions is essential and is the subject of continued work.

Supplementary Material Available: A list of observed and calculated structure factors, bond distances and angles, and positional–thermal

parameters for both structures (31 pages). Ordering information is given on any current masthead page.

References and Notes

(1) F. A. Cotton, *Chem. Soc. Rev.*, **4**, 27 (1975), and references cited therein.

(2) For some recent examples see R. J. Klinger, W. Butter, and M. D. Curtis, *J. Am. Chem. Soc.*, **97**, 3535 (1975); F. A. Cotton, M. W. Extine, and R. H. Niswander, *Inorg. Chem.*, **17**, 692 (1978); W. I. Bailey, Jr., M. H. Chisholm, F. A. Cotton, C. A. Murillo, and L. A. Rankel, *J. Am. Chem. Soc.*, **100**, 802 (1978); M. H. Chisholm, R. L. Kelly, F. A. Cotton, and M. W. Extine, *ibid.*, **100**, 2256 (1978).

(3) J. San Filippo, Jr., H. J. Sniadoch, and R. L. Grayson, *Inorg. Chem.*, **13**, 2121 (1974); J. San Filippo, Jr., *Inorg. Chem.*, **11**, 3140 (1972).

(4) This composition is attained for the compound only after removal of solvent and drying in vacuo. Anal. Calcd for Mo₂Cl₄(P(C₆H₅)₃)₂(CH₃OH)₂: Mo, 20.80; Cl, 15.37; C, 49.48; H, 4.15. Found: Mo, 20.54; Cl, 15.42; C, 50.34; H, 4.45.

(5) The crystal structure analysis revealed three sites occupied by unbound solvent molecules, but less than full occupation of these sites makes *n* = 2.2.

(6) The crystals were found to be triclinic, *P*Ī, *Z* = 1, *a* = 11.547 (6) Å, *b* = 12.152 (5) Å, *c* = 9.458 (4) Å, *α* = 103.87 (5)°, *β* = 112.47 (4)°, *γ* = 104.33 (5)°. At the present stage of refinement all nonhydrogen atoms have been located and full-matrix least-squares refinement including anisotropic temperature factors has resulted in conventional descrepancy indices of *R* = 0.066 and *R*ᵥᵥ = 0.087. No attempt has been made to locate H atom positions.

(7) F. A. Cotton, J. M. Troup, T. R. Webb, D. H. Williamson, and G. Wilkinson, *J. Am. Chem. Soc.*, **96**, 3824 (1974).

(8) J. A. Potenza, R. J. Johnson, and J. San Filippo, Jr., *Inorg. Chem.*, **15**, 2215 (1976).

(9) J. V. Brencic and P. Segedin, *Z. Anorg. Allg. Chem.*, **423**, 266 (1976).

(10) Other important bond distances and angles found in the molecule are Mo–Cl (av), 2.404 (2) Å; Mo–P, 2.539 (3) Å; Mo–Mo–Cl (av), 107.20 (6)°; Mo–Mo–P, 97.58 (6); Mo–Mo–O, 113.70 (16)°.

(11) Anal. Calcd for MoCl₂(P(C₆H₅)₃): Mo, 22.36; Cl, 16.52. Found: Mo, 22.60; Cl, 17.30.

(12) Refinement of the structure of Mo₄Cl₈(P(C₄H₉)₃)₄ is still incomplete, but all nonhydrogen atom positions have been determined and the basic structural unit Mo₄Cl₈P₄ is the same in all essential features as that determined for Mo₄Cl₈(P(C₂H₅)₃)₄. Crystals of the latter grown from benzene were found to be monoclinic, *a* = 14.274 (2) Å, *b* = 12.564 (1) Å, *c* = 14.427 (2) Å, *β* = 122.80 (1)°, *P*2₁/*c*, *Z* = 2. Using 2378 data of limited quality with intensities *I* > 3σ(*I*) the refinement has converged with *R* = 0.126 and *R*ᵥᵥ = 0.158. In the final refinement cycles anisotropic temperature factors were included for all nonhydrogen atoms except for the four C atoms of two ethyl groups, which had unusually large temperature factors.

(13) Other important distances and angles in the Mo₄Cl₈(PEt₃)₄ molecule follow: Mo(1)–Cl(1), 2.425 (5); Mo(2)–Cl(2), 2.421 (6); Mo(1)–Cl(3′), 2.381 (6); Mo(1)–Cl(4′), 2.427 (6); Mo(2)–Cl(3), 2.373 (5); Mo(2)–Cl(4), 2.422 (5); Mo(1)–P(1), 2.558 (6); Mo(2)–P(2), 2.556 (7) Å; Mo(1)–Mo(2)–Mo(1′), 90.6 (1)°; Mo(2)–Mo(1)–Mo(2′), 89.4°.

(14) The Mo–Mo single bond distance is known to vary markedly depending on the nature of all ligands present, from a minimum value of about 2.5 Å to a maximum of about 3.2 Å; ref 16.

(15) Representative of compounds having Mo–Mo triple bonds unsupported by any bridging ligands are Mo₂(NMe₂)₆ (ref 17), Mo₂(CH₂SiMe₃)₆ (ref 18), and Mo₂(OSiMe₃)₆(NHMe₂)₂ (ref 19), with Mo–Mo bond distances of 2.211 (2), 2.167, and 2.242 (1) Å, respectively. The comparison of distances in Mo₄Cl₈(PEt₃)₄ and Mo₂(OSiMe₃)₆(NHMe₂)₂ is especially pertinent because in both cases the Mo atoms are coordinated to four ligands.

(16) F. A. Cotton, *J. Less-Common Met.*, **54**, 3 (1977).

(17) M. H. Chisholm, F. A. Cotton, B. A. Frenz, W. W. Reichert, L. W. Shive, and B. R. Stults, *J. Am. Chem. Soc.*, **98**, 4469 (1976).

(18) F. Huq, W. Mowat, A. Shortland, A. C. Skapski, and G. Wilkinson, *Chem. Commun.*, 1079 (1971).

(19) M. H. Chisholm, F. A. Cotton, M. W. Extine, and W. W. Reichert, *J. Am. Chem. Soc.*, **100**, 153 (1978).

(20) In support of this is the loss of the band at 558 nm giving rise to the blue color of the dimer and assigned as the *δ* → *δ** transition; in the yellow tetramer strong bands are observed at 420 nm (*ε* 2.2 × 10³) and 308 (1.7 × 10⁴).

(21) Anal. Calcd for MoCl₂(CH₃OH): Mo, 48.24; Cl, 35.7; C, 6.03; H, 2.01. Found: Mo, 48.2; Cl, 34.6; C, 6.08; H, 2.09.

Synthesis and Reactions of (η⁵-Cyclopentadienyl)tricarbonylhydridovanadate. A Comparative Mechanistic Study of Its Organic Halide Reduction Reactions with Those of Tri-n-butyltin Hydride

Robert J. Kinney,[1a] William D. Jones,[1b] and Robert G. Bergman*[1c]

Contribution No. 5755 from the Laboratories of Chemistry, California Institute of Technology, Pasadena, California, 91125, and the Department of Chemistry, University of California, Berkeley, California 94720. Received June 5, 1978

Abstract: The complex PPN⁺[CpV(CO)₃H]⁻ (PPN-3; Cp ≡ η⁵-C₅H₅) has been prepared in 70% yield by sodium reduction of CpV(CO)₄ (1) followed by protonation of the resulting dianion [CpV(CO)₃]²⁻ (2) with water and cation exchange with PPN⁺Cl⁻. The physical properties and chemical reactions of 3 have been investigated. The sodium salt of 3 is contact ion paired in the solid state and in THF; dissociation of solvent-separated pairs occurs on conversion to the PPN⁺ salt or dissolution in polar solvents such as HMPA. Treatment of dianion 2 with methyl iodide gives the related salt PPN⁺[CpV(CO)₃CH₃]⁻, which may also be isolated and characterized. Hydride 3 reacts with a wide range of organic halides, resulting in substitution of the halogen atom by the hydrogen of 3. The organometallic products of these reactions are the vanadium halides PPN⁺[CpV(CO)₃X]⁻ (8). In some cases a second organometallic product is observed; this material is the binuclear bridging hydride PPN⁺[CpV(CO)₃]₂H⁻ (10), and it is formed by reaction of the kinetic product 8 with starting 3 present in the reduction solutions. Irradiation of 1 in the presence of 3 provides an alternate route to bridging hydride 10. Competition experiments against PPh₃ have shown that 3 reacts more rapidly than the phosphine with transient, coordinatively unsaturated CpV(CO)₃, but thermodynamically PPh₃ is the better ligand. The borohydride salt PPN⁺[CpV(CO)₂BH₄]⁻ has also been prepared, by treating 1 with NaBH₄ and by treating hydride 3 with BH₃·THF. The mechanism of the reaction between 3 and organic halides has been investigated in detail, and compared in several cases with halide reductions carried out using tri-n-butyltin hydride. Relative reactivity, stereochemistry, cyclization, and trapping studies demonstrate that in almost all cases, the reduction reaction proceeds via free-radical intermediates. As in the R₃SnH case, these intermediates are generated in a chain process, and are trapped by hydrogen transfer from 3. The absolute rate constant for this transfer step can be estimated to be 2 × 10⁷ M⁻¹ s⁻¹, nearly an order of magnitude larger than the rate constant for hydrogen transfer from tri-n-butyltin hydride. Reduction of cyclopropylcarbinyl bromide appears to be exceptional, and probably proceeds by a two-electron mechanism.

Organotransition metal hydrides are not, in general, very "hydridic". Such complexes often suffer proton and hydrogen

atom abstraction, and participate easily in insertion reactions involving M–H addition across carbon–carbon double and