Multiple Cluster CH Activations and Transformations of Furan by Triosmium Carbonyl Complexes

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Multiple Cluster CH Activations and Transformations of Furan by Triosmium Carbonyl Complexes

Richard D. Adams*, Joseph Kiprotich and Mark D. Smith

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Reaction of $Os_3(CO)_{10}(NCMe)_2$ with the triosmium furyne complex $Os_3(CO)_9(\mu_3,\eta^2\text{-}C_4H_2O)(\mu\text{-}H)_2$, 1 yielded the bis-triosmium complex 2 containing a bridging furyenyl ligand by CH activation at the uncoordinated C – C double bond. Heating 2 led to additional CH activation with formation of the first furdiyne C_4O ligand in the complex $Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}2,3\text{-}\mu_3\text{-}\eta^2\text{-}4,5\text{-}C_4O)Os_3(CO)_9(\mu\text{-}H)_2$, 3. The furdiyne ligand in 3 was subsequently ring-opened and decarbonylated to yield products 4 and 5 containing novel bridging C_3 ligands. Complex 2 also undergoes ring opening to yield an intermediate $Os_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}\mu\text{-}\eta^2\text{-}CH\text{-}C\text{-}CH\text{-}C{=}O)Os_3(CO)_{10}(\mu\text{-}H)$, 6 which was also decarbonylated thermally to yield 4 and 5. All products were characterized by a combination of IR, NMR, mass spec and single-crystal X-ray diffraction analyses.

Furans are among the principal products obtained from the upgrading of biomass feedstocks and are key intermediates in the formation of higher-value products including biofuels.[1] Reactions leading to the opening of five-membered furan rings have presented some challenges,[2] but can be achieved in combination with the catalytic addition of hydrogen to the ring.[3]

In recent studies, we have found that multiple additions of triosmium carbonyl cluster complexes to o-carboranes can lead to opening of their very stable cage structures.[4] We have now investigated the nature of multiple additions of triosmium carbonyl cluster complexes to furan and found that this leads not only to multiple CH activations including the formation of the first example of what could reasonably be called the first "furdiyne" ligand, the smallest diyne ring reported here-to-date, by complete dehydrogenation of the furan ring, but also to facile opening and decarbonylation of the furan ring itself under mild conditions. The reaction of the triosmium furyne complex $Os_3(CO)_9(\mu_3,\eta^2\text{-}C_4H_2O)(\mu\text{-}H)_2$,[5] **1** with $Os_3(CO)_{10}(NCMe)_2$ in a cyclohexane solution heated to reflux for 4 h yielded three products: $Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}2,3\text{-}\mu\text{-}\eta^2\text{-}4,5\text{-}C_4HO)Os_3(CO)_{10}(\mu\text{-}H)$, **2** (63 % yield), $Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}2,3\text{-}\mu_3\text{-}\eta^2\text{-}4,5\text{-}C_4O)Os_3(CO)_9(\mu\text{-}H)_2$, **3** (11 % yield) and $Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}C\text{-}C\text{-}C\text{-}\mu_3\text{-}\eta^2)Os_3(CO)_9(\mu\text{-}H)_2$, **4** (13 % yield). All three products were characterized by a combination of IR, NMR, mass spec and single-crystal X-ray diffraction analyses. There are two independent molecules in the asymmetric crystal unit of compound **2**. Both molecules are structurally similar. An ORTEP diagram of the molecular structure of **2** is shown in Figure 1.

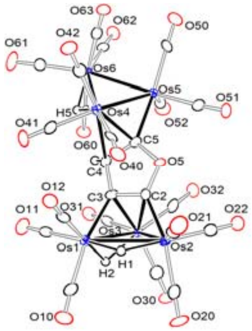

Figure 1. An ORTEP diagram of the molecular structure of $Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}2,3\text{-}\mu\text{-}\eta^2\text{-}4,5\text{-}C_4HO)Os_3(CO)_{10}(\mu\text{-}H)$, **2** showing 50% thermal ellipsoid probability. There are two independent molecules in the asymmetric crystal unit. Selected interatomic bond distances (Å) are as follows: Os(1) – Os(2) = 3.0814(5), Os(1) – Os(3) = 2.8512(5), Os(2) – Os(3) = 2.7811(5), Os(1) – C(3) = 2.141(9), Os(2) – C(2) = 2.031(9), *Os(3) – C(2) = 2.397(8), Os(3) – C(3) = 2.245(8), Os(5) – C(5) =* 2.101(9), Os(4) – C(5) = 2.346(9), Os(4) – C(4) = 2.496(9), C(2) – C(3) = 1.406(12), C(4) – C(5) = 1.395(12), C2A – C3A 1.398(12), C4A – C5A 1.409(12), O5 – C2 = 1.386(10), O5 – C5 = 1.431(10), O5A – C2A = 1.363(10), O5A - C5A = 1.427(9).

Compound **2** contains two triangular triosmium carbonyl clusters mutually coordinated to a single furynenyl ligand. The C – C triple bond, C2 – C3, of the furynenyl ligand is coordinated to the face of

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[*] *Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208 USA. E-mail:ADAMSRD@mailbox.sc.edu*

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x the Os1-Os2-Os3 cluster in the di-σ+π-coordination mode and the C4 – C5 enyl bond is σ-π-coordinated to the Os4 – Os5 edge of the Os4-Os5-Os6 cluster.

The coordinated triple and double bonds are of very similar lengths: C(2) – C(3) = 1.406(12) Å, C(4) – C(5) = 1.395(12) Å, (for molecule 2, C2A – C3A 1.398(12) Å, C4A – C5A 1.409(12) Å) but interestingly, the two C – O bonds are significantly different, O5 – C2 = 1.386(10) Å, O5 – C5 = 1.431(10) Å (O5A – C2A = 1.363(10) Å, O5A - C5A = 1.427(9) Å). Compound **2** was formed by the oxidative – addition of the olefinic CH bond at the C5 position of the furyne ligand in **1**. The double bond then became π-coordinated to Os4.

An ORTEP diagram of the molecular structure of **3** is shown in Figure 2. Compound **3** also contains two triangular triosmium clusters. Each cluster is coordinated to a pair of carbon atoms in a five-membered C_4O heterocycle that could formally be regarded as a furdiyne or "oxacyclopentadiyne" ligand. This species has not yet been observed in the free state. The C2 – C3 triple bond is coordinated to the Os1-Os2-Os3 cluster in the di-σ+π-coordination mode as in **2** and the C4 – C5 triple bond is similarly coordinated in a di-σ+π-coordination mode to the Os4-Os5-Os6 cluster. The C – C bond distances, C(2) – C(3) = 1.392(10) Å and C(4) – C(5) = 1.415(10) Å, are similar to C – C triple bond distances found in **1** (1.389(10) Å), see Supporting Information) and **2**, see above. The C - O bond distances are equal in length, O5 – C2 = 1.405(8) Å, O5 – C5 = 1.397(8) Å and similar to those found in **1** and **2**, but slightly longer than those found in the free furan molecule, 1.368(6) Å.[6] Compound **3** was shown to be formed directly from **2** in a separate test (9.5 % yield) which involves the loss of a carbonyl ligand from the Os4-Os5-Os6 cluster of **2** and was followed by an activation of the remaining C-H bond on C(4) of the enyl group that leads to the formation of the hydrido ligand and the second C – C triple bond between the atoms C(4) and C(5).

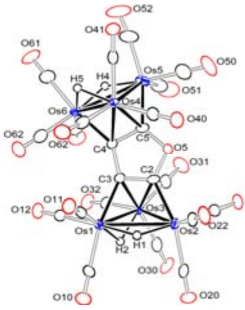


Figure 2. An ORTEP diagram of the molecular structure of $Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}2,3\text{-}\mu_3\text{-}\eta^2\text{-}4,5\text{-}C_4O)Os_3(CO)_9(\mu\text{-}H)_2$, **3** showing 50% thermal ellipsoid probability. Selected interatomic bond distances (Å) are as follow: Os(1) – Os(2) = 3.0695(4), Os(1) – Os(3) = 2.8480(4), Os(2) – Os(3) = 2.7782(4), Os(1) – C(3) = 2.131(7), Os(2) – C(2) = 2.040(7), Os(3) – C(2) = 2.336(7), Os(3) – C(3) = 2.310(7), Os(5) – C(5) = 2.041(7), Os(4) – C(5) = 2.325(7), Os(4) – C(4) = 2.320(7), Os(6) – C(4) = 2.131(7), C(4) – C(5) = 1.415(10), C(2) – C(3) = 1.392(10), C(3) – C(4) = 1.493(9), O5 – C2 = 1.405(8), O5 – C5 = 1.397(8).

Multiple CH activations by metal complexes are extremely rare. A series of four CH activations by two clusters on a single molecule as represented by the formation of the sequence of compounds **1** to **2** and then to **3** is unprecedented.

Small ring cycloalkynes are of interest because of the destabilizing strain introduced into the molecule by the triple bond(s) that introduces unusual reactivity.[7] It has been shown that the addition of metal atoms to the triple bonds of cycloalkynes allows for the stabilization of smaller cycloalkynes as ligands vis-a-vis the free forms.[8] The smallest cyclodiyne reported to date is a zirconocene-bis(methoxy)benzdiyne complex reported by Buchwald a number of years ago.[9] The five-membered furdiyne ring found in **3** brings ring smallness to an unprecedented new small size for a "cyclodiyne" grouping.

An ORTEP diagram of the molecular structure of **4** is shown in Figure 3. Compound **4** contains two triangular triosmium clusters that are linked by a bridging C_3 ligand. C_3 ligands have been observed previously but never as fully coordinated as the one found in **4**.[10] The C_3 group bridges all three metal atoms in each cluster to form a bis ($\mu_3\text{-}\eta^2$) bridge between them. The C_3 ligand in **4** is nonlinear, C(2) – C(3) – C(4) = 143.9(6)°. Both C – C bonds are short, C(2) – C(3) = 1.359(8) Å, C(3) – C(4) = 1.361(8) Å and indicative of unsaturation. It could be described as a dimetalla-allenylidene ligand. The two terminal carbon atoms, C(2) and C(4), are each bonded to three osmium atoms in one Os_3 cluster. The central carbon C(3) is bonded to one osmium atom in each cluster, Os(2) – C(3) = 2.432(6) Å, Os(4) – C(3) = 2.420(6) Å.

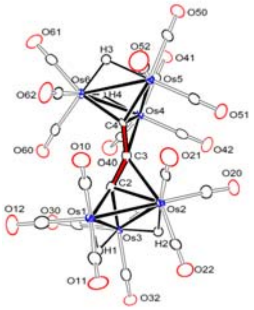
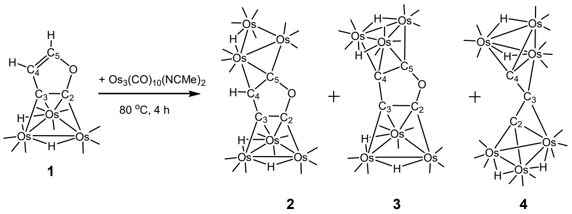


Figure 3. An ORTEP diagram of the molecular structure of $Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}\mu_3\text{-}\eta^2\text{-}C\text{-}C\text{-}C)Os_3(CO)_9(\mu\text{-}H)_2$, **4** showing 60% thermal ellipsoid probability. Selected interatomic bond distances (Å) and angles (deg) are as follow: Os(1) – Os(2) = 2.7848(4), Os(1) – Os(3) = 2.8821(3), Os(2) – Os(3) = 2.9107(3), Os(1) – C(2) = 2.070(6), Os(2) – C(2) = 2.233(6), Os(3) – C(2) = 2.075(6), Os(2) – C(3) = 2.432(6), Os(4) – C(4) = 2.226(5), Os(5) – C(4) = 2.026(5), Os(6) – C(4) = 2.108(6), Os(4) – C(3) = 2.420(6), Os(4) – Os(5) = 2.7944(3), Os(4) – Os(6) = 2.8978(4), Os(5) – Os(6) = 2.8930(3), C(2) – C(3) = 1.359(8), C(3) – C(4) = 1.361(8), C(2) – C(3) – C(4) = 143.9(6).

The C_3 ligand was formed by a ring-opening decarbonylation of the furdiyne ring in **3**. These transformations are summarized in Scheme 1.When compound **3** was heated to reflux in a toluene-d_8 solution at 80° C for 75 h, compound **4** (9% yield) and the new compound $Os_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}\eta^2\text{-}\mu\text{-}\eta^2\text{-}C{=}C{=}C)Os_3(CO)_{10}(\mu\text{-}H)$, **5** (79% yield) were formed. Compound **5** was also characterized by single-crystal X-ray diffraction analysis. An ORTEP diagram of the molecular structure of **5** is shown in Figure 4.



Scheme 1. A summary of the conversion of **1** to **3**, **4**, and **5** and the interconversions between **3**, **4**, and **5**.

Like **4**, compound **5** contains two triangular triosmium clusters that are linked by a bridging C_3 ligand, but in contrast to the structure of **4**, the C_3 group in **5** bridges all three metal atoms in one cluster (Os1-Os2-Os3) by one of the terminal carbon atoms C(1) and only two of the metal atoms, Os5 and Os6, by the other terminal carbon atom C(3) in the other cluster Os4-Os5-Os6, Os(5) – C(3) = 2.186(13) Å and Os(6) – C(3) = 2.144(13) Å. This difference can be attributed to the different number of CO ligands the two triosmium clusters. Cluster Os1-Os2-Os3 contains only nine carbonyl ligands and the cluster Os4-Os5-Os6 contains ten carbonyl ligands. The C_3 ligand in **5** is virtually linear, C(1) – C(2) – C(3) = 177.3(14)° and the C – C bond distances are significantly different, C*(1)* – C*(*2) = 1.390(19) Å, C(2) – C(3) = 1.23(2) Å. The central carbon C(3) is not bonded to any of the metal atoms. Accordingly, the C*(1)* – C*(*2) bond is represented as a single bond because it is bonded to three metal atoms and one carbon atom. The C(2) – C(3) bond is formulated as a double bond because it is bonded to only two metal atoms and one carbon atom C(1) but it may contain considerable triple bond character to complete the bonding at C2. As with the formation of **4**, the C_3 ligand in **5** was formed by a ring-opening decarbonylation of the furdiyne ring in **3** which may in turn have been facilitated by ring strain in the cyclodiyne ligand. Not too surprisingly, when compound **5** was heated to 105 °C in solution over a period of 10 days, it was converted to **4** in 74% yield by simple decarbonylation. A summary of these transformations are shown in Scheme 2.

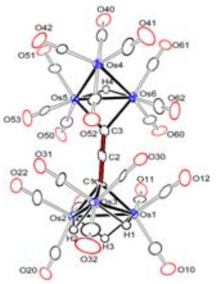
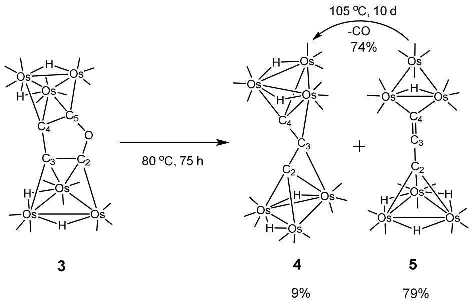


Figure 4. *An ORTEP diagram of the molecular structure of $Os_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}\eta^1\text{-}\mu\text{-}\eta^1\text{-}C\text{-}C{=}C)Os_3(CO)_{10}(\mu\text{-}H)$,* ***5*** *showing 60% thermal ellipsoid probability. Selected interatomic bond distances (Å) and angles (deg) are as follow: Os(1) – Os(2) = 2.8652(7), Os(1) – Os(3) = 2.8932(7), Os(2) – Os(3) = 2.8934(7), Os(1) – C(1) = 2.129(14), Os(2) – C(1) = 2.148(12), Os(3) – C(1) = 2.114(13), Os(6) – C(3) = 2.144(13), Os(5) – C(3) = 2.186(13), C(1) – C(2) = 1.390(19), C(2) – C(3) = 1.23(2), Os(4) – Os(5) = 2.8404(7), Os(4) – Os(6) = 2.8472(7), Os(5) – Os(6) = 2.7868(7), C(1) – C(2) = 1.390(19), C(2) – C(3) = 1.23(2), C(1) – C(2) – C(3) = 177.3(14).*



Scheme 2. A summary of the transformations of **3**.

When compound **2** was heated to reflux in a heptane solution at 98° C for 5 h, compounds **3**, **4** and **5** (8% yield) together with a small amount of the new compound $Os_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}\mu\text{-}\eta^2\text{-}CH\text{-}C\text{-}CH\text{-}C{=}O)Os_3(CO)_{10}(\mu\text{-}H)$, **6** (2.5% yield) were formed. Compound **6** is one of the most interesting compounds of the series even though it was obtained in the lowest yield. An ORTEP diagram of the molecular structure of **6** is shown in Figure 5. The molecule contains two triosmium carbonyl cluster groupings linked by a CHCCHC=O chain. The three carbon atoms C2, C3 and C3 from C-terminus form a triple bridge on the Os1-Os2-Os3 cluster. The C2 - C3 pair could be viewed as an alkynyl group with an H atom on carbon C2, δ = 9.13 and a carbon C4 on C3, C3 – C4 = 1.398(9) Å. Atoms C(2) and C(3) (C-C = 1.379(9) Å) bridge the three metal atoms. Atom C4 is also bonded to Os1, Os(1) – C(4) = 2.329(6) Å and it contains one hydrogen atom, δ = 3.87. Atom C4 is bonded to the carbonyl group C5 – O5, C(5) – O(5) = 1.280(7) Å which serves as a bridge across the Os(4) – Os(6) edge, Os(4) – O(5) = 2.117(4) Å, Os(6) – C(5) = 2.058(6) Å, of the second Os_3 cluster.

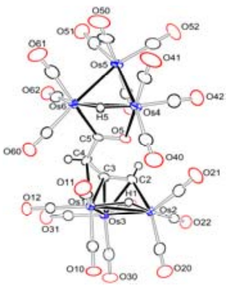
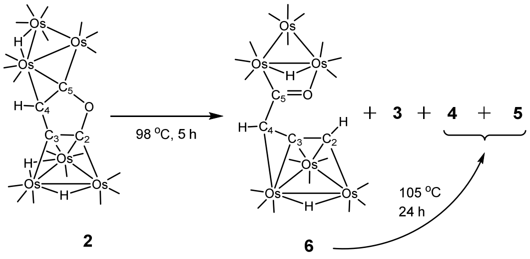


Figure 5. An ORTEP diagram of the molecular structure of $Os_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2,\mu\text{-}\eta^2\text{-}CHCCHC{=}O)Os_3(CO)_{10}(\mu\text{-}H)$, **6** showing 60% thermal ellipsoid probability. Selected interatomic bond distances

(Å) are as follow: Os(1) – Os(2) = 3.0026(4), Os(1) – Os(3) = 2.8255(4), Os(2) – Os(3) = 2.8056(4), Os(1) – C(4) = 2.329(6), Os(1) – C(3) = 2.267(6), Os(3) – C(3) = 2.092(6), Os(3) – C(2) = 2.272(7), Os(2) – C(2) = 2.048(7), Os(4) – O(5) = 2.117(4), Os(6) – C(5) = 2.058(6), Os(4) – Os(6) = 2.9131(4), Os(4) – Os(5) = 2.8293(4), Os(5) – Os(6) = 2.8776(4), Os(4) – O(5) = 2.117(4), Os(6) – C(5) = 2.058(6), C(2) – C(3) = 1.379(9), C(3) – C(4) = 1.398(9), C(4) – C(5) = 1.476(8).

Compound **6** was decarbonylated and converted to **4** and **5** when heated to 105 ^{o}C. The products and their transformations derived from **2** are shown in Scheme 3.



Scheme 3. Conversions of 2 to compounds 3, 4, 5 and 6.

In this work we have shown that two trisomium cluster complexes working in concert can activate all four CH bonds on the furan molecule resulting, in limit, to the formation of the remarkable furdiyne ligand, the smallest cyclodiyne ligand observed to date, in the complex **3**, Scheme 1. This cyclodiyne ring can be opened and decarbonylated by mild heating to yield the complexes **4** and **5** containing novel C_3 ligands bridging between the two triosmium clusters. Interestingly, the bridging C_4HO furynenyl ligand precursor complex **2** can also undergo an opening of the furynenyl ring without decarbonylation to yield the complex **6**, but the CHCCHC=O ligand in **6** will also decarbonylate and dehydrogenate when heated to yield the complexes **4** and **5**, Scheme 2.

Conflicts of interest

"There are no conflicts to declare".

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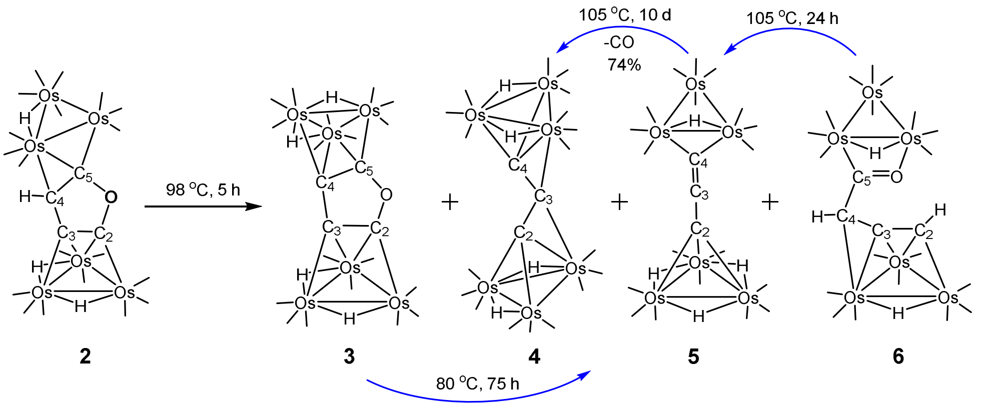

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Abstract: Reaction of $Os_3(CO)_{10}(NCMe)_2$ with the triosmium furyne complex $Os_3(CO)_9(\mu_3,\eta^2\text{-}C_4H_2O)(\mu\text{-}H)_2$, **1** yielded the bis-triosmium complex **2** containing a bridging furynenyl ligand by CH activation at the uncoordinated C – C double bond. Heating **2** led to additional CH activation with formation of the first furdiyne C_4O ligand in the complex $Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}2,3\text{-}\mu_3\text{-}\eta^2\text{-}4,5\text{-}C_4O)Os_3(CO)_9(\mu\text{-}H)_2$, **3**. The furdiyne ligand in **3** was subsequently ring-opened and decarbonylated to yield products **4** and **5** containing novel bridging C_3 ligands. Complex **2** also undergoes ring opening to yield an intermediate $Os_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}\mu\text{-}\eta^2\text{-}CH\text{-}C\text{-}CH\text{-}C{=}O)Os_3(CO)_{10}(\mu\text{-}H)$, **6** which was also decarbonylated thermally to yield **4** and **5**.