

ALKOXIDES OF MOLYBDENUM AND TUNGSTEN: METAL–METAL BONDS AND ORGANOMETALLIC CHEMISTRY *

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Summary

Recent developments in the chemistry of alkoxides of molybdenum and tungsten are described. Two aspects of particular emphasis are (i) metal–metal bonds and (ii) the potential role of alkoxide ligands in organometallic chemistry.

It is my pleasure to participate in the celebration of Professor R.C. Mehrotra's 60th anniversary by contributing to this volume. Though I have not yet met Professor Mehrotra, through personal correspondence, the literature and through my mentor, Professor D.C. Bradley, FRS, we are intimately related by common associations and interests, not the least of which is metal alkoxide chemistry. It is to this field of inorganic chemistry that I turn my thoughts and describe historically some of my own interests and involvements.

Though my thesis work with Professor Bradley was not directed within the field of metal alkoxide chemistry, that subject permeated the atmosphere of the laboratory. My first contribution to the field arose from a serendipitous preparation of a mixed metal alkoxide, $\text{LiCr}(\text{OBu}^t)_4$ [1]. Based upon magnetic and spectroscopic data, this mixed metal alkoxide was shown to contain trivalent chromium ($\text{Cr}(3+)$) in the unusual tetrahedral environment. Subsequently, I discovered that molybdenum did not form a related compound. LiOBu^t and a dinuclear compound, $\text{Mo}_2(\text{OBu}^t)_6$, were rather difficult to separate by either crystallization or sublimation. During my time as a graduate student, I never succeeded in separating the two compounds. I was, however, able to show that $\text{Mo}_2(\text{OBu}^t)_6$ was diamagnetic and gave only one ^1H signal in the ^1H NMR spectrum. Furthermore, in the mass spectrometer, there was a strong molecular ion, $\text{Mo}_2(\text{OBu}^t)_6^+$, followed by many other Mo_2 -containing ions. Indeed, the virtual absence of any mononuclear ion was quite striking.

* Dedicated to Prof. R.C. Mehrotra on the occasion of his sixtieth birthday (February 16th, 1982).

I suggested the possibility of a compound of the form $(\text{Bu}^t\text{O})_3\text{Mo}\equiv\text{Mo}(\text{OBu}^t)_3$. The possibility that the two molybdenum atoms could be united by a metal—metal triple bond in the absence of alkoxy bridges was a radical departure from classical metal alkoxide theories [2], though only a few years earlier Cotton [3] had proposed the existence of a metal—metal quadruple bond in the $\text{Re}_2\text{Cl}_8^{2-}$ anion. Why not then a $\text{Mo}\equiv\text{Mo}$ bond?

After completing my thesis work with Professor Bradley, I moved to Canada where I spent three years with Professor H.C. Clark at the University of Western Ontario, learning organoplatinum chemistry [4] and in general gaining my first experiences with organometallic chemistry. It was there, in Canada, that I read with considerable interest of the X-ray structural characterization [5] of $(\text{Me}_3\text{SiCH}_2)_3\text{Mo}\equiv\text{Mo}(\text{CH}_2\text{SiMe}_3)_3$, the first structurally characterized member of what is now a large group of compounds containing $\text{Mo}\equiv\text{Mo}$ bonds unbridged by ligand atoms. I felt convinced that $\text{Mo}_2(\text{OBu}^t)_6$ had to be related to $\text{Mo}_2(\text{CH}_2\text{SiMe}_3)_6$ and, furthermore, that there should exist related ditungsten compounds.

The demonstration of this, however, befell my first graduate students, Bill Reichert and Mike Extine, at Princeton University. There, through a very productive collaboration with Professor F.A. Cotton, Robert A. Welch, Distinguished Professor of Chemistry at Texas A & M University, and his group, we discovered a rich field of dimolybdenum and ditungsten chemistry surrounding a central $(\text{M}\equiv\text{M})^{6+}$ unit [6]. The early parts of this story have now been covered in the literature by reviews and I restrict my subsequent comments to various aspects of the chemistry of the alkoxides.

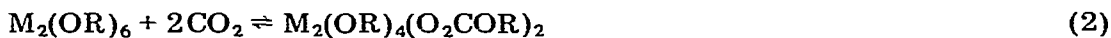
The presence of the $\text{M}\equiv\text{M}$ bond in $\text{M}_2(\text{OR})_6$ compounds [7] unbridged by alkoxy-ligands was quite remarkable in view of the well known ability of alkoxide ligands to bridge metal atoms. This point is further emphasized when one realizes that the metal atoms in $\text{M}_2(\text{OR})_6$ compounds are capable of coordinating donor ligands as shown by eq. 1.



L = N or P donor ligand

The position of equilibrium in eq. 1 is dependent on the bulkiness of R and L and varies significantly from M = Mo to M = W. For example, when R = *i*-Pr and L = pyridine, the equilibrium lies well to the right in hexane solutions for M = W [8] and well to the left when M = Mo [9], though crystalline adducts $\text{M}_2(\text{OPr}^i)_6(\text{py})_2$ have been obtained for both metals.

Another example of the unsaturated nature of these compounds is seen in their reversible reactions with CO_2 , eq. 2 [10], which gives rise to four-coordinate metal atoms.



Recognizing the unsaturated nature of these $\text{M}\equiv\text{M}$ -containing compounds, we initiated investigations of their reactivity towards small unsaturated organic molecules.

With carbon monoxide, $\text{M}_2(\text{OR})_6$ compounds react to give initially (and reversibly) μ -CO adducts. These adducts are, however, exceedingly reactive

and only $\text{Mo}_2(\text{O}^t\text{Bu})_6(\text{CO})$ has been well characterized [11]. However, in the presence of pyridine, compounds of formula $\text{M}_2(\text{OR})_6(\text{py})_2(\mu\text{-CO})$ have been characterized for $\text{R} = \text{Pr}^i$ and Ne ($\text{Ne} = \text{CH}_2\text{CMe}_3$) [12], see Fig. 1. These compounds may be viewed as inorganic analogues of cyclopropenones: there are exceedingly low C—O stretching frequencies, $\nu(\text{CO}) = 1650 \text{ cm}^{-1}$ ($\text{M} = \text{Mo}$) and 1550 cm^{-1} ($\text{M} = \text{W}$). The M—M distances in the $\mu\text{-CO}$ adducts are ca. 2.5 \AA , typical of $\text{M}=\text{M}$ bonds, and longer by ca. 0.3 \AA than $\text{M}\equiv\text{M}$ distances.

Addition of alkynes leads to polymerization of the alkyne. In the presence of pyridine, simple alkyne adducts $\text{Mo}_2(\text{OR})_6(\text{py})_2(\text{ac})$ have been isolated where $\text{R} = \text{Pr}^i$ and Ne and $\text{ac} = \text{HCCH}$, MeCCH and MeCCMe [13]. The role of steric factors, which is of such great importance in the coordination chemistry of metal alkoxides, is seen here. Related compounds could not be isolated with the bulky O^tBu ligands, whereas for the less sterically demanding neopentoxy ligands it was possible to isolate a compound $\text{Mo}_2(\text{ONe})_6(\mu\text{-C}_4\text{H}_4)(\text{py})$ in which the $\mu\text{-C}_4\text{H}_4$ ligand is formed by the coupling of two acetylene molecules, see Fig. 2. In these reactions, we see a return to a pseudo octahedral coordination for molybdenum. This is a general trend observed for all oxidative-addition reactions which always proceed with the formation of alkoxy bridges. Other oxidative-additions to $\text{M}_2(\text{OR})_6$ compounds are shown in eq. 3 through 6 below [14,15,17]:

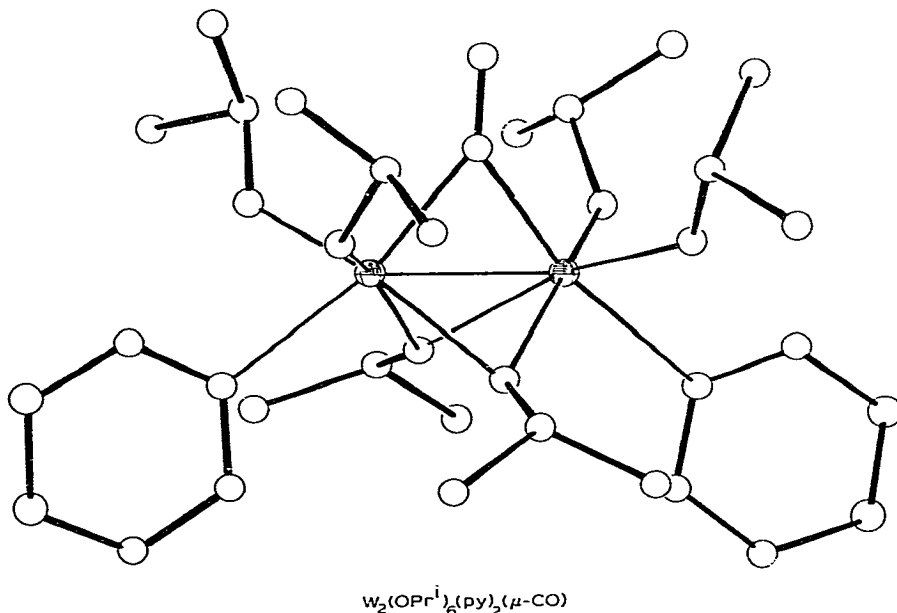
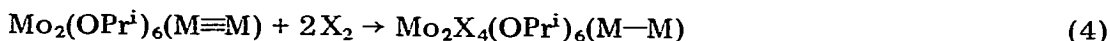
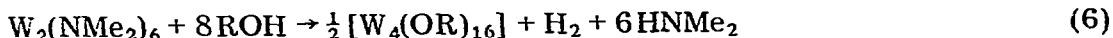
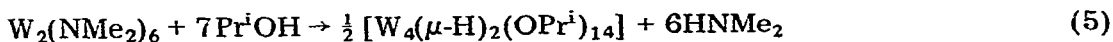


Fig. 1. An ORTEP view of the $\text{W}_2(\text{OPr}^i)_6(\text{py})_2(\mu\text{-CO})$ molecule. The $\text{Mo}_2(\text{OPr}^i)_6(\text{py})_2(\mu\text{-CO})$ molecule is isostructural and, in both compounds, the M—M distance is $2.495(1) \text{ \AA}$.



where R = Me or Et

In reactions 3 and 4, metal-metal triple bonds are transformed to double and single bonds, respectively. In reactions 5 and 6, oxidation of the metal occurs and we observe cluster formation. The structure of $\text{W}_4(\text{OEt})_{16}$, shown in Fig. 3, is particularly interesting to chemists familiar with the development of metal alkoxide structural theories. The basic fusing of four MO_6 octahedra is seen in the structure of the titanium alkoxides $[\text{Ti}(\text{OR})_4]_4$, where R = Me [18] and Et [19]. For tungsten, the presence of four d^2 ions provides eight electrons for W_4 cluster bonding and these are evidently efficiently used since the W-W distances are markedly shorter, by ca. 0.7 Å, than the Ti-Ti distances in $[\text{Ti}(\text{OEt})_4]_4$.

The ability of the dinuclear alkoxides, $\text{M}_2(\text{OR})_6(\text{M}\equiv\text{M})$, to act as building blocks for cluster synthesis is further demonstrated by reactions 7 and 8 [20,21].



where R = Prⁱ and Ne

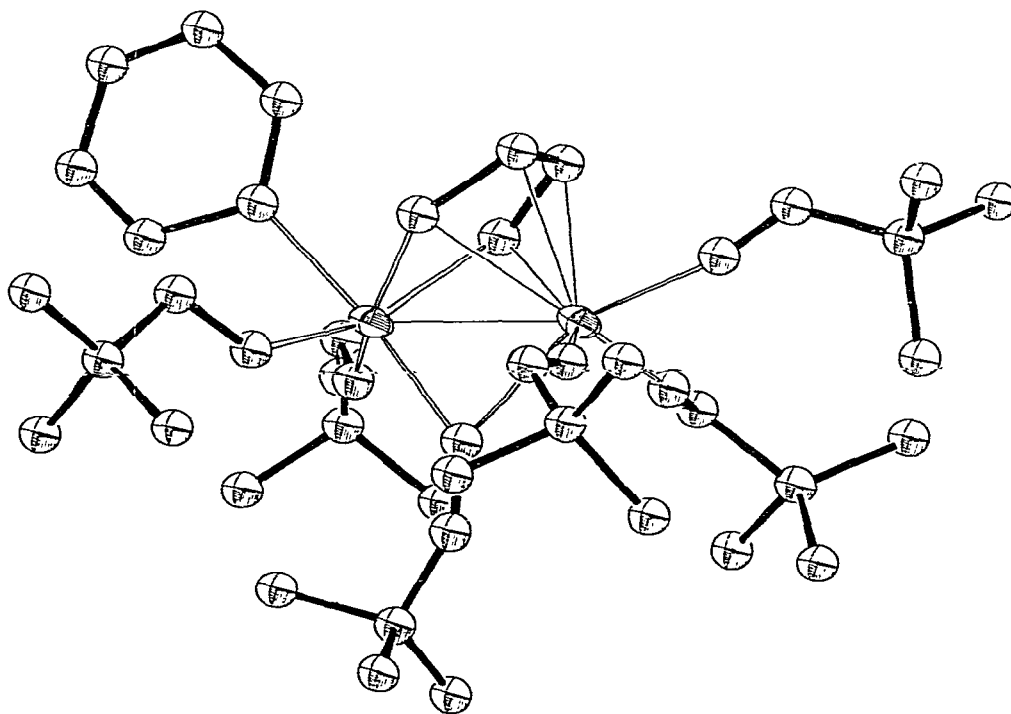


Fig. 2. An ORTEP view of the $\text{Mo}_2(\text{ONe})_6(\mu\text{-C}_4\text{H}_4)(\text{py})$ molecule showing the $\mu\text{-C}_4\text{H}_4$ ligand formed by the coupling of two HCCH molecules.

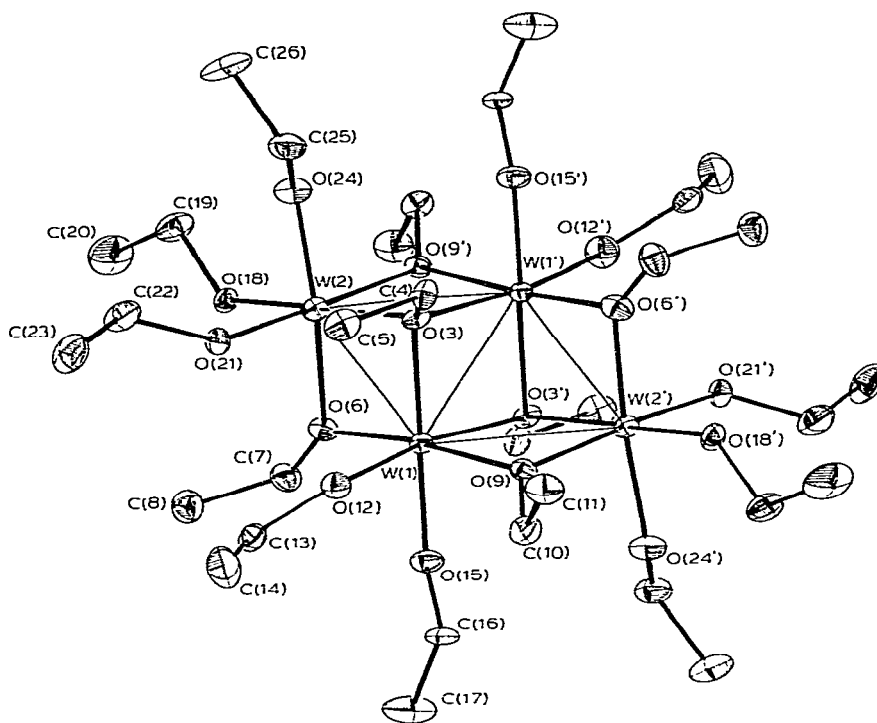


Fig. 3. An ORTEP view of the $W_4(OEt)_{16}$ molecule. Pertinent bond distances (with those for the analogous titanium complex in square brackets) are $W(1)-W(2) = 2.645(2)$ [3.34], $W(1)-W(1') = 2.763(2)$ [3.42], $W(1)-W(2') = 2.936(2)$ [3.50], $W-O$ (terminal) = 1.96 (average), $W-O(\mu_2) = 2.02$ (average), and $W-O(\mu_3) = 2.18$ (average) Å.



where $X = Cl$ and Br

The $Mo_3O(OR)_{10}$ compounds have a triangulo Mo_3 unit ($Mo-Mo = 2.55$ Å) [see Fig. 4] capped by bridging oxo and alkoxy ligands. The six electrons, formerly located in the $Mo \equiv Mo$ bond, are distributed in cluster molecular orbitals ($a^2 + e^4$) in the Mo_3 unit which leads to a net $Mo-Mo$ bond order of one.

The structures of $Mo_4Cl_4(OPr^i)_8$ and $Mo_4Br_4(OPr^i)_8$ are shown in Figs. 5 and 6, respectively. In reaction 8, the replacement of OPr^i ligands leads to the coupling of two $Mo \equiv Mo$ bonds to give a square 12-electron Mo_4 cluster, formally an inorganic analogue of cyclobutadiene, when $X = Cl$, and a butterfly or opened-tetrahedral 12-electron Mo_4 cluster when $X = Br$. Though it is not obvious why the Mo_4 cluster geometry should differ for the two halides, simple symmetry arguments allow one to rationalize how 12 electrons may be used in $M-M$ cluster bonding in both structures. The $Mo-Mo$ distance in $Mo_4Cl_4(OPr^i)_8$, 2.378(1) Å, is significantly shorter than that in $Mo_4Br_4(OPr^i)_8$, 2.50 Å (average: five short distances), which is consistent with the view that the $Mo-Mo$ bond order in the former is 1.5 and close to one in the latter. The structure of $Mo_4F_4(OBu^t)_8$, which one might think should be closely related, contains two

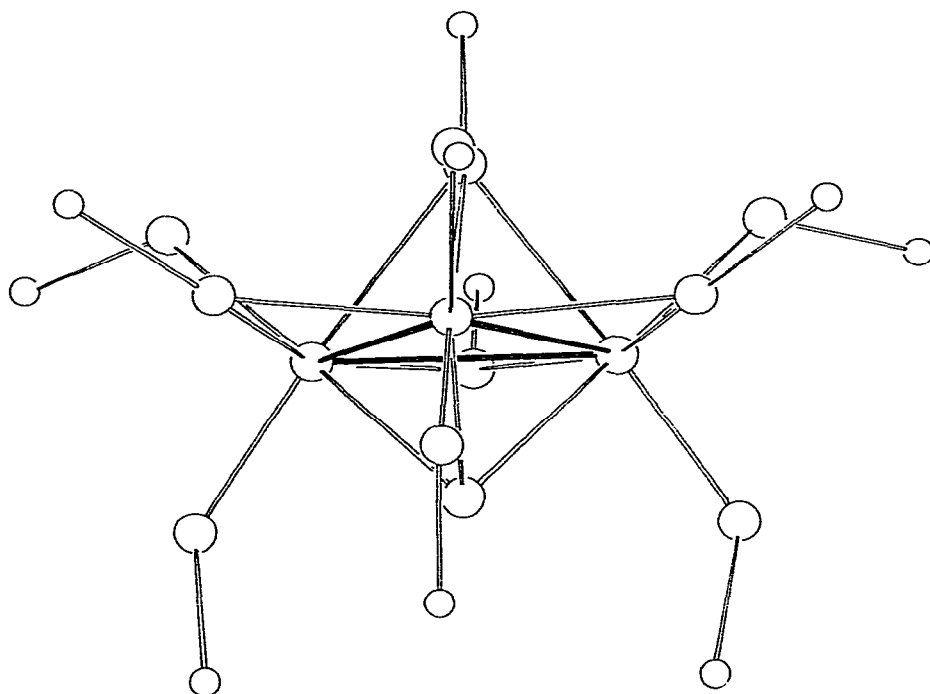


Fig. 4. An ORTEP view of the central $\text{Mo}_3(\mu_3\text{-O})(\mu_3\text{-OC})(\mu_2\text{-OC})_3(\text{OC})_6$ skeleton of the $\text{Mo}_3(\text{O})(\text{ONe})_{10}$ molecule.

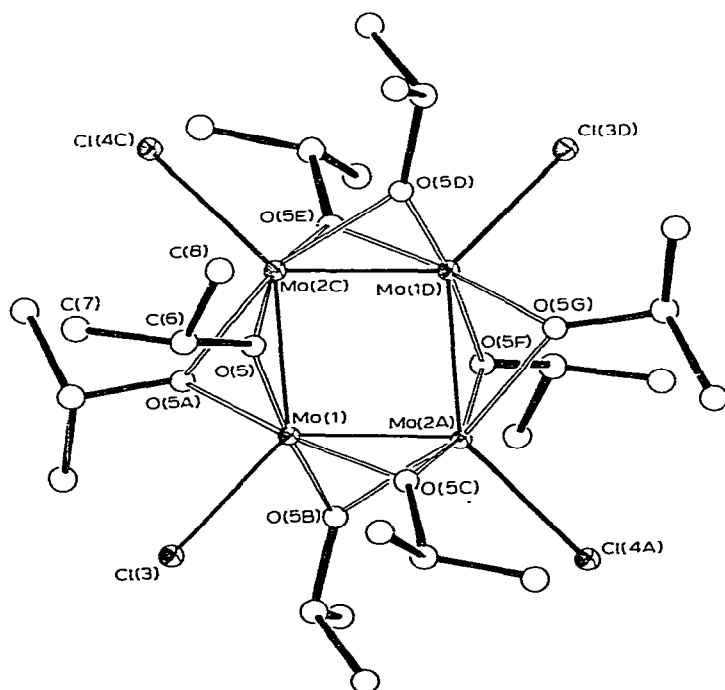


Fig. 5. An ORTEP view of the $\text{Mo}_4\text{Cl}_4(\text{OPr}^i)_8$ molecule emphasizing the virtual D_{4h} symmetry.

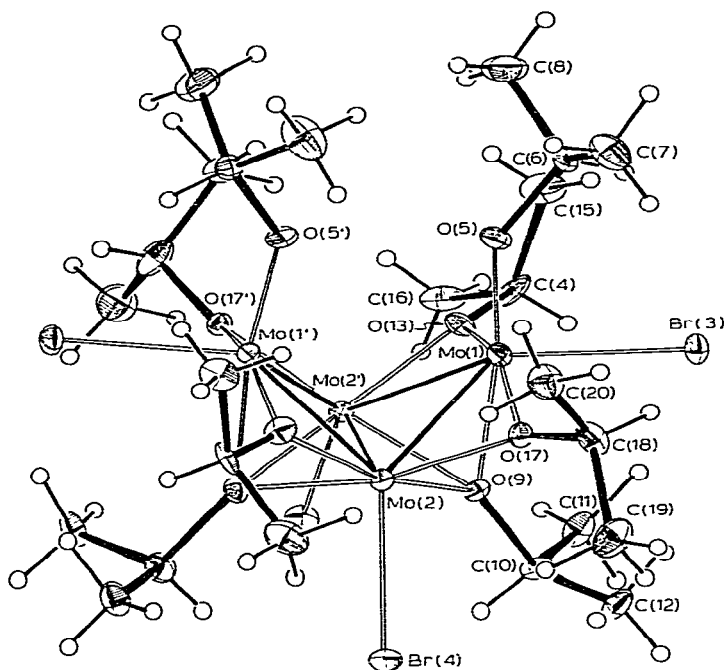


Fig. 6. An ORTEP view of the $\text{Mo}_4\text{Br}_4(\text{OPr}^i)_8$ molecule emphasizing the virtual C_{2v} symmetry of the molecule.

unbridged $\text{Mo}\equiv\text{Mo}$ bonds brought together by fluoride bridges [22]. Clearly for $\text{Mo}\equiv\text{Mo}$ bonds, two plus two makes four in more ways than one!

Finally, I should like to emphasize the potential role that alkoxide ligands might play in organometallic chemistry. As is evident from this short discourse, alkoxides, acetylenes and carbon monoxide are all capable of coexisting at dinuclear centers of molybdenum and tungsten. Whereas most organometallic ligands are π -acceptors, alkoxides are strong π -donors and this has already been shown to influence the ground state properties of CO in $\text{Mo}(\text{OBU}^t)_2(\text{py})_2(\text{CO})_2$ [23] and bpy in $\text{Mo}(\text{OPr}^i)_2(\text{bpy})_2$ [24], where by bpy = 2,2'-bipyridyl. It is possible that this strong π -donating property could induce interesting reactivity patterns in other ligands. This point is clearly worthy of further investigation.

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