

# Exploring the peri-, chemo-, and regioselectivity of addition of technetium metal oxides of the type $\text{TcO}_3\text{L}$ ( $\text{L} = \text{Cl}^-$ , $\text{O}^-$ , $\text{OCH}_3$ , $\text{CH}_3$ ) to substituted ketenes: a DFT computational study

Issahaku Ahmed, Richard Tia, and Evans Adei

**Abstract:** The addition of  $\text{TcO}_3\text{L}$  ( $\text{L} = \text{Cl}$ ,  $\text{O}^-$ ,  $\text{OCH}_3$ ,  $\text{CH}_3$ ) to substituted ketenes along various addition pathways was studied with density functional theory calculations to explore the peri-, chemo-, and regioselectivity of the reactions. In the reactions of  $\text{TcO}_3\text{L}$  with dimethyl ketene, the results show that for  $\text{L} = \text{O}^-$  and  $\text{CH}_3$ , [1 + 1] addition to form a triplet zwitterionic intermediate is the preferred first step; for  $\text{L} = \text{Cl}$ , the [3 + 2]<sub>C=C</sub> addition across the O–Tc–Cl bond is the preferred first step and for  $\text{L} = \text{OCH}_3$  the [3 + 2]<sub>C=C</sub> addition across the O–Tc–OCH<sub>3</sub> bond is the preferred first step. In the reactions of  $\text{TcO}_3\text{Cl}$  with substituted ketenes, [1 + 1] addition to form a triplet zwitterionic intermediate is the preferred first step for  $\text{X} = \text{Ph}$ ,  $\text{CN}$ , and  $\text{Cl}$ ; the [3 + 2]<sub>C=C</sub> addition across the O–Tc–O bond of the complex is the preferred first step for  $\text{X} = \text{H}$ , while the [3 + 2]<sub>C=C</sub> addition across the O–Tc–CH<sub>3</sub> bond is the preferred first step. Reactions involving a change in the oxidation state of metal have high activation barriers, while reactions that do not involve a change in oxidation state have low activation barriers. Reactions of ketenes with  $\text{TcO}_3\text{L}$  complexes have lower activation barriers for the preferred addition pathways than those of the  $\text{ReO}_3\text{L}$  complexes reported in the literature. Thus, the  $\text{TcO}_3\text{L}$  complexes may be better catalysts for the activation of the C=C bonds of substituted ketenes than the reported  $\text{ReO}_3\text{L}$  complexes.

**Key words:** ketene, technetium, oxidation, computational.

**Résumé :** Nous avons étudié l'addition des complexes  $\text{TcO}_3\text{L}$  ( $\text{L} = \text{Cl}$ ,  $\text{O}^-$ ,  $\text{OCH}_3$ ,  $\text{CH}_3$ ) sur des cétones substitués et divers mécanismes par lesquels s'effectuent ces additions à l'aide de calculs de la théorie de la fonctionnelle de la densité en vue d'explorer la périsélectivité, la chimiosélectivité et la régiosélectivité de ces réactions. Dans les réactions des complexes  $\text{TcO}_3\text{L}$  avec le diméthylcétène, les résultats montrent que, dans le cas où  $\text{L} = \text{O}^-$  et  $\text{CH}_3$ , l'addition [1 + 1] formant un intermédiaire zwitterionique à l'état triplet est l'étape initiale la plus favorable; alors que, dans le cas où  $\text{L} = \text{Cl}$ , c'est l'addition [3 + 2]<sub>C=C</sub> sur la liaison O–Tc–Cl qui est l'étape initiale la plus favorable et, dans le cas où  $\text{L} = \text{OCH}_3$ , l'étape initiale la plus favorable est l'addition [3 + 2]<sub>C=C</sub> sur la liaison O–Tc–OCH<sub>3</sub>. En outre, dans les réactions du  $\text{TcO}_3\text{Cl}$  avec des cétones substitués, l'addition [1 + 1] formant un intermédiaire zwitterionique à l'état triplet est l'étape initiale la plus favorable lorsque  $\text{X} = \text{Ph}$ ,  $\text{CN}$  et  $\text{Cl}$ ; dans le cas où  $\text{X} = \text{H}$ , c'est l'addition [3 + 2]<sub>C=C</sub> sur la liaison O–Tc–O du complexe qui est l'étape initiale la plus favorable, alors que sur la liaison O–Tc–CH<sub>3</sub>, c'est l'addition [3 + 2]<sub>C=C</sub> qui est l'étape initiale la plus favorable. Les réactions faisant intervenir un changement de l'état d'oxydation de l'atome métallique présentent des barrières d'activation élevées, alors que celles qui ne font intervenir aucun changement d'état d'oxydation présentent des barrières d'activation basses. Les mécanismes d'addition favorisés dans les réactions entre des cétones et des complexes  $\text{TcO}_3\text{L}$  présentent des barrières d'activation moins élevées que celles qui ont été rapportées dans la littérature pour les mêmes réactions avec des complexes  $\text{ReO}_3\text{L}$ . Les complexes  $\text{TcO}_3\text{L}$  pourraient donc être de meilleurs catalyseurs que les complexes  $\text{ReO}_3\text{L}$  connus pour effectuer l'activation des liaisons C=C de cétones substitués. [Traduit par la Rédaction]

**Mots-clés :** cétène, technétium, oxydation, computationnel.

## Introduction

Ketenes are excellent precursors for catalytic asymmetric reactions, creating chiral centers mainly through addition across their C=C bonds. Ketenes represent one of the keystone reactive intermediates of organic chemistry due to their unusual and unique spectrum of chemical reactivity.<sup>1</sup> Due to their electrophilic nature, ketenes readily react with nucleophiles to form zwitterionic enolates that form the basis for much of asymmetric chemistry. The high reactivity of ketenes with organic substitutes has led to increasing interest in their reactivity with metal complexes.<sup>2</sup> There are issues of periselectivity ([3 + 2] versus [2 + 2] or [1 + 1] addition), stereoselectivity (*cis* and *trans* isomers for the transition states and products), chemoselectivity (addition across the C=C or C=O moiety), and regioselectivity involved in the addition of transition metal oxo complexes to ketenes.

Catalyzed reactions of group VII (manganese, technetium, and rhenium) are of great importance for their tendency toward epoxidation and dihydroxylation. Studies have shown that transition metal catalyzed processes have high selectivity and efficiency. Unlike ketenes, reactions of transition metal oxo complexes with olefins have been extensively explored and the issues of periselectivity settled.<sup>3–23</sup>

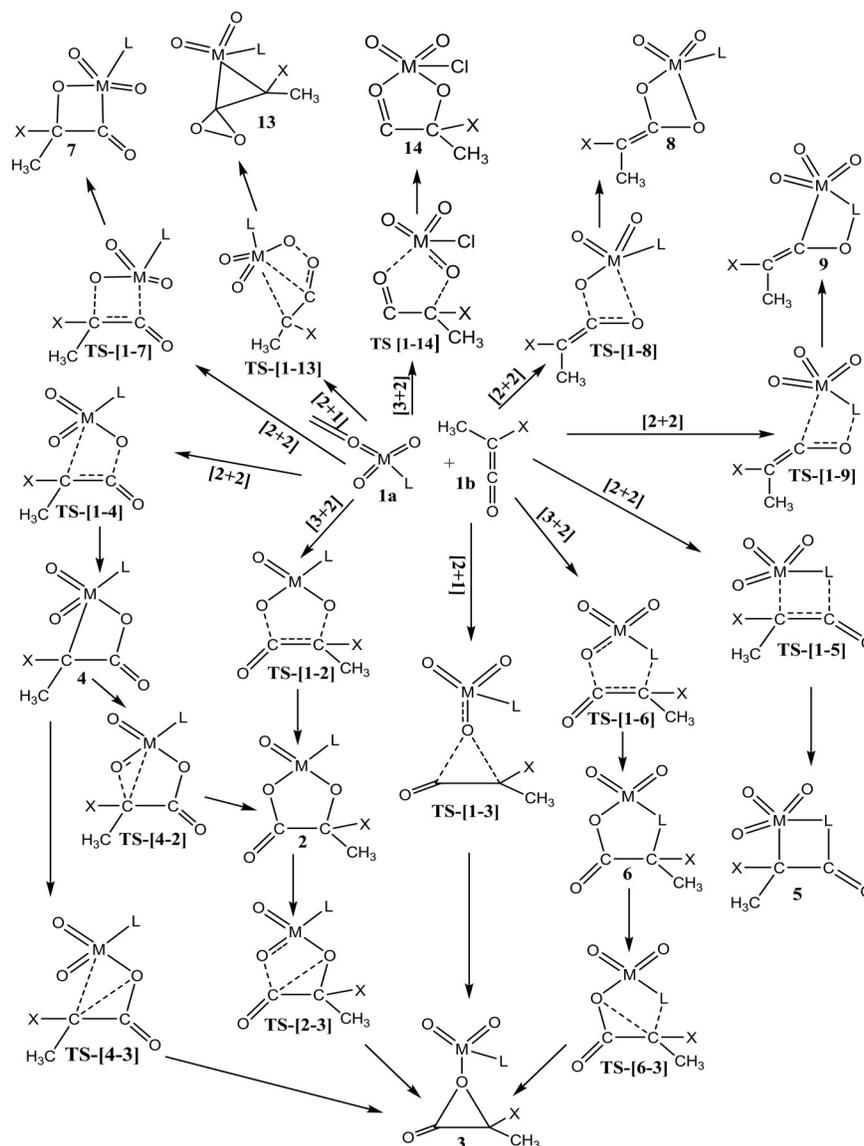
A number of studies have been conducted on the periselectivity, chemoselectivity, and regioselectivity of the addition of ketenes to rhenium oxo complexes. Middleditch et al.<sup>24</sup> studied the reactions of rhenium oxo complexes with diphenyl ketene and concluded that the [3 + 2] addition pathway was the most preferred and that addition across the ketene C=C double bond is preferred over addition across the ketene C=O double bond. Deubel et al.<sup>25</sup> studied the chemo- and periselectivity of the addition of rhenium oxo complexes to ketene

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**Scheme 1.** Proposed pathways for the concerted additions of  $LTcO_3$  ( $L = O^-, Cl^-, CH_3, OCH_3$ ) to substituted ketene (dimethyl ketene) and possible rearrangements.

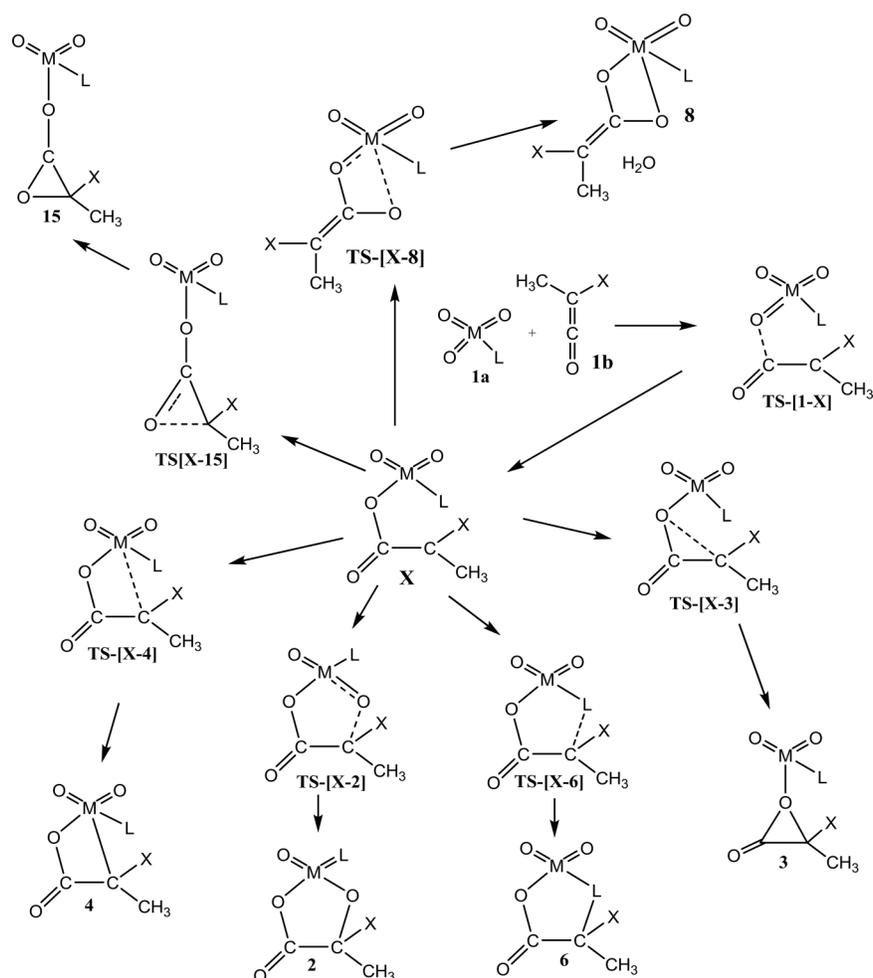


and found that the reactions of  $ReO_3L$  ( $L = O^-, H_3PN, Me, Cp$ ), which are O-nucleophilic and metal-electrophilic, favor  $[2 + 2]$  addition and that when  $L = O^-$  and  $H_3PN$ , addition across  $C=O$  is preferred, while addition across  $C=C$  bonds is preferred with softer ligands such as methyl and cyclopentadienyl. An exploratory predictive mechanistic study recently conducted by Ahmed et al.<sup>26</sup> on the peri-, chemo-, and regio selectivity of the addition of transition metal oxo complexes  $ReO_3L$  ( $L = Cl, O^-, OCH_3, CH_3$ ) to substituted ketenes  $O=C(CH_3)(X)$  ( $X = CH_3, H, CN, Ph$ ) showed that  $[2 + 2]$  addition pathway (across the  $C=C$  or  $C=O$  bond depending on the ligand) is the most preferred in the reactions of dimethyl ketene with all of the metal complexes studied. This is consistent with the works of Deubel et al.<sup>25</sup> In the reactions of  $ReO_3Cl$  with all of the substituted ketenes, the study showed that the  $[2 + 2]$  pathway is also the most preferred except when  $X = Cl$ , which is chemoselective towards the  $[3 + 2]$  addition pathway. The study demonstrated that these reactions have the potential to afford dioxirane precursors,  $CO_2$ , chlorohydrin precursors, and esters (lactone).

To date, there is no report on the reaction of ketenes with technetium oxo complexes. All of the reported experimental and theoretical works are on the rhenium oxo complexes. Meanwhile, the works

of Aniyagei et al.<sup>21–23</sup> have shown that the additions of technetium oxo complexes to olefins afford reactions with lower activation barriers and higher selectivity for the preferred pathways compared to reactions catalyzed by the similar rhenium oxo complexes. It is therefore envisaged that this might be the case in the oxidations of ketenes with group VIIB oxo complexes, i.e., that the oxidation of substituted ketenes with technetium oxo complexes might afford reactions with lower activation barriers and better selectivity than those catalyzed by rhenium oxo complexes, as was seen to be the case in the oxidations of olefins. This therefore is the motivation for this work, which seeks to explore the peri-, chemo-, and regioselectivity of the addition of technetium oxo complexes of the type  $TcO_3L$  ( $L = Cl, O^-, CH_3O, CH_3$ ) to substituted ketenes  $O=C(CH_3)(X)$  ( $X = H, CH_3, Cl, CN, Ph$ ) (Schemes 1 and 2). The rearrangements of the intermediates are also explored. As an exploratory predictive mechanistic study, it is aimed at investigating the various plausible pathways for ketene reactions with technetium oxo complexes. The results will be useful in the design of technetium oxo complexes as catalysts for the selective oxidations of substituted ketenes, beyond the reported  $ReO_3L$  complexes.

**Scheme 2.** Proposed pathways for the stepwise additions of  $\text{LTcO}_3$  ( $\text{L} = \text{O}^-, \text{Cl}^-, \text{CH}_3, \text{OCH}_3$ ) to substituted ketene (dimethyl ketene) and possible rearrangements.



### Details of calculation

All calculation were performed with the Spartan '10 V1.1.0 code from Wavefunction, Inc.<sup>27</sup> at the DFT B3LYP/LACVP\* and MO6/LACVP\* levels of theory. The B3LYP functional is a Hartree-Fock DFT hybrid functional, while the MO6 is metahybrid exchange correlation that has been recommended for application in organometallic and inorganometallic chemistry.<sup>28</sup> The LACVP\* basis set is a relativistic effective core potential. It describes the atoms hydrogen to argon with the 6-31G\* basis, while heavier atoms are described with the LANL2DZ basis set, which uses Dunning's all-electron valence double zeta basis set (D95V) for first row elements<sup>29</sup> and Wadt and Hay's Alamos ECP plus double zeta basis set for the atoms sodium to lanthanum and hafnium to bismuth.<sup>30–32</sup>

Molecules were constructed using Spartan's graphical model builder, minimized interactively using an appropriate molecular mechanics force field<sup>33</sup> and optimized fully without any symmetry restrictions. A normal mode analysis was performed to verify that the equilibrium geometries have no imaginary frequencies.

The transition state structures were located by a series of constrained geometry optimizations in which the forming and breaking bonds are fixed at various lengths, while the remaining internal coordinates will be optimized. The approximate stationary points located from such a procedure were then fully optimized using the standard transition state optimization procedure in Spartan. All transition states were shown to have a Hessian matrix with a single negative eigenvalue, characterized by an imaginary vibrational frequency along the reaction coordinate. An intrinsic reaction coordi-

nate calculation was carried out to ensure that transition states smoothly connect reactants and products.

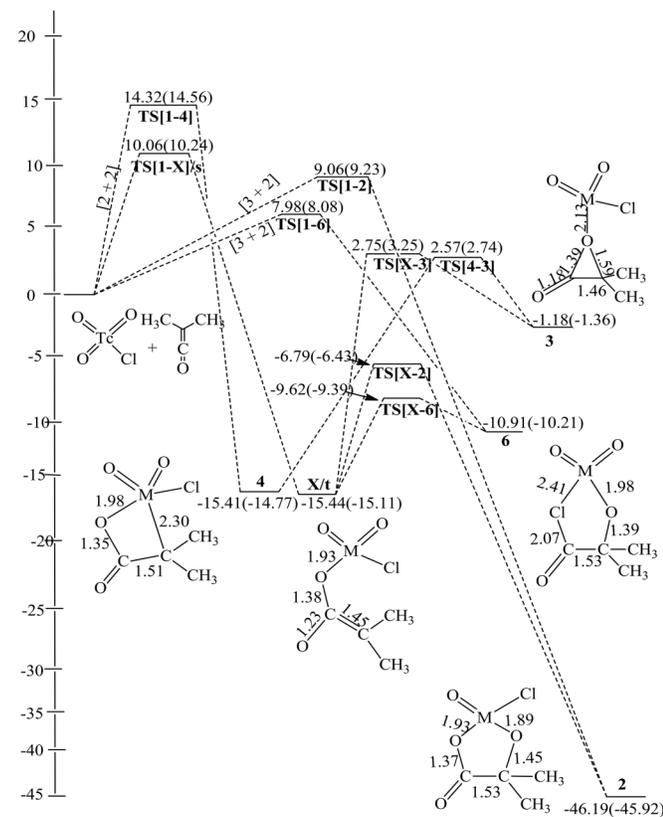
### Results and discussion

The study is in two main parts. The following four sections look at the reactions of  $\text{TcO}_3\text{L}$  ( $\text{L} = \text{Cl}^-, \text{O}^-, \text{OCH}_3, \text{CH}_3$ ) with dimethyl ketene. The subsequent four sections look at the reactions of  $\text{TcO}_3\text{Cl}$ , the least selective of the technetium complexes explored here, with a series of substituted ketenes  $\text{O}=\text{C}=\text{C}(\text{CH}_3)(\text{X})$  ( $\text{X} = \text{H}, \text{CH}_3, \text{Cl}, \text{CN}, \text{Ph}$ ). This will help elucidate the effects of substituents on the metal complex and the ketene on the mechanism of the reactions.

#### Reaction of $\text{TcO}_3\text{Cl}$ with dimethyl ketene

Figure 1 shows the optimized geometries and the energy profile of the reaction between  $\text{TcO}_3\text{Cl}$  and dimethyl ketene ( $(\text{CH}_3)_2\text{C}=\text{C}=\text{O}$ ). The singlet structure of  $\text{TcO}_3\text{Cl}$  was 62.69 kcal/mol more stable than the triplet structure when both species were computed as neutral structures. The concerted [3 + 2] addition of the  $\text{O}=\text{Tc}=\text{O}$  bond of the metal oxide across the  $\text{C}=\text{C}$  of the ketene to form metalla-2,5-dioxolane-4,4-dimethyl-3-one on the singlet potential energy surface (PES) species  $\text{2}$  (Fig. 1) has an activation barrier of 9.06 kcal/mol and exothermicity of 46.19 kcal/mol at the B3LYP level of theory through a transition state  $\text{TS-[1-2]}$ . Our earlier work<sup>26</sup> on rhenium oxo complexes yielded an activation barrier of 22.59 kcal/mol and exothermicity of 16.95 kcal/mol for the formation of the rhenium complex analogue of species  $\text{2}$ . The MO6 level of theory gives an activation barrier of 5.86 kcal/mol and reaction energy of  $-55.50$  kcal/mol. The

**Fig. 1.** Energetics of the reaction of  $\text{TcO}_3\text{-Cl}$  with dimethyl ketene on the singlet PES. Energies in kcal/mol at the B3LYP level of theory. Zero-point energy corrections in parentheses.



formation of the five-membered metallacycle **6** (Fig. 1) through concerted  $[3 + 2]$  addition of the  $\text{O}=\text{Tc}=\text{Cl}$  bond of the metal oxide across the  $\text{C}=\text{C}$  bond of the ketene on the singlet PES has an activation barrier of 7.97 kcal/mol and reaction energy of  $-10.91$  kcal/mol. Both species **2** and **6** could also arise from stepwise addition pathway with overall activation barrier of 10.06 kcal/mol.

The concerted  $[2 + 2]$  addition of the  $\text{Tc}=\text{O}$  bond of the metal oxide across the  $\text{C}=\text{C}$  of the ketene to form species **4** (Fig. 1) has an activation barrier of 14.32 kcal/mol and exothermicity of 15.41 kcal/mol. A spin crossover was seen in the stepwise pathway from the singlet reactants through a singlet transition state  $\text{TS}[\text{1-X}]/\text{s}$  to form a triplet zwitterionic intermediate  $\text{X}/\text{t}$  with an activation barrier of 10.06 kcal/mol and exothermicity of 15.44 kcal/mol at the B3LYP level of theory.

Localizing a zwitterionic intermediate in a gas-phase calculation might seem surprising, since zwitterions are more likely formed in solution or liquid phase than in the gas phase. However, there is ample evidence in the literature to indicate that zwitterions can exist in the gas phase. For example, Julian and Jarrold<sup>34</sup> have concluded from ab initio calculations that the ground state for neutral, isolated molecules in the gas phase can be zwitterionic under appropriate conditions and that the common assumption that charge separation is inherently unfavorable in the gas phase may need to be revisited, even for molecules in the absence of a net charge. The zwitterionic intermediate located is unstable; additional stabilization can be expected from solvation effects.

The formation of the ester precursor (species **3**) could arise from two possible pathways: the formation of species **4** through concerted  $[2 + 2]$  addition of the  $\text{Re}=\text{O}$  bond of the metal oxide across the  $\text{C}=\text{C}$  of the ketene followed by rearrangement to form **3** with an overall activation barrier of 17.98 kcal/mol and reaction energy of  $-1.18$  kcal/mol or the stepwise formation of the zwitterionic

intermediate species  $\text{X}/\text{t}$  followed by rearrangement to form the species with an overall activation energy of 18.19 kcal/mol.

The most plausible overall addition pathway on this PES is the concerted  $[3 + 2]$  addition of the  $\text{O}=\text{Tc}=\text{Cl}$  bond of the metal oxide across the  $\text{C}=\text{C}$  of the ketene to form the five-membered metallacycle species **6**. This is consistent with the work of Middleitch<sup>24</sup> where only products arising from formal  $[3 + 2]$  addition were isolated in the reactions of  $\text{ReO}_3\text{L}$  with diphenyl ketene. The order of feasibility is  $[3 + 2]_{\text{C}=\text{C}} > [2 + 2]_{\text{C}=\text{C}}$ . The most plausible pathway towards the formation of the lactone precursor **3** is through the formation of species **4** followed by subsequent rearrangement to form **3** with an overall activation barrier of 17.98 kcal/mol. No  $[2 + 2]$  or  $[3 + 2]$  addition across the  $\text{C}=\text{O}$  of the ketene (i.e.,  $[2 + 2]_{\text{C}=\text{O}}$  or  $[3 + 2]_{\text{C}=\text{O}}$ ) was obtained.

In the work of Deubel et al.,<sup>25</sup> the lowest activation barriers were found to be between 10 and 20 kcal/mol, which are generally higher than the barriers for the reactions of  $\text{TcO}_3\text{Cl}$  with dimethyl ketene reported here. Therefore, this reaction is kinetically more feasible than the  $\text{ReO}_3\text{L}$ -catalyzed reactions reported by Deubel et al.<sup>25</sup> and Ahmed et al.<sup>26</sup>

The calculated activation and reaction energies for some selected addition pathways (Table 1) at the MO6 level of theory are lower than those at the B3LYP level of theory, which is consistent with the work of Linder and Brinck<sup>35</sup> and Ahmed et al.<sup>26</sup> but the MO6 results do not change the preferred addition pathway.

#### Reaction of $\text{TcO}_4^-$ with dimethyl ketene

Figure 2 shows the relative energies of the main stationary points (reactants, transition states, intermediates, and products) involved in the reaction between  $\text{TcO}_4^-$  and dimethyl ketene and some of the optimized structures. The energetics are summarized in Table 2. The singlet structure of  $\text{TcO}_4^-$  is 51.77 kcal/mol more stable than the triplet structure when both species were computed as anionic structures. On the singlet PES, the concerted  $[3 + 2]$  addition of the  $\text{O}=\text{Re}=\text{O}$  bond of the metal oxide across the  $\text{C}=\text{C}$  bond of the ketene to form metalla-2,5-dioxolane-4,4-dimethyl-3-one (Fig. 2) has an activation barrier of 8.68 kcal/mol and exothermicity of 45.17 kcal/mol at the B3LYP level of theory through transition state  $\text{TS}[\text{1-2}]$ . The MO6 level of theory gives an activation barrier of 3.62 kcal/mol and exothermicity of 55.24 kcal/mol. In the work of Deubel et al.<sup>25</sup> involving rhenium oxo complexes, the activation barrier was found to be 28.4 kcal/mol and exothermicity 0.1 kcal/mol. Our earlier work<sup>26</sup> on rhenium oxo complexes gave an activation barrier of 20.16 kcal/mol and exothermicity of 17.43 kcal/mol. The barriers for the rhenium oxo complexes are significantly higher than those of the technetium complexes reported here. Species **2** could also arise from a stepwise addition pathway through intermediate  $\text{X}$  with an overall barrier of about 20.70 kcal/mol.

Species **4** (Fig. 2) formed through concerted  $[2 + 2]$  addition of the  $\text{Tc}=\text{O}$  bond of the metal oxide across the  $\text{C}=\text{C}$  bond of the ketene with an activation energy of 7.75 kcal/mol and exothermicity of 17.42 kcal/mol, respectively, at the B3LYP level. At the MO6 level, the barrier is 2.37 kcal/mol and the reaction energy is  $-29.52$  kcal/mol. Deubel et al.<sup>25</sup> obtained a barrier of 12.4 kcal/mol and exothermicity of 8.3 kcal/mol. The technetium metal catalyst gives lower activation barriers and the reaction energies are more exothermic compared to that of the rhenium metal. Species **4** rearranges through transition state  $\text{TS}[\text{4-2}]$  with an activation barrier of 26.14 kcal/mol to form species **2** at the B3LYP level of theory.

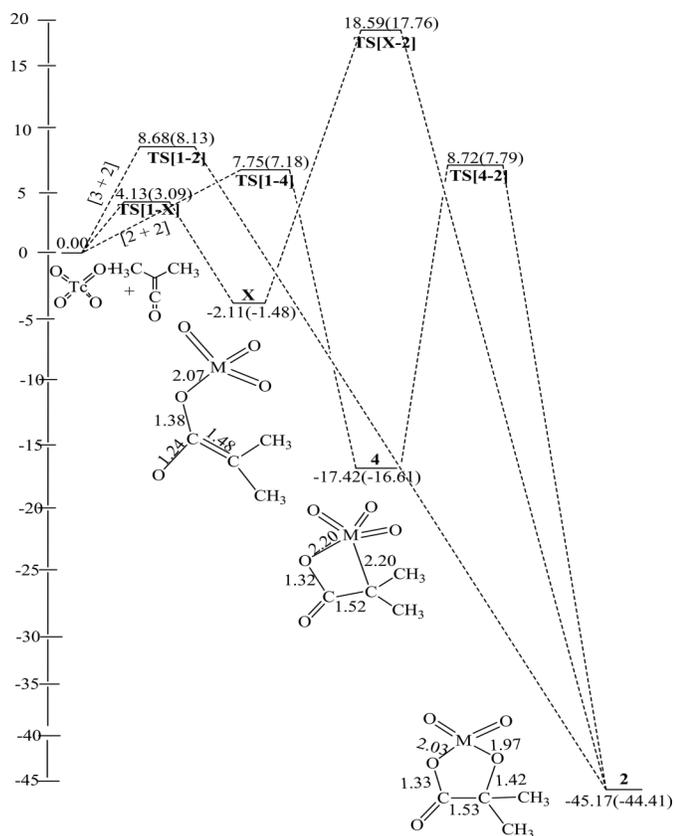
The zwitterionic intermediate  $\text{X}/\text{s}$  (Fig. 2) localizes as a singlet intermediate through transition state  $\text{TS}[\text{1-X}]/\text{s}$  with an energy barrier of 4.13 kcal/mol and reaction energy of  $-2.11$  kcal/mol.

The most feasible overall addition pathway on this PES is the concerted  $[2 + 2]$  addition of the  $\text{Tc}=\text{O}$  bond of the metal oxide across the  $\text{C}=\text{C}$  of the ketene to form the four-membered metallacycle species **4**, while the most feasible route for the formation of **2** is the one-step  $[3 + 2]$  addition pathway. The barrier for the  $[1 + 1]$  addition pathway to form the triplet zwitterionic intermediate

**Table 1.** Calculated activation energies and reaction energies for the addition pathways in the reaction of  $\text{TcO}_3\text{Cl}$  with dimethyl ketene at the B3LYP and MO6 levels of theory.

Chlorine ligand		Activation energy (kcal/mol)		Reaction energy (kcal/mol)	
Reaction path	Addition	B3LYP	MO6	B3LYP	MO6
1-2	$[3 + 2]_{\text{C}=\text{C}}$	9.06 (9.23)	5.86 (5.98)	-46.19 (-45.92)	-55.50 (-54.81)
1-4	$[2 + 2]_{\text{C}=\text{C}}$	14.32 (14.56)	5.32 (5.72)	-15.41 (-14.77)	-27.31 (-26.10)
1-6	$[3 + 2]_{\text{C}=\text{O}}$	7.98 (8.08)	4.65 (5.13)	-10.91 (-10.21)	-19.49 (-18.58)
1-X	$[1 + 1]$	10.06 (10.24)	4.53 (5.04)	-15.44 (-15.11)	-21.76 (-21.19)
4-3	Rearrangement	17.98 (18.15)	23.91 (24.24)	14.23 (13.41)	17.00 (15.97)
X-2	Rearrangement	8.65 (9.01)	-32.56 (-32.01)	-30.75 (-29.98)	-33.74 (-33.09)
X-3	Rearrangement	18.19 (18.69)	12.31 (12.94)	14.26 (13.39)	11.45 (10.37)
X-6	Rearrangement	5.82 (6.05)	3.02 (3.87)	4.53 (4.16)	2.27 (1.95)

Note: Zero-point energy corrections in parentheses.

**Fig. 2.** Energetics of the reaction of  $\text{TcO}_4^-$  with dimethyl ketene on the singlet PES. Energies in kcal/mol at the B3LYP level of theory. Zero-point energy corrections in parentheses.

$\text{X/t}$  is the preferred first step in these reactions; however, the conversion of  $\text{X/t}$  to **2** involves a very high barrier.

The calculated energy barriers for the formation of species **2**, **4**, and  $\text{X/s}$ , are lower compared to the chlorine ligand analogues of the metal oxide (Fig. 1). Also, the reaction of the  $\text{TcO}_4^-$  with dimethyl ketene is more selective (fewer competitive pathways) compared to that of  $\text{ReO}_3\text{Cl}$ .

Attempts to locate transition states leading to the formation of species **3**, **8**, **13**, and **14** were not successful. The calculated activation and reaction energies for some selected addition pathways (Table 2) at the MO6 level of theory are lower than those at the B3LYP level just as is the case of the chlorine ligand. No addition pathway across the  $\text{C}=\text{O}$  bond of the ketene was found to be feasible. Thus, the metal complex adds selectively across the  $\text{C}=\text{C}$  bonds of the ketene rather than  $\text{C}=\text{O}$  bonds. Comparing the oxidation of ketenes with  $\text{TcO}_4^-$  and  $\text{ReO}_4^-$ , the technetium metal catalyst comparatively

is a better catalyst for its propensity to give a kinetically and thermodynamically controlled reaction system in the formation of similar analogues than the rhenium metal.

### Reaction of $\text{TcO}_3-\text{OCH}_3$ with dimethyl ketene

The optimized geometries and the energy profile of the reaction of  $\text{TcO}_3-\text{OCH}_3$  with dimethyl ketene are shown in Fig. 3 and the energetics are summarized in Table 3. The singlet structure of  $\text{TcO}_3-\text{CH}_3$  was 47.13 kcal/mol more stable than the triplet structure when both species were computed as neutral structures. The concerted  $[3 + 2]$  addition of the  $\text{O}=\text{Tc}=\text{O}$  bond of the metal oxide across the  $\text{C}=\text{C}$  bond of the ketene to form metalla-2,5-dioxolane-4,4-dimethyl-3-one on the singlet PES species **2** (Fig. 3) through transition state  $\text{TS-[1-2]}$  has an activation energy of 21.09 kcal/mol and exothermicity of 43.11 kcal/mol at the B3LYP level of theory. The MO6 level of theory gives an activation barrier of 7.88 kcal/mol and reaction energy of 52.39 kcal/mol. The five-membered metallacycle **6** (Fig. 3) formed through concerted  $[3 + 2]$  addition of the  $\text{O}=\text{Tc}=\text{O}$  bond of the metal oxide across the  $\text{C}=\text{C}$  bond of the ketene on the singlet PES has an activation barrier of 11.26 kcal/mol and reaction energy of -31.90 kcal/mol. The preference of the  $[3 + 2]$  over the  $[2 + 2]$  is consistent with the work of Herrmann<sup>36</sup> and Middleditch<sup>24</sup> on the rhenium complex. An activation energy of 13.47 kcal/mol is obtained in the formation of the triplet zwitterionic intermediate  $\text{X/t}$  through transition state  $\text{TS-[1-X]/s}$  at the B3LYP level of theory with an exothermicity of 12.76 kcal/mol. This intermediate  $\text{X/t}$  undergoes cyclization to form species **3** and **8** through transition states  $\text{TS-[X-3]/s}$  and  $\text{TS-[X-8]/s}$  with respective activation energies of 21.98 and 25.12 kcal/mol at the B3LYP level of theory.

### Reaction of $\text{TcO}_3-\text{CH}_3$ with dimethyl ketene

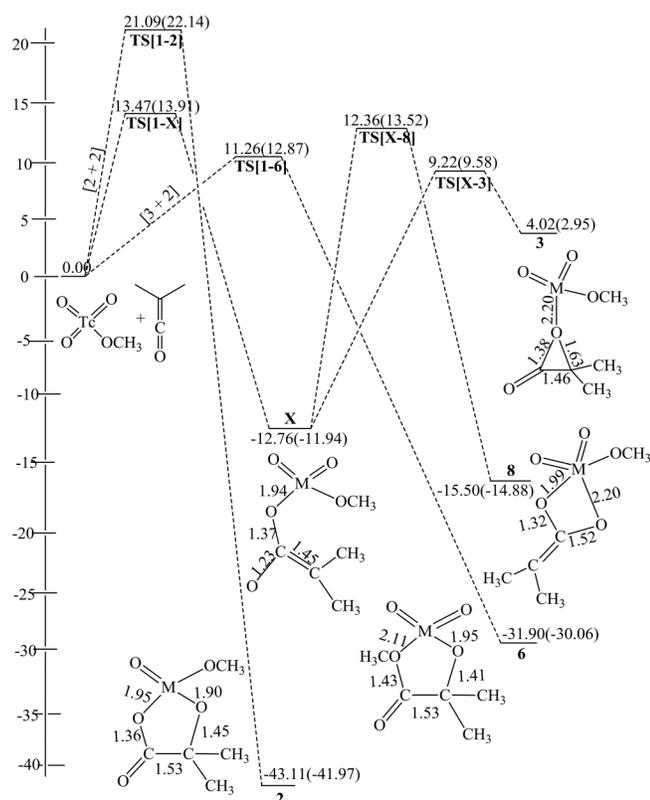
The optimized geometries and the energy profile of the reaction between  $\text{TcO}_3-\text{CH}_3$  and dimethyl ketene are shown in Fig. 4 and the energetics are summarized in Table 4. The singlet structure of  $\text{ReO}_3-\text{CH}_3$  is 49.78 kcal/mol more stable than the triplet structure; both species were computed as neutral structures. On the singlet PES, the concerted  $[3 + 2]$  addition of the  $\text{O}=\text{Tc}=\text{O}$  bond of the metal oxide across the  $\text{C}=\text{C}$  of the ketene to form metalla-2,5-dioxolane-4,4-dimethyl-3-one species **2** (Fig. 4) has an activation barrier of 20.57 kcal/mol and exothermicity of 32.44 kcal/mol at the B3LYP level of theory through transition state  $\text{TS-[1-2]}$ . The MO6 level of theory gave 17.35 and 44.02 kcal/mol, respectively. The work of Deubel et al.<sup>25</sup> on the rhenium complex gave an activation energy of 44.5 kcal/mol and the reaction energy was endothermic by 16.3 kcal/mol, while that of Ahmed et al.<sup>26</sup> gave a barrier of 33.95 kcal/mol and exothermicity of 1.20 kcal/mol. This indicates that activating the bonds of ketenes with  $\text{TcO}_3-\text{CH}_3$  is more feasible than with  $\text{ReO}_3-\text{CH}_3$ .

The formation of species **4** (Fig. 4) through concerted  $[2 + 2]$  addition of the  $\text{Tc}=\text{O}$  bond of the metal oxide across the  $\text{C}=\text{C}$  bonds of the ketene has an activation barrier of 19.45 kcal/mol and reaction energy of -17.65 kcal/mol. The work of Deubel et al.<sup>25</sup> on the rhenium

**Table 2.** Calculated activation energies and reaction energies for the addition pathways in the reaction of  $\text{TcO}_4^-$  with dimethyl ketene at the B3LYP and MO6 levels of theory.

Oxygen ligand		Activation energy (kcal/mol)		Reaction energy (kcal/mol)	
Reaction path	Addition	B3LYP	MO6	B3LYP	MO6
1-2	$[3 + 2]_{\text{C}=\text{C}}$	8.68 (8.13)	3.62 (3.22)	-45.17 (-44.41)	-55.24 (-54.84)
1-4	$[2 + 2]_{\text{C}=\text{C}}$	7.75 (7.18)	2.37 (2.07)	-17.42 (-16.61)	-29.52 (-29.02)
1-X	$[1 + 1]$	4.13 (3.09)	1.51 (1.01)	-2.11 (-1.48)	-6.34 (-5.45)
X-2	Rearrangement	20.70 (19.87)	16.18 (15.13)	-43.06 (-42.27)	-48.90 (-48.12)
4-2	Rearrangement	26.14 (25.21)	33.08 (32.16)	-27.75 (-27.13)	-25.72 (-24.34)

Note: Zero-point energy corrections in parentheses.

**Fig. 3.** Energetics of the reaction of  $\text{TcO}_3\text{-OCH}_3$  with dimethyl ketene on the singlet PES. Energies in kcal/mol at the B3LYP level of theory. Zero-point energy corrections in parentheses.

complex with ketenes gave an activation barrier of 20.2 kcal/mol for the *cis* isomer and 23.6 kcal/mol for the *trans* isomer and a reaction energy of -6.3 and -9.9 kcal/mol, respectively. This again indicates that reactions with the technetium complex are more favorable than those with the rhenium complex. Species 4 also rearranges to form species 2 through transition state TS[4-2] with an energy barrier of 17.11 kcal/mol. An activation energy of 47.71 kcal/mol and reaction energy of 26.07 kcal/mol are involved in the formation of an open-shell intermediate species 9 (Fig. 4) through concerted  $[2 + 2]$  addition of the  $\text{Tc-CH}_3$  bond of the metal oxide across the  $\text{C}=\text{O}$  bond of the ketene.

Dioxirane precursor species 13 is formed through the direct  $[1 + 2]$  addition of one of the oxygens of the metal oxide across the  $\text{C}=\text{O}$  bond of the ketene with an activation barrier of 111.41 kcal/mol and endothermicity of 67.66 kcal/mol at the B3LYP level of theory. Since the energy barrier is so high and 13 is predicted to be so unstable, this reaction is not likely to occur. Species 13 may be so unstable due to the presence of the two highly strained rings.

The most feasible first step is the formation of the triplet zwitterionic intermediate. It is seen that the selectivity of the  $\text{TcO}_3\text{-}$

$\text{CH}_3$  reaction is almost the same as that of the  $\text{TcO}_3\text{-Cl}$  and  $\text{TcO}_3\text{-OCH}_3$  systems but it has relatively higher energy barriers.

Considering all of the reactions of  $\text{TcO}_3\text{L}$  ( $\text{L} = \text{Cl}^-$ ,  $\text{O}^-$ ,  $\text{OCH}_3$ ,  $\text{CH}_3$ ) with dimethyl ketene, the oxygen ligand system ( $\text{TcO}_4^-$  with dimethyl ketene (Fig. 2)) has the lowest activation barriers and the cleanest reaction surface and hence the highest selectivity. The ability of  $\text{MO}_4^-$  ( $\text{M} = \text{Mn}$ ,  $\text{Re}$ ,  $\text{Tc}$ ) to catalyze the oxidation of olefins selectively to fewer products was noted in the work of Aniaeyei et al.<sup>21-23</sup> where the reactions of  $\text{MnO}_4^-$ ,  $\text{ReO}_4^-$ , and  $\text{TcO}_4^-$  with ethylene had lower barriers for fewer reaction pathways leading to high selectivity.

In the reactions of dimethyl ketenes with  $\text{TcO}_3\text{L}$ , the trend in the selectivity of the reactions with respect to ligand L is  $\text{O}^- > \text{CH}_3 > \text{CH}_3\text{O}^- > \text{Cl}^-$ .

In the reactions of all of the  $\text{TcO}_3\text{Cl}$  complexes with dimethyl ketene, structure 7, which is a regioisomer of 4 formed from  $[2 + 2]_{\text{C}=\text{C}}$  addition of the ketene across the  $\text{Tc-O}$  bond such that the carbonyl carbon of the ketene is bonded to the metal, is not found. Thus, 4 is the only viable regioisomer from the  $[2 + 2]_{\text{C}=\text{C}}$  addition (Table 5).

### Reaction of $\text{TcO}_3\text{Cl}$ with methyl ketene

Even though all of the metal catalysts from the previous sections selectively catalyzed specific reactions, the reactions of one of the less selective metal catalysts (i.e.,  $\text{TcO}_3\text{Cl}$ ) is explored in the following sections with a series of substituted methyl ketenes to study the effects of the substituents on the ketene on the reactivity and selectivity of these reactions.

Table 6 shows the activation and reaction energies of the main stationary points involved in the reaction between  $\text{TcO}_3\text{Cl}$  and methyl ketene (the optimized geometries and the energy profile of the reaction of  $\text{TcO}_3\text{Cl}$  and methyl ketene are shown in the electronic supporting information Fig. S1 (see Supplementary material section)). From Table 6, it is seen that replacing one of the methyl groups on the ketene with hydrogen raises the activation barrier for the formation of the hydro analogue of species 2 by 2.02 kcal/mol and the reaction becomes less exothermic by 2.27 kcal/mol. The formation of the triplet zwitterionic intermediate X/t sees an increase in activation barrier by 1.34 kcal/mol and a decrease in exothermicity by 3.84 kcal/mol. The rearrangement of the triplet zwitterionic intermediate X/t to form species 2/s has the energy barrier increased by 3.87 kcal/mol.

The formation of the lactone precursor species 3 has a 6.33 kcal/mol increase in the activation barrier and a 2.10 kcal/mol increase in reaction energy, while the rearrangement of the triplet intermediate X/t to form species 6/s is no longer feasible for this system because no transition state is found. The formation of the ester precursor species 3 could arise from a single pathway just as in the reaction of  $\text{TcO}_3\text{Cl}$  with dimethyl ketene.

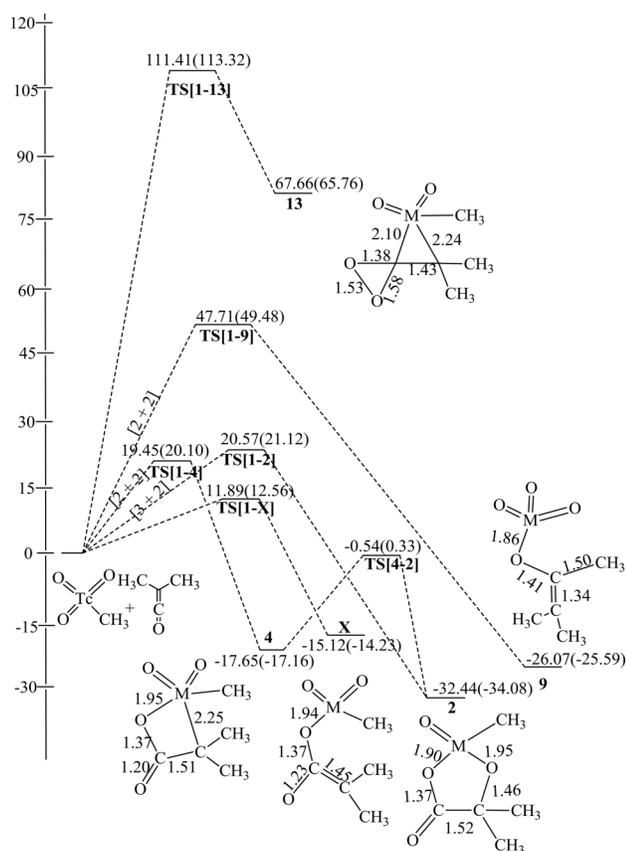
The most plausible addition pathway on this PES is the concerted  $[3 + 2]$  addition of the  $\text{O}=\text{Re}=\text{O}$  bond of the metal oxide across the  $\text{C}=\text{C}$  of the ketene to form the five-membered metallocycle species 2 just as is the case for the parent system (dimethyl ketene).

Upon replacement of the methyl group with hydrogen, the corresponding minima of species 4 and 6 could not be located. There-

**Table 3.** Calculated activation and reaction energies for the addition pathways in the reaction of  $\text{TcO}_3\text{-OCH}_3$  with dimethyl ketene at the B3LYP and MO6 levels of theory.

Methoxy ligand		Activation energy (kcal/mol)		Reaction energy (kcal/mol)	
Reaction path	Addition	B3LYP	MO6	B3LYP	MO6
1-2	$[3 + 2]_{\text{C}=\text{C}}$	21.09 (22.14)	7.88 (8.16)	-43.11 (-41.97)	-52.39 (-51.65)
1-6	$[3 + 2]_{\text{C}=\text{C}}$	11.26 (12.87)	7.30 (7.93)	-31.90 (-30.06)	-42.20 (-41.86)
1-X	$[1 + 1]$	13.47 (13.91)	11.75 (12.44)	-12.76 (-11.94)	-20.31 (19.47)
X-3	Rearrangement	21.98 (22.34)	25.23 (25.78)	16.78 (15.59)	13.09 (12.57)
X-8	Rearrangement	25.12 (26.28)	25.79 (26.67)	-2.72 (-2.10)	-6.28 (-6.23)

Note: Zero-point energy corrections in parentheses.

**Fig. 4.** Energetics of the reaction of  $\text{TcO}_3\text{-CH}_3$  with dimethyl ketene on the singlet PES. Energies in kcal/mol at the B3LYP level of theory. Zero-point energy corrections in parentheses.

fore, it is seen to be no longer feasible. However, for this system, a concerted  $[2 + 2]$  addition of the  $\text{Tc}=\text{O}$  bond of the metal oxide across the  $\text{C}=\text{O}$  bond of the ketene to form an open-shell intermediate species **9** is located. The energy barriers for the formation of similar analogues in the methyl ketene system are similar to those of the dimethyl ketene system. There is not much difference in the selectivity of this reaction compared to the former; however, three plausible elementary steps are seen for this system against four plausible elementary steps for the dimethyl system. Therefore, replacing a dimethyl ketene with methyl ketene decreases the number of plausible elementary steps and hence increases the selectivity but does not really affect the reactivity.

#### Reaction of $\text{TcO}_3\text{Cl}$ with chloromethyl ketene

In the reaction of  $\text{TcO}_3\text{Cl}$  with chloromethyl ketene, structure **4** (Scheme 1) does not appear to be a viable intermediate, since it was not located at all. However, its regioisomer, i.e., **7**, formed from  $[2 + 2]_{\text{C}=\text{C}}$  addition of the ketene across the  $\text{Tc}-\text{O}$  bond such

that it was found that the carbonyl carbon of the ketene is bonded to the metal. The barrier for the formation of **7** is 0.02 kcal/mol higher than that for the formation of **4** involving dimethyl ketene, and the corresponding exothermicity decreases by 10.40 kcal/mol. An increase in the activation barrier of 1.40 kcal/mol for the formation of the triplet zwitterionic intermediate **X/t** is seen and the reaction energy is seen to be more exothermic by 3.29 kcal/mol. The cyclization of the triplet zwitterionic intermediate **X/t** to form species **2/s** increased in activation barrier by 3.8 kcal/mol.

The triplet intermediate **X/t** also cyclizes to form species **2** with an increase in the activation barrier of about 7.67 kcal/mol and a decrease in exothermicity of 1.15 kcal/mol. Also, species **X/t** cyclizes in the formation of species **6** with an increase in the energy barrier of 7.65 kcal/mol and the reaction energy decreases in endothermicity by 4.14 kcal/mol. No concerted addition pathway towards the formation of species **2** and **6** is seen. Formation of the ester precursor **3** is also not located.

An activation barrier of about 74.11 kcal/mol is computed in the formation of the dioxirane precursor **13** with an endothermicity of 66.22 kcal/mol. This species **13** is not located for the methyl ketene and dimethyl ketene.

The most feasible first step is the  $[1 + 1]$  addition pathway to form the triplet zwitterionic intermediate. This system has the most selective reaction surface compared to dimethyl and methyl ketene systems. This makes the chloromethyl ketene reaction surface with the metal catalyst ( $\text{TcO}_3\text{Cl}$ ) potentially more selective compared to the two former systems.

#### Reaction of $\text{TcO}_3\text{Cl}$ with cyanomethyl ketene

As in the case of the chloromethyl ketene, structure **4** does not seem to be a viable intermediate in the reactions of  $\text{TcO}_3\text{Cl}$  with cyanomethyl ketene but its regioisomer **7** is located. The barrier for the formation of **7** is 40.36 kcal/mol higher than that for the formation of **4** involving dimethyl ketene and the corresponding reaction energy from  $-15.44$  to  $11.89$  kcal/mol. The formation of the triplet zwitterionic intermediate **X/t** also sees a 1.44 kcal/mol increase in the activation barrier and a change in reaction energy from an exothermicity of 15.44 kcal/mol to an endothermicity of 9.88 kcal/mol. The triplet zwitterionic intermediate **X/t** then cyclizes through singlet transition state **TS-[X-8]/s** to form species **8/s** with an energy barrier of 15.93 kcal/mol and reaction energies of  $-16.83$  kcal/mol.

The formation of the carbon monoxide and chlorohydrin precursor species **C/s** (Fig. S3) through direct  $[3 + 2]$  addition of  $\text{Tc}=\text{O}$  of the metal oxide across the  $\text{C}=\text{C}=\text{O}$  of cyanomethyl ketene has an activation barrier of 28.46 kcal/mol and exothermicity of 18.34 kcal/mol. These reactions seem possible only in the  $\text{TcO}_3\text{Cl}$ -cyanomethyl ketene case. The formation of the dioxirane precursor **13** (Scheme 1), just as in the case of chloromethyl ketene, has an activation barrier of 122.07 kcal/mol and endothermicity of 73.88 kcal/mol, making this reaction highly unlikely. The formation of the three-membered ring lactone is not possible, just as in the case of the chloromethyl ketene system. It is realized that the

**Table 4.** Calculated activation energies and reaction energies for the addition pathways in the reaction of  $\text{TcO}_3\text{-OCH}_3$  with dimethyl ketene at the B3LYP and MO6 levels of theory.

Methyl ligand		Activation energy (kcal/mol)		Reaction energy (kcal/mol)	
Reaction path	Addition	B3LYP	MO6	B3LYP	MO6
<b>1-2</b>	$[3 + 2]_{\text{C}=\text{C}}$	20.57 (21.12)	17.35 (18.04)	-32.44 (-34.08)	-44.02 (-43.43)
<b>1-4</b>	$[2 + 2]_{\text{C}=\text{C}}$	19.45 (20.10)	10.27 (10.94)	-17.65 (-17.16)	-30.06 (-28.99)
<b>1-9</b>	$[2 + 2]_{\text{C}=\text{O}}$	47.71 (49.48)	28.36 (29.76)	-26.07 (-25.59)	-27.82 (-25.58)
<b>1-13</b>	$[1 + 2]$	111.41 (113.32)	103.58 (105.37)	67.66 (65.76)	57.03 (58.49)
<b>1-X</b>	$[1 + 1]$	11.89 (12.56)	9.55 (10.65)	-15.12 (-14.23)	-20.74 (-21.96)
<b>4-2</b>	Rearrangement	17.11 (17.98)	19.01 (19.79)	-14.79 (-15.04)	-13.96 (-14.08)

Note: Zero-point energy corrections in parentheses.

**Table 5.** Comparison of the peri-, chemo-, and regioselectivity of the reactions of technetium: activation barriers and reaction energies for the various reactions of the technetium and rhenium complexes with dimethyl ketene.

Reaction path	Addition	Activation energy (kcal/mol)	Reaction energy (kcal/mol)
<b>Chlorine ligand</b>			
<b>1-2</b>	$[3 + 2]_{\text{C}=\text{C}}$	9.06 (9.23)	-46.19 (-45.92)
<b>1-4</b>	$[2 + 2]_{\text{C}=\text{C}}$	14.32 (14.56)	-15.41 (-14.77)
<b>1-6</b>	$[3 + 2]_{\text{C}=\text{C}}$	7.98 (8.08)	-10.91 (-10.21)
<b>4-3</b>	Rearrangement	17.98 (18.15)	14.23 (13.41)
<b>1-X</b>	$[1 + 1]$	10.06 (10.24)	-15.44 (-15.11)
<b>X-2</b>	Rearrangement	8.65 (9.01)	-30.75 (-29.98)
<b>X-3</b>	Rearrangement	18.19 (18.69)	14.26 (13.39)
<b>X-6</b>	Rearrangement	5.82 (6.05)	4.53 (4.16)
<b>Methoxy ligand</b>			
<b>1-2</b>	$[3 + 2]_{\text{C}=\text{C}}$	21.09 (22.14)	-43.11 (-41.97)
<b>1-6</b>	$[3 + 2]_{\text{C}=\text{C}}$	11.26 (12.87)	-31.90 (-30.06)
<b>1-X</b>	$[1 + 1]$	13.47 (13.91)	-12.76 (-11.94)
<b>X-3</b>	Rearrangement	21.98 (22.34)	16.78 (15.59)
<b>X-8</b>	Rearrangement	25.12 (26.28)	-2.72 (-2.10)
<b>Oxygen ligand</b>			
<b>1-2</b>	$[3 + 2]_{\text{C}=\text{C}}$	8.68 (8.13)	-45.17 (-44.41)
<b>1-4</b>	$[2 + 2]_{\text{C}=\text{C}}$	7.75 (7.18)	-17.42 (-16.61)
<b>1-X</b>	$[1 + 1]$	4.13 (3.09)	-2.11 (-1.48)
<b>X-2</b>	Rearrangement	20.70 (19.87)	-43.06 (-42.27)
<b>4-2</b>	Rearrangement	26.14 (25.21)	-27.75 (-27.13)
<b>Methyl ligand</b>			
<b>1-2</b>	$[3 + 2]_{\text{C}=\text{C}}$	20.57 (21.12)	-32.44 (-34.08)
<b>1-4</b>	$[2 + 2]_{\text{C}=\text{C}}$	19.45 (20.10)	-17.65 (-17.16)
<b>1-9</b>	$[2 + 2]_{\text{C}=\text{O}}$	47.71 (49.48)	-26.07 (-25.59)
<b>1-13</b>	$[1 + 2]$	111.41 (113.32)	67.66 (65.76)
<b>1-X</b>	$[1 + 1]$	11.89 (12.56)	-15.12 (-14.23)
<b>4-2</b>	Rearrangement	17.11 (17.98)	-14.79 (-15.04)

Note: Zero-point energy corrections in parentheses.

formation of species **2** and **6** is no longer feasible due to the presence of a more electronegative substituent (CN) compared to the methyl group.

The most feasible first step is the  $[1 + 1]$  addition to form the triplet zwitterionic intermediate.

This system has energy barriers similar to those for the dimethyl ketene, methyl ketene, and chloromethyl ketene systems for the identified species. However, this system has fewer feasible reaction pathways on the singlet PES than the dimethyl ketene and methyl ketene systems but more than the chloromethyl ketene system. This makes the cyanomethyl ketene reaction surface with the metal catalyst ( $\text{TcO}_3\text{Cl}$ ) more selective compared to dimethyl ketene and methyl ketene but less selective compared to chloromethyl ketene even though they are all selective. Also, it is the only substituted ketene that yields the species **C/s**.

### Reaction of $\text{TcO}_3\text{Cl}$ with methyl phenyl ketene

The activation and reactions energies involved in the reaction between  $\text{TcO}_3\text{Cl}$  and methyl phenyl ketene (Fig. S4 shows the optimized geometries and relative energies of the main stationary points involved in the reaction between  $\text{TcO}_3\text{Cl}$  and methyl phenyl ketene) are also shown in Table 6. It is seen that the formation of the phenyl analogue of species **2** by replacing one of the methyl groups on the ketene with a phenyl group leads to the raising of the activation energy by 0.86 kcal/mol but a decrease of the exothermicity of the reaction energy by 7.33 kcal/mol. Also seen is a decrease in the activation barrier of about 0.78 kcal/mol in the formation of the triplet zwitterionic intermediate **X/t** with the reaction energy changing from -15.44 to 11.25 kcal/mol. The triplet zwitterionic intermediate **X/t** then cyclizes to form species **8/s** with an energy barrier of 6.76 kcal/mol and exothermicity of 30.53 kcal/mol. A single addition pathway towards the formation of species **3** was identified (Fig. S4) through rearrangement of species **2** with an activation energy of about 51.53 kcal/mol and endothermicity of 57.80 kcal/mol.

The most plausible addition pathway on this PES is the concerted  $[3 + 2]$  addition of the  $\text{O}=\text{Tc}=\text{O}$  bond of the metal oxide across the  $\text{C}=\text{C}$  of the ketene to form the species **2** intermediate. There are no longer local minima corresponding to intermediates **4** and **6**; this is attributed to the presence of a bulkier and more electronegative substituent (Ph) compared to the methyl group.

### Rationalizing the PESs of the reaction of $\text{TcO}_3\text{Cl}$ with the substituted ketenes

Table 7 shows the nature of the partial charges on the  $\text{C}=\text{C}=\text{O}$  atoms of the parent ketene obtained from the electrostatic potential map of the various substituted ketenes. The substituted ketenes with the same consecutive positive or negative charge on the  $\text{C}=\text{C}=\text{O}$  atoms of the parent ketene with the substituent having same charge (positive or negative) produce less selective PES in the reaction between  $\text{TcO}_3\text{Cl}$  with the substituted ketenes. This is noted for the dimethyl ketene, methyl ketene, and cyanomethyl ketene metal catalysts. However, a clean PES is seen for those substituted ketenes with alternating charges on the  $\text{C}=\text{C}=\text{O}$  of the parent ketene with the substituent having different charges. This is also noted for chloromethyl ketene and methyl phenyl ketene. In the reaction of  $\text{TcO}_3\text{Cl}$  with the substituted ketenes ( $\text{O}=\text{C}=\text{C}(\text{CH}_3)(\text{X})$ ,  $\text{X} = \text{H}, \text{CH}_3, \text{Cl}, \text{CN}, \text{Ph}$ ), the addendums (adding atoms), which are positive-on-negative (thus, positives from the metal catalyst and negatives from the ketene), yielded lower barriers and the preferred pathway is  $[3 + 2]$  addition across the  $\text{C}=\text{C}$  of the substituted ketenes, just as in the case of the reaction of  $\text{TcO}_3\text{L}$  ( $\text{L} = \text{Cl}^-, \text{OCH}_3$ ) with dimethyl ketene except for  $\text{X} = \text{Cl}$  whose lower barrier is a  $[2 + 2]$  addition across the  $\text{C}=\text{C}$  of the ketene with electrostatic potential map charges of the addendums being positive-on-negative at one end (oxygen from metal

**Table 6.** Calculated activation energies and reaction energies for the [3 + 2] and [2 + 2] additions of TcO<sub>3</sub>Cl with the substituted ketenes (O=C=C(CH<sub>3</sub>)(X), X = H, CH<sub>3</sub>, Cl, CN, Ph) across the C=C and C=O bonds of ketene at the B3LYP level of theory.

Reaction path	Addition	Activation energy (kcal/mol)					Reaction energy (kcal/mol)				
		X = CH <sub>3</sub>	X = H	X = Cl	X = CN	X = Ph	X = CH <sub>3</sub>	X = H	X = Cl	X = CN	X = Ph
1-2	[3 + 2] <sub>C=C</sub>	9.06	11.08			9.95	-46.19	-43.92			-38.86
1-4	[2 + 2] <sub>C=C</sub>	14.32		44.34	54.68		-15.41		-5.01	11.89	
1-5	[2 + 2] <sub>C=C</sub>										
1-6	[3 + 2] <sub>C=C</sub>	7.97					-10.91				
1-8	[2 + 2] <sub>C=O</sub>										
1-9	[2 + 2] <sub>C=O</sub>		20.91					-1.73			
1-14	[3 + 2] <sub>C=C=O</sub>										
1-13	[1 + 2] <sub>C=O</sub>			74.11	122.07				66.22	73.88	
1-C	[3 + 2] <sub>C=C=O</sub>				28.46					-18.34	
1-X	[1 + 1]	10.06	11.40	11.46	11.50	9.28	-15.44	-11.60	-18.73	9.88	11.25
X-2	Rearrangement	8.48	12.35	16.15			-30.75	-32.32	29.60		
X-3	Rearrangement	18.19	24.52				14.26	16.36			
X-6	Rearrangement	5.82		13.47			4.53		0.39		
X-8	Rearrangement		8.78		15.93	6.76		3.50		-16.83	-30.53
2-3	Rearrangement					51.53					57.80
4-2	Rearrangement										
4-3	Rearrangement	18.01					14.23				

**Table 7.** Nature of partial charges on the C=C=O atoms of the parent ketene obtained from the electrostatic potential map (EPM) of various substituted ketenes.

Ketene	Nature of EPM charges on C=C=O	Nature of PES
Dimethyl ketene		Less selective
Methyl ketene		Less selective
Cyanomethyl ketene		Less selective
Chloromethyl ketene		Selective
Methyl phenyl ketene		Selective

catalyst-on-carbon from ketene) and positive-on-positive at the other adding end (the metal of the catalyst-on-carbon of the ketene).

In all of the reactions studied, it was found that the postulated formation of **14** by [3 + 2] addition of the C=C=O bond of the ketenes across the Tc–O bond of TcO<sub>3</sub>Cl is not possible.

### Comparison of the reactions of TcO<sub>3</sub>L and ReO<sub>3</sub>L with dimethyl ketene

Table 8 shows the activation barriers and reaction energies for the first step of the various reactions of TcO<sub>3</sub>L and ReO<sub>3</sub>L with dimethyl ketene for the various ligands studied in this work and in our earlier reported work.<sup>26</sup> It is seen from the table that for all of the ligands, the activation barriers for the formation of similar analogues are lower for the technetium complexes than for the rhenium complexes and reaction energies for technetium are more exothermic than those for rhenium. It is also seen from the table that the reactions of the technetium complexes are more selective than the reactions of the rhenium complexes, since there are fewer com-

petitive reaction pathways with the technetium complexes than with the rhenium complexes. A similar trend was seen by Aniaeyei et al.<sup>21–23</sup> for the reactions of group VIIB transition metal oxides with ethylene. These results imply that technetium oxo complexes will most likely efficiently and selectively catalyze specific reactions in the oxidation of ketenes and olefins more so than the rhenium oxo complexes. Therefore, technetium oxo complexes may be better catalysts for specific oxidation reactions of ketenes and olefins than rhenium complexes.

### Summary and conclusion

(1) The periselectivity in the reactions of metal oxides (TcO<sub>3</sub>L) with substituted ketenes depends on the ligand L and (or) the type of substituents on the ketene. The [2 + 2] addition across the C=C of the ketenes is the preferred pathway in the reaction of TcO<sub>3</sub>L (L = O<sup>-</sup>, CH<sub>3</sub>) with dimethyl ketene, while the [3 + 2] addition across the C=C is the preferred pathway for L = Cl<sup>-</sup> and OCH<sub>3</sub>. In the reaction of TcO<sub>3</sub>Cl with the substituted ketenes (O=C=C(CH<sub>3</sub>)(X), X = H, CH<sub>3</sub>, Cl, CN, Ph), the [3 + 2] pathway is the most preferred for X = H, CH<sub>3</sub>, Ph, and CN, whereas for X = Cl, the [2 + 2] pathway is the most preferred.

(2) Chemoselectivity (C=C versus C=O) of the [2 + 2] addition of TcO<sub>3</sub>L also depends on the ligand L. For L = O<sup>-</sup>, Cl<sup>-</sup>, and CH<sub>3</sub>, the addition across the C=C bond of the dimethyl ketene was the most favored (7.75, 14.32, and 19.45 kcal/mol, respectively), while none of the ligands prefer addition across C=O. No [2 + 2] addition pathways were located for L = OCH<sub>3</sub>.

(3) The chemoselectivity of the [2 + 2] addition of TcO<sub>3</sub>Cl with the substituted ketenes depends on the substituent on the ketene. For X = H and CN, addition across the C=O bond of the metal oxide is the most favored, whereas for X = CH<sub>3</sub>, Cl, and Ph, addition across the C=C is the most favored. Thus, chemoselectivity of the addition of metal oxides to ketenes depends on the ligand and (or) the substituent of the ketene.

(4) The regioselectivity of the [2 + 2]<sub>C=C</sub> addition is such that it is the addition leading to a bond between the middle carbon of the ketene and the metal center that is possible for the reactions of all of the TcO<sub>3</sub>L with dimethyl ketene. Its regioisomer, which has a bond between the carbonyl carbon of the ketene and the metal center, is possible only in the reaction of TcO<sub>3</sub>Cl with chloromethyl ketene and cyano metal ketene.

(5) The order in the activation energies of the preferred [3 + 2] and [2 + 2] pathways for addition of dimethyl ketenes to the metal complexes TcO<sub>3</sub>L with respect to changing ligand L is

**Table 8.** Comparison of the peri-, chemo-, and regioselectivity of the reactions of technetium and rhenium: activation barriers and reaction energies for the first step of the various reactions of the technetium and rhenium complexes with dimethyl ketene.

Metal	Reaction path	Addition	Activation barrier (kcal/mol)				Reaction energy (kcal/mol)			
			-Cl	-O-	OCH <sub>3</sub>	CH <sub>3</sub>	-Cl	-O-	OCH <sub>3</sub>	CH <sub>3</sub>
Tc	1-2	[3 + 2] <sub>C=C</sub>	9.06 (9.23)	8.68 (8.13)	21.09 (22.14)	20.57 (21.12)	-46.19 (-45.92)	-45.17 (-44.41)	-43.11 (-41.97)	-32.44 (-34.08)
	1-6	[3 + 2] <sub>C=C</sub>	7.98 (8.08)		11.26 (12.87)		-10.91 (-10.21)		-31.90 (-30.06)	
	1-4	[2 + 2] <sub>C=C</sub>	14.32 (14.56)	7.75 (7.18)		19.45 (20.10)	-15.41 (-14.77)	-17.42 (-16.61)		-17.65 (-17.16)
	1-8	[2 + 2] <sub>C=O</sub>								
	1-9	[2 + 2] <sub>C=O</sub>				47.71 (49.48)				-26.07 (-25.59)
	1-14									
Re <sup>a</sup>	1-X	[1 + 1]	10.06 (10.24)	4.13 (3.09)	13.47 (13.91)	11.89 (12.56)	-15.44 (-15.11)	-2.11 (-1.48)	-12.76 (-11.94)	-15.12 (-14.23)
	1-2	[3 + 2] <sub>C=C</sub>	22.59 (23.08)	20.16 (20.68)	24.79 (25.14)	33.95 (33.92)	-16.95 (-13.81)	-17.43 (-14.50)	-16.16 (-12.91)	-1.20 (1.25)
	1-6	[3 + 2] <sub>C=C</sub>	24.07 (24.78)		24.13 (24.73)		1.31 (3.72)		-6.59 (-3.18)	
	1-4	[2 + 2] <sub>C=C</sub>	13.64 (14.62)	12.54 (11.83)	41.69 (42.79)	20.71 (21.82)	-8.22 (-6.12)	-12.13 (-10.67)	-17.35 (-14.69)	-15.43 (-12.62)
	1-8	[2 + 2] <sub>C=O</sub>	18.68 (19.05)	6.40 (6.53)	17.87 (18.26)	18.38 (18.81)	-6.14 (-4.60)	-8.36 (-6.60)	-3.46 (-1.56)	-6.99 (-5.03)
	1-9	[2 + 2] <sub>C=O</sub>	19.10 (19.82)		18.08 (19.17)	50.00 (50.31)	-12.79 (-11.18)		-12.22 (-9.88)	-26.78 (-24.01)
	1-14	[3 + 2] <sub>C=C=O</sub>	21.48 (21.88)			24.18 (25.08)	12.93 (13.43)			15.74 (16.01)
	1-X	[1 + 1]	17.94 (17.77)		22.39 (21.18)	18.08 (18.19)	0.23 (0.77)		3.93 (4.45)	1.98 (2.58)

Note: Zero-point energy corrections in parentheses.

<sup>a</sup>Data from Ahmed et al.<sup>26</sup>

O<sup>-</sup> < Cl < CH<sub>3</sub> < CH<sub>3</sub>O<sup>-</sup>, while the order in reaction energies is CH<sub>3</sub> < CH<sub>3</sub>O<sup>-</sup> < O<sup>-</sup> < Cl. For the reactions of substituted ketenes with TcO<sub>3</sub>Cl, the order in activation barriers for the preferred addition pathways is CH<sub>3</sub> < Ph < H < Cl < CN, while the reaction energies follow the order Cl < CH<sub>3</sub> < H < Ph < CN.

(6) In the reactions of dimethyl ketenes with TcO<sub>3</sub>L, the trend in the selectivity of the reactions is Cl<sup>-</sup> < CH<sub>3</sub>O<sup>-</sup> < CH<sub>3</sub> < O<sup>-</sup>, while the trend in selectivity is CH<sub>3</sub> < H < CN < Cl < Ph in the reactions of TcO<sub>3</sub>Cl with substituted ketenes (O=C=C(CH<sub>3</sub>)(X), X = H, CH<sub>3</sub>, Cl, CN, Ph).

(7) Reactions involving a change in oxidation state of metal from the reactant to the product have high activation barriers, while reactions that do not involve a change in oxidation state have low activation barriers. The changes in oxidation state were observed for substituents or ligands with an electron-withdrawing or electron-donating inductive effect.

(8) For both [3 + 2] and [2 + 2] additions, low activation barriers are obtained when the substituent on the ketene is electron-donating, while high activation barriers are obtained when the substituent is electron-withdrawing. Due to the difficulty in the formation of an endocyclic O–O bond, the [3 + 2] addition of the O=M=O bond of the metal complex across the C=O of the ketenes was not possible.

(9) The reactions of substituted ketenes with TcO<sub>3</sub>L complexes have lower activation barriers for the preferred [3 + 2] and [2 + 2] addition pathways than those of the ReO<sub>3</sub>L complexes reported in the literature. Thus, the TcO<sub>3</sub>L complexes may be better catalysts for the activation of the C=C bonds of substituted ketenes than the reported ReO<sub>3</sub>L complexes.

## Supplementary material

Supplementary material is available with the article through the journal Web site at <http://nrcresearchpress.com/doi/suppl/10.1139/cjc-2015-0295>.

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