



# Theoretical feasibility of CO-activation and Fischer–Tropsch chain growth on mono- and diatomic Ru complexes

Cathrin Welker<sup>a,b</sup>, Noko S. Phala<sup>c</sup>, John R. Moss<sup>b</sup>, Michael Claeys<sup>a</sup>, Eric van Steen<sup>a,\*</sup>

<sup>a</sup> Centre for Catalysis Research, Department of Chemical Engineering, University of Cape Town, Private Bag X3, Rondebosch 7701, South Africa

<sup>b</sup> Department of Chemistry, University of Cape Town, Private Bag X3, Rondebosch 7701, South Africa

<sup>c</sup> Process Research, Anglo Research, PO Box 106, Crown Mines 2025, South Africa

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## ABSTRACT

Thermodynamic analyses of different proposed reaction pathways to determine the thermodynamic feasibility of FT reactions on a mono- and diatomic Ru-complex as model catalysts were performed.  $\text{Ru}(\text{CO})_5$  and  $\text{Ru}_2(\text{CO})_9$  were taken as starting complexes. The calculations illustrate that a minimum of two adjacent metal atoms is required for C–O bond cleavage and chain growth in the Fischer–Tropsch synthesis. The CO-insertion mechanism seems to be thermodynamically most feasible reaction pathway on diatomic Ru-clusters.

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## 1. Introduction

The Fischer–Tropsch (FT) synthesis is the catalytic conversion of synthesis gas ( $\text{H}_2/\text{CO}$  mixture) over a metallic catalyst yielding long chain hydrocarbons [1]. Catalysts with Ru as the catalytically active component are known to be the most active ones for this reaction [2]. Originally considered as a structure-insensitive reaction, recent publications on supported Co, Fe, Rh and Ru catalysts showed that crystallites below a certain size in the nano-meter range display lower metal surface area specific activity (turn over number) [3–8]. The origin of this behaviour is not clear. Investigation of Fischer–Tropsch activity over homogeneous complexes may give some indications to the origin of this phenomenon.

There have been several attempts to investigate the possibility to conduct homogeneously catalysed Fischer–Tropsch synthesis using organometallic clusters [9–11]. Such studies can be considered as extreme cases of metal dispersion with all metal atoms exposed to the reactants. Claeys et al. [12,13] detected some FT activity over supported Ru-complexes containing a minimum of two adjacent metal atoms. In their studies, a mono-atomic Ru-complex, however, did not show any Fischer–Tropsch activity.

The theoretical feasibility of CO-activation and chain growth on a single metal centre and two adjacent metal atoms is reported

here. These active centres containing one or two metal atoms are expressed as organometallic Ru-complexes. Reaction pathways for the Fischer–Tropsch synthesis based on experimental findings are proposed starting with known organometallic compounds.

## 2. Methodology

### 2.1. Proposed reaction pathways

All possible reaction pathways for the mono- and diatomic model systems under consideration are based on commonly postulated pathways, viz. CO-insertion, carbide, enol, alkoxy and alkenyl mechanisms [14–16]. As a starting point, the transformation of the ligands on the Ru-centre is envisaged to take place in accordance with the empirical principles established in organometallic chemistry. The proposed intermediates have generally 18 valence electrons for the transition metal and reactive species have 16 valence electrons. The proposed pathways leading to the generation of the catalytically active species, the generation of a chain starter and for chain growth are formulated, as is common practice for polymerization reactions [14–16]. Additional limitations include a minimum number of 5 or 6 ligands on a Ru-centre (with one ligand for the Ru–Ru bond in the diatomic Ru-complexes) and a number of C-atoms equal or exceeding the number of O-atoms. Carboxyl–Ru-compounds ( $\text{Ru}-\text{OR}$ ) or hydroxyl–Ru-compounds ( $\text{Ru}-\text{OH}$ ) are not considered.

\* Corresponding author. Tel.: +27 21 650 3796; fax: +27 21 650 5501.

E-mail address: [evs@chemeng.uct.ac.za](mailto:evs@chemeng.uct.ac.za) (E. van Steen).

### 2.1.1. Reaction pathway over a mono-atomic Ru-complex

$\text{Ru}(\text{CO})_5$  [18] as the simplest mono-atomic Ru-complex was used as starting compound for the proposed mono-atomic FT reaction pathways. Product desorption steps were included to allow comparison of theoretical selectivities with experimental observations done in homogeneous environment.

A scheme was developed to calculate all possible Ru-complexes for a given H, C and O atom number on a single Ru-atom. Plausible ligands consisting of C, H and O atoms ( $-\text{H}$ ;  $\equiv\text{C}$ ;  $\equiv\text{CH}$ ;  $=\text{CH}_2$ ;  $-\text{CH}_3$ ;  $-\text{CHO}$ ;  $-\text{COOH}$ ;  $-\text{CH}_2\text{CHO}$ ;  $=\text{CHOH}$ ;  $-\text{COCH}_3$ ;  $=\text{CO}$ ) were added to a Ru-centre, with the restriction that the number of valence electrons ( $N_{\text{VE}}$ ) equals 18 and 16, respectively, based on empirical organometallic chemistry rules [17]. A set of numerical equations was solved for a given molecule  $\text{Ru}_x\text{C}_y\text{O}_z\text{H}_z$ . In this equation set, the possible ligands were replaced with letters in alphabetical order (alphabetical numbering system:  $\text{H} = \text{a}$ ;  $\text{C} = \text{b}$ ;  $\text{CH} = \text{c}$ ;  $\text{CH}_2 = \text{d}$ ;  $\text{CH}_3 = \text{e}$ ;  $\text{CHO} = \text{f}$ ;  $\text{COOH} = \text{g}$ ;  $\text{CH}_2\text{CHO} = \text{h}$ ;  $\text{CH}_2\text{OH} = \text{i}$ ;  $\text{CHOH} = \text{j}$ ;  $\text{COCH}_3 = \text{k}$ ;  $\text{CO} = \text{l}$ ). Each ligand was multiplied by the number of donating electrons to the Ru-centre (see Eqs. (1)–(3)). The total amount of valence electrons on the Ru-centre was calculated using Eq. (4), including 8 fixed valence electrons for the  $4d^8$  Ru-system. A valid solution was obtained when the different restrictions were satisfied (i.e. the number of O-atoms equal or less the number of C-atoms, maximum amount of ligands restricted to 6).

$$N(\text{H}) = 1a + 1c + 2d + 3e + 1f + 1g + 3h + 3i + 2j + 3k \quad (1)$$

$$N(\text{O}) = 1f + 2g + 1h + 1i + 1j + 1k + 1l \quad (2)$$

$$N(\text{C}) = 1b + 1d + 1e + 1f + 1g + 2h + 1i + 1j + 2k + 1l \quad (3)$$

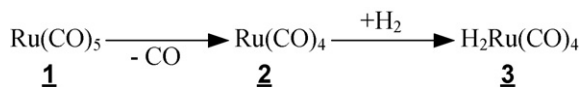
$$N_{\text{VE}} = 8 + 1a + 3b + 3c + 2d + 1e + 1f + 1g + 1h + 1i + 2j + 1k + 2l = 16 \text{ or } 18 \quad (4)$$

The generated complexes were ordered in 3 different reaction pathways (A, B, and C). It was confirmed that no additional reaction pathways are possible. The large number of possible complexes in a diatomic Ru-complex made it impractical to do the same exercise for the diatomic systems.

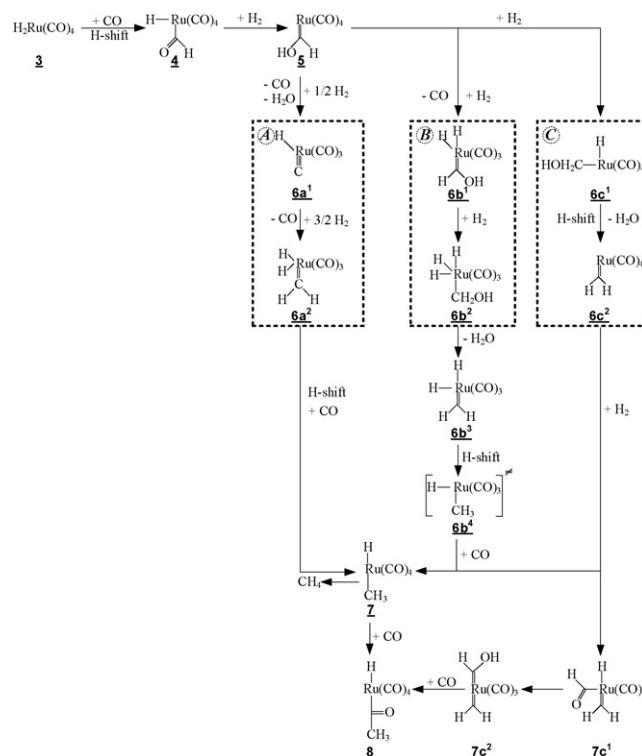
**2.1.1.1. Generation of the starter of the catalytic cycle.** The first step is the transformation of the model catalyst  $\text{Ru}(\text{CO})_5$  (1) via CO-desorption into the 16 valence electron species  $\text{Ru}(\text{CO})_4$  (2). Hydrogenation of  $\text{Ru}(\text{CO})_4$  generates  $\text{H}_2\text{Ru}(\text{CO})_4$  (3), which is regarded as the starter of the catalytic cycle (see Scheme 1). Compounds 1 and 3 are well-known and characterized, whereas species 2 has been identified [18–24].

The catalytic cycle starts from  $\text{H}_2\text{Ru}(\text{CO})_4$  and involves the generation of the chain starter and then chain growth (see Scheme 2). Several possible desorption routes have been included that lead to the formation of products, such as methane, methanol and formaldehyde.

**2.1.1.2. Generation of the chain starter.** The generation of the chain starter is based on the enol mechanism [25–27]. CO-adsorption on  $\text{H}_2\text{Ru}(\text{CO})_4$  (3) with a simultaneous migration of Ru bonded hydrogen towards a CO-ligand generates a Ru-aldehyde species (4). The simultaneous action is required to keep the number of



Scheme 1. Generation of chain started over mono-atomic Ru-complex.



Scheme 2. Proposed reaction pathways A, B and C divided in the generation of the chain starter and the first step of chain growth for the Fischer-Tropsch synthesis over mono-atomic clusters.

valence electrons constant. The aldehyde group undergoes a tautomerisation to a Ru-enol species (5). From here, 3 different reaction pathways have been proposed for the generation of the chain starter including a C–O bond cleavage.  $\text{HRu}(\text{CO})_4\text{CH}_3$  (7) is regarded as the chain starter. Although  $\text{HRu}(\text{CO})_4\text{CH}_3$  has not been isolated, the Os analogue is known and has been studied [28]. Similar reduction mechanisms of M-CO via M-CHO into M-CH<sub>3</sub> are known in homogeneous environments [29]. Methyl surface species on bulk catalyst surfaces during FT synthesis are proposed in the alkyl mechanism [30–33] and have been observed on surfaces involved in CO-hydrogenation [32].

**2.1.1.3. Reaction pathway A.** Along reaction pathway A,  $\text{H}_2\text{O}$  and CO desorb from the Ru-enol species with simultaneous H-addition to form a Ru-methylidyne ( $\text{Ru}=\text{C}$ ) ( $6a^1$ ), which is a typical intermediate in the carbide-mechanism [1,15,34]. Methylidyne are known for Ru as well as various other transition metals such as e.g. Rh [35] and W [36]. It is unlikely that this is an elementary reaction, and may thus not be feasible on a mono-atomic Ru-complex. Hydrogenation of this ‘carbide’-intermediate and simultaneous desorption of a CO-ligand leads to the Ru-methylene  $\text{H}_2\text{Ru}(\text{CO})_3\text{CH}_2$  ( $6a^2$ ), again a suggested compound for Ru [37]. H-shift and CO-adsorption lead to the formation of the chain starter  $\text{HRu}(\text{CO})_4\text{CH}_3$  (7).

**2.1.1.4. Reaction pathway B.** Along reaction pathway B,  $\text{H}_2$ -adsorption and simultaneous CO-desorption yields  $\text{H}_2\text{Ru}(\text{CO})_3(\text{CHOH})$  ( $6b^1$ ). CO-assisted desorption of this species may lead to the formation of formaldehyde and  $\text{H}_2\text{Ru}(\text{CO})_4$  or to the formation of methanol and  $\text{Ru}(\text{CO})_4$ , which can be transformed into  $\text{H}_2\text{Ru}(\text{CO})_4$  by hydrogenation (not shown). Another  $\text{H}_2$ -addition will saturate the  $\text{Ru}=\text{C}$  bond, generating a Ru-alkoxy species ( $6b^2$ ), followed by  $\text{H}_2\text{O}$  condensation on the alkoxy group to a Ru-methylene ( $6b^3$ ). H-shift from the Ru-centre to the unsat-

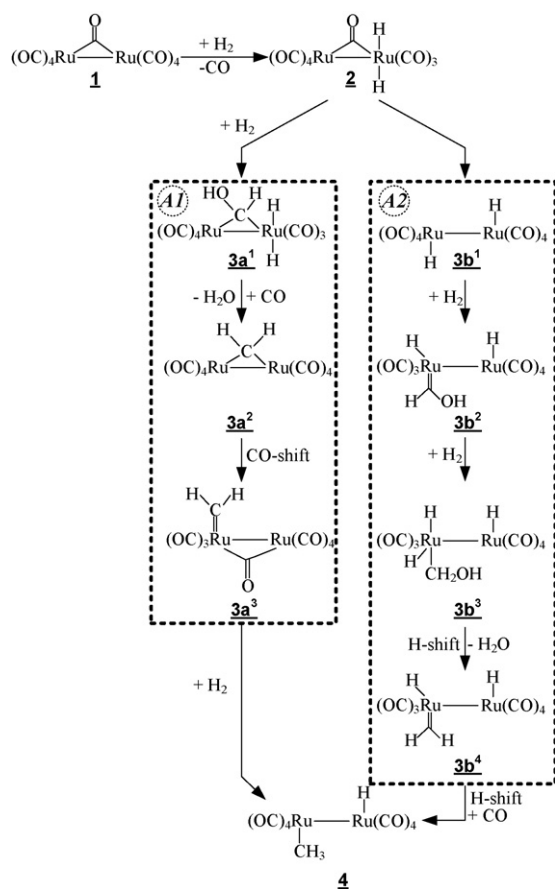
urated methylene group generates a 16 valence electron transition state species **6b**<sup>4</sup>, and CO-addition forms the chain starter (**7**). All reaction steps along this pathway B can be elementary.

**2.1.1.5. Reaction pathway C.** The C–O bond cleavage along reaction pathway C yields another Ru-methylene intermediate (**6c**<sup>2</sup>). This species is formed via a Ru-methoxy (**6c**<sup>1</sup>) involving H-shift and H<sub>2</sub>O-elimination. Methylene groups as intermediates during Fischer–Tropsch synthesis are proposed in the alkyl and in the alkenyl mechanism [15,38]. The Ru-methylene adsorbs another H<sub>2</sub>-molecule to either generate the chain starter (**7**), or a Ru-aldehyde species (**7c**<sup>1</sup>) and keeping the methylene group on the Ru. The second pathway by-passes the chain starter and goes directly via tautomerisation to **7c**<sup>2</sup> and finishes with another CO-insertion forming a C<sub>2</sub>-keto ligand on the Ru (**8**).

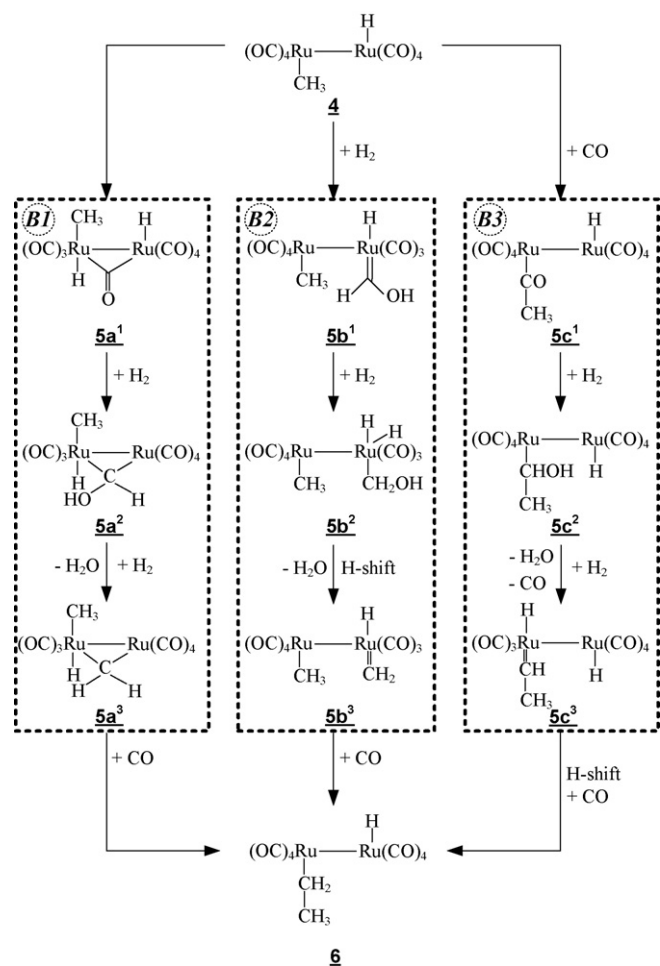
### 2.1.2. Reaction pathway over a diatomic Ru-complex

Ru<sub>2</sub>(CO)<sub>9</sub> (**1**) was taken as the starting compound for the proposed reaction pathways in the Fischer–Tropsch synthesis over a diatomic Ru-complex. Ru<sub>2</sub>(CO)<sub>9</sub> has been identified spectroscopically and the osmium analogue Os<sub>2</sub>(CO)<sub>9</sub> has been isolated and characterized [39].

The first step is H<sub>2</sub>-activation and adsorption with simultaneous CO-desorption generating compound **2** (see Scheme 3). The osmium analogue H<sub>2</sub>O<sub>2</sub>(CO)<sub>8</sub> is a known and characterized compound [40]. Two different reaction pathways (A1 and A2) for the formation of the chain starter (**4**) are proposed. The osmium analogue of the chain starter **4** HO<sub>s</sub>(CO)<sub>4</sub>Os(CO)<sub>4</sub>CH<sub>3</sub> is a known compound [28]. Three different reaction pathways are proposed for



**Scheme 3.** Generation of the chain starter for the along reaction pathways A1 and A2.

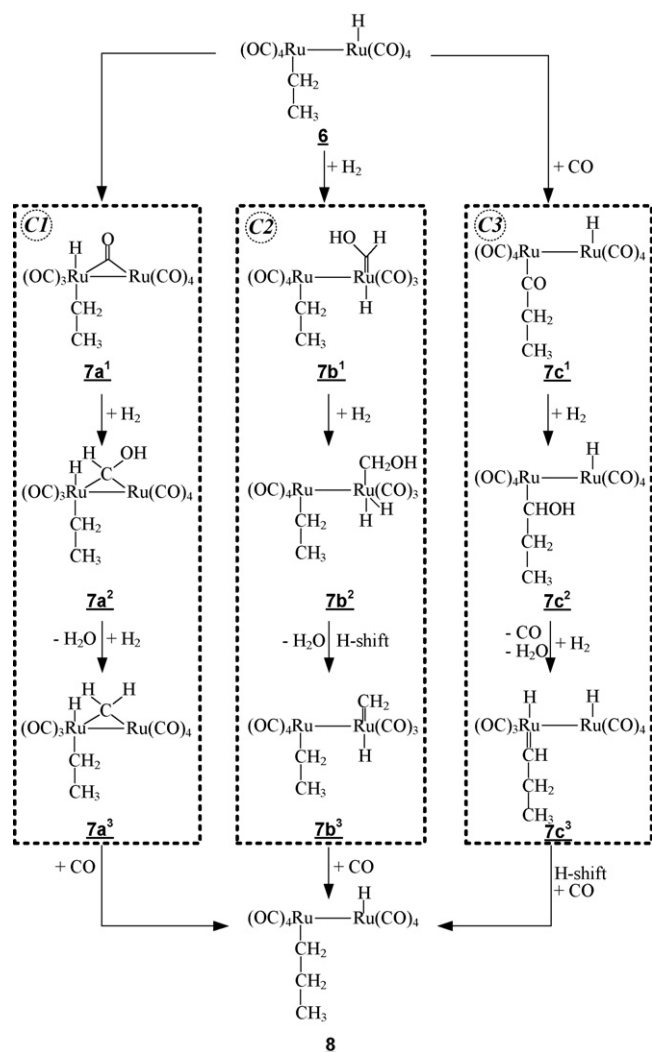


**Scheme 4.** Reaction pathways B1, B2 and B3 for chain growth in the Fischer–Tropsch synthesis over di-atomic Ru-clusters.

the first and second part of chain growth (B1/B2/B3 and C1/C2/C3; see Schemes 4 and 5). All proposed reaction steps can be elementary and all intermediates have 18 valence electrons.

**2.1.2.1. Reaction pathways A1, B1 and C1.** Reaction pathways A1, B1 and C1 follow the same reaction sequence, where the C–O bond cleavage occurs on the bridging CO-ligands. Therefore, along reaction pathways B1 and C1, the first step is the transformation of a terminal CO-ligand from compounds **4** and **6** into a bridging CO-ligand. H<sub>2</sub>-addition on the bridging CO reduces it to a bridging Ru-methoxy (**3a**<sup>1</sup>, **5a**<sup>2</sup>, **7a**<sup>2</sup>). The next step is H<sub>2</sub>O desorption with simultaneous H<sub>2</sub>-addition along reaction pathways B1 and C1 and, respectively, CO-adsorption with simultaneous H<sub>2</sub>O desorption along reaction pathway A1 generating a bridging Ru-methylene (**3a**<sup>2</sup>, **5a**<sup>3</sup>, **7a**<sup>3</sup>), which are known compounds [41]. Along pathway A1, the bridging methylene-ligand transforms into a terminal methyldiene ligand, forcing a rearrangement of a terminal carboxyl into a bridging position (**3a**<sup>3</sup>). H<sub>2</sub>-addition on the unsaturated Ru=CH<sub>2</sub> generates the chain starter Ru(CO)<sub>4</sub>(CH<sub>3</sub>)RuH(CO)<sub>4</sub> (**4**). Along reaction pathways B2 and C2 the bridging methylene-ligand shifts directly to a terminal position, generating the Ru-alkyl compounds with longer hydrocarbon chains (**6**, **8**).

**2.1.2.2. Reaction pathways A2, B2 and C2.** The C–O bond cleavage along reaction pathways A2, B2 and C2 is based on the enol mechanism [25–27]. Along pathway A2 an additional step is included,



**Scheme 5.** Reaction pathways C1, C2 and C3 for chain growth in the Fischer–Tropsch synthesis over di-atomic Ru-clusters.

where the Ru-enol (**3b<sup>2</sup>**) is formed over  $\text{H}_2\text{Ru}(\text{CO})_4$  (**3b<sup>1</sup>**) via  $\text{H}_2$ -addition. In mechanisms B2 and C2 the Ru-enol (**5b<sup>1</sup>**, **7b<sup>1</sup>**) is directly generated via hydrogenation of a CO-ligand from the Ru-alkyls **4**, **6**.  $\text{H}_2$ -addition reduces the Ru-enol to a Ru-methoxy (**3b<sup>3</sup>**, **5b<sup>2</sup>**, **7b<sup>2</sup>**). H-shift from a terminal hydrogen to the unsaturated  $\text{Ru}=\text{C}$  of the Ru-methoxy with simultaneous  $\text{H}_2\text{O}$  desorption, yields Ru-methylenes **3b<sup>4</sup>**, **5b<sup>3</sup>** and **7c<sup>3</sup>**. Along pathway A2, a H-atom rearranges to the methylene with a simultaneous CO-adsorption, forming the chain starter **4**. The methylene-ligand inserts into the Ru-alkyl ligand of the adjacent Ru-atom and CO adsorbs along reaction pathways B2 and C2, leading to the formation of the Ru-alkyl compounds **6** and **8**.

**2.1.2.3. Reaction pathways B3 and C3.** CO-insertion in the Ru–C bond of the Ru-alkyl ligand of the compounds **4** and **6** are proposed for reaction pathways B3 and C3. The generated Ru-keto (**5c<sup>1</sup>**, **7c<sup>1</sup>**) is hydrogenated to a Ru-methoxy (**5c<sup>2</sup>**, **7c<sup>2</sup>**),  $\text{H}_2\text{O}$  and CO desorb,  $\text{H}_2$  adsorbs and a Ru-alkylidene (**5c<sup>3</sup>**, **7c<sup>3</sup>**) is generated. H-shift and CO-adsorption on the unsaturated hydrocarbon bond generates, based on the CO-insertion mechanism, the Ru-alkyl species with a hydrocarbon chain length of respectively two (**6**) and three (**8**).

## 2.2. Computational details

To investigate the feasibility of the proposed mechanisms, geometry optimization calculations based on the density functional theory (DFT) were performed on each intermediate. The calculations were done using Materials Studio<sup>®</sup>, employing DFT-GGA (general gradient approximation) as implemented in the DMol code [42,43]. The Ru core,  $[\text{Kr}]5s^2$ , was treated using an effective core potential (ECP) [44,45] and for the valence electrons,  $5p^{14}d^5$ , a double numerical basis set with polarization (DNP) was used. For H, C and O all electrons were included in the calculations. Geometry optimization calculations were done for different multiplicities to investigate the minimum electronic energy,  $E_{\text{elec}}$ . All calculations were performed in the gas phase using the BLYP functional. Stationary points were characterized as local minima by ensuring the absence of imaginary frequencies in the vibrational analysis, which also enabled correction of the electronic energies for zero-point vibrational energies. The energy convergence tolerance was  $2.0 \times 10^{-5}$  Ha, the basis set cut-off radius was 4.3 Å, the maximal force 0.004 Ha/Å, and the maximum displacement 0.005 Å. Electronic smearing was used in cases where the convergence was problematic.

The minimum electronic energies,  $E_{\text{elec}}$ , are static energies at 0K. These results were used to calculate the enthalpy, H, and entropy, S, of each compound extrapolated to other temperatures ( $T=25\text{--}1000$  K) using standard thermo-chemical approximations. The energies reported are at a temperature of 475 K, which is a typical reaction temperature for Ru-based FT synthesis. The amounts of H, C, O and Ru atoms were kept constant for every reaction step and all the surrounding molecules were taken into account in the stability calculation.

## 3. Results and discussion

### 3.1. Validity of the theoretical method

The minimum electronic energy,  $E_{\text{elec}}$ , was calculated for different multiplicities of different species to investigate ground state spin-states and possibilities of spin-crossing during the reaction. However, for all species the lowest spin-state was found to have the lowest energy.

The validation of the theoretical method was performed using the first three compounds of the proposed reaction mechanisms. Four different DFT functionals in the DMol<sup>3</sup> code were tested: BLYP (LYP [46] and B88 NLDA [47]), BP (PW91 [48] and B88 NLDA), PW91 and PBE [49]. The properties investigated were: Ru–C, C–O and Ru–H bond lengths for the known species, IR C–O frequencies for  $\text{Ru}(\text{CO})_5$  and the bond dissociation energy (BDE) for the first reaction step. BLYP and BP appeared to be the most appropriate functionals (see Table 1). The main calculations were therefore performed with the BLYP function.

A similar validation analysis was performed for the diatomic reaction mechanism (data not shown) based on literature data of the starting compound  $\text{Ru}_2(\text{CO})_9$ . Bond lengths and angles were compared with each other, ensuring that the used basis set is also appropriate for this system.

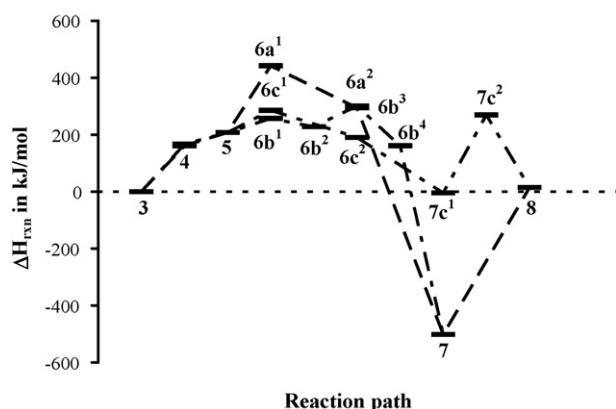
### 3.2. Analysis of reaction pathways over mono-atomic Ru-complexes

Three different reaction pathways are proposed to yield the chain starter (**7**) (see Scheme 2). The numerical calculations have shown that the proposed pathways cover the entire range of possible reaction pathways. Fig. 1 shows the change in the enthalpy

**Table 1**

Calculated (DFT-BLYP) and literature data (experimental and calculated) of the known compounds in the proposed reaction pathway over mono-atomic Ru-complexes

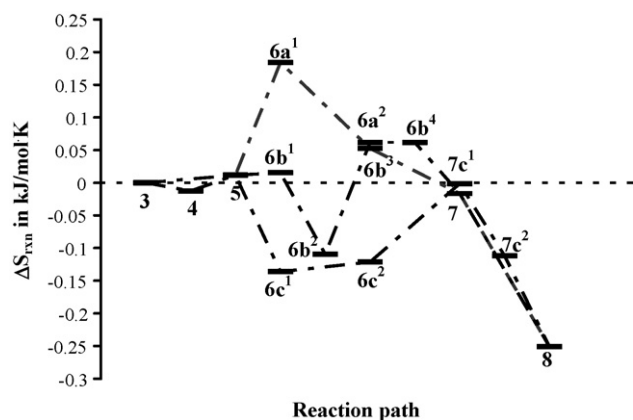
Compound	$\nu_{\text{CO}}$ (cm <sup>-1</sup> )	CO <sub>ax</sub> (Å)	CO <sub>eq</sub> (Å)	Ru–C <sub>ax</sub> (Å)	Ru–C <sub>eq</sub> (Å)	Ru–H (Å)	BDE (kJ/mol)
Ru(CO) <sub>5</sub>	2001/2017.8	1.154	1.159	1.978	1.977		118.72 <sup>a</sup>
		1.142	1.147	1.950	1.969		115.56 [19]
	1999/2035			1.95	1.96		[21]
				1.943	1.952		[18]
				1.162	1.165	1.987	1.971
Ru(CO) <sub>4</sub>		1.160	1.159	1.996	1.957		a
		1.161	1.171	1.951	1.904		[20]
		1.160	1.164	1.987	1.971		[23]
H <sub>2</sub> Ru(CO) <sub>4</sub>		1.152	1.151	1.965	1.998	1.652	a
		1.149	1.150	1.950	1.988	1.651	[24]

<sup>a</sup> This study.**Fig. 1.** Enthalpy of reaction,  $\Delta H_{\text{rxn}}$ , in kJ/mol for the different intermediates proposed along the reaction pathways A, B and C over mono-atomic Ru-clusters at 475 K.

relative to the enthalpy of the starter of the catalytic chain, H<sub>2</sub>Ru(CO)<sub>4</sub> (**3**), and the change in the entropy of the three proposed reaction pathways is shown in Fig. 2.

### 3.2.1. Formation of the starter of the catalytic chain

The formation of the starter of the catalytic chain is thermodynamically not favoured. Especially, CO-dissociation from Ru(CO)<sub>5</sub> to 16 valence electron species Ru(CO)<sub>4</sub> is highly unfavoured (at 475 K:  $\Delta H_{\text{rxn}} = 120$  kJ/mol;  $\Delta G_{\text{rxn}} = 47$  kJ/mol). The postulated consecutive formation of the starter of the catalytic chain, H<sub>2</sub>Ru(CO)<sub>4</sub>,

**Fig. 2.** Entropy of reaction,  $\Delta S_{\text{rxn}}$ , in kJ/molK for the different intermediates proposed along the reaction pathways A, B and C over mono-atomic Ru-clusters at 475 K.

from Ru(CO)<sub>4</sub> is exothermic (at 475 K:  $\Delta H_{\text{rxn}} = -85$  kJ/mol;  $\Delta G_{\text{rxn}} = -18$  kJ/mol). However, the overall generation of the starter of the catalytic chain from Ru(CO)<sub>5</sub> is not favoured.

### 3.2.2. Formation of the chain starter

All proposed reaction pathways require the formation of the Ru-enol species (**5**) from the starter of the catalytic cycle (**3**) over a Ru-aldehyde species (**4**) via tautomerisation. Both reactions are endothermic ( $\Delta H_{\text{rxn}} = 63$  kJ/mol) and entropically demanding ( $\Delta S_{\text{rxn}} = -135$  J/molK) making the reactions thermodynamically not favoured.

### 3.2.3. Reaction pathway A

The formation of an intermediate Ru–C species (**6a**<sup>1</sup>) as postulated along reaction pathway A is highly endothermic ( $\Delta H_{\text{rxn}} = 441$  kJ/mol). Furthermore, the transformation of the Ru-enol species (**5**) into the Ru–C species is not expected to be an elementary reaction step, due to the complexity of the reaction. Thus, the formation of this carbide analogue is highly unlikely. The hydrogenation of this ‘carbide’-intermediate yielding H<sub>2</sub>RuCH<sub>2</sub>(CO)<sub>3</sub> (**6a**<sup>2</sup>) is also endothermic. The consecutive formation of the chain starter HRu(CO)<sub>4</sub>CH<sub>3</sub> (**7**) is highly exothermic.

### 3.2.4. Reaction pathway B

Along reaction pathway B the Ru-enol species (**5**) is converted in an endothermic reaction ( $\Delta H_{\text{rxn}} = 256$  kJ/mol) into H<sub>2</sub>Ru(CO)<sub>3</sub>(CHOH) (**6b**<sup>1</sup>), followed by a slightly less endothermic H<sub>2</sub>-addition ( $\Delta H_{\text{rxn}} = 227$  kJ/mol), generating H<sub>3</sub>Ru(CO)<sub>3</sub>(CH<sub>2</sub>OH) (**6b**<sup>2</sup>). H<sub>2</sub>O desorption leads to the formation of H<sub>2</sub>Ru(CO)<sub>3</sub>CH<sub>2</sub> (**6b**<sup>3</sup>) ( $\Delta H_{\text{rxn}} = 300$  kJ/mol). The formation of the 16 valence electron transition-state species **6b**<sup>4</sup> is less endothermic ( $\Delta H_{\text{rxn}} = 160$  kJ/mol). This transition-state species adsorbs another CO to form the chain starter (**7**) ( $\Delta H_{\text{rxn}} = -500$  kJ/mol), making the overall conversion of the starter of the catalytic cycle (**3**) into species **7** highly exothermic. The formation of the chain starter (**7**) via the different intermediates, which can be generated in elementary reaction steps along reaction pathway B, does not seem to be thermodynamically favoured due to high expected activation energies of larger than 250 kJ/mol.

### 3.2.5. Reaction pathway C

The C–O bond cleavage in the Ru-enol species (**5**) yielding a Ru-methylene intermediate (**6c**<sup>2</sup>) as proposed for reaction pathway C is endothermic ( $\Delta H_{\text{rxn}} = 189$  kJ/mol). The Ru-methylene intermediate forms via a Ru-alkoxy species (**6c**<sup>1</sup>) ( $\Delta H_{\text{rxn}} = 285$  kJ/mol), possibly via elementary reaction steps. It should however be noted that the formation of **6c**<sup>1</sup> is highly endothermic.

Starting from **6c**<sup>3</sup>, chain growth was also proposed by avoiding the highly exothermic formation of the chain starter **7**.

H<sub>2</sub>-activation leads to **7c**<sup>1</sup> in a slightly exothermic reaction. **7c**<sup>1</sup> tautomerises into **7c**<sup>2</sup>, before generating HRu(CO)<sub>4</sub>COCH<sub>3</sub> (**8**) by shifting the enol-ligand in the methylene group. The tautomerisation of complex **7c**<sup>1</sup> into **7c**<sup>2</sup> is again highly endothermic ( $\Delta H_{\text{rxn}} = 285$  kJ/mol).

### 3.2.6. Discussion of reaction pathways over mono-atomic Ru-complexes

From a thermodynamic point of view reaction pathways B and C involve reaction intermediates with the lowest energy. Both proposed reaction pathways invoke reaction steps which may occur stepwise on a single Ru-atom as an elementary reaction step. However, these elementary reaction steps also involve the formation of 16 valence electron intermediates. Some of the reaction steps require reaction energies of >200 kJ/mol. This means that the activation barrier for these reaction steps is expected to be at least 200 kJ/mol. Hence, the formation of the chain starter and thus FT synthesis on a mono-atomic Ru centre is not feasible. The formation of H<sub>2</sub>Ru(CO)<sub>3</sub>(CHOH) (**6b**<sup>1</sup>) requires the least amount of energy and could be feasible at high reaction temperatures. However, the step to generate species **6b**<sup>4</sup> is not feasible with a reaction energy of >300 kJ/mol.

From H<sub>2</sub>Ru(CO)<sub>3</sub>(CHOH) (**6b**<sup>1</sup>) desorption of methanol CH<sub>3</sub>OH or formaldehyde CH<sub>2</sub>O is thermodynamically favoured. The reverse reaction to generate the Ru-enol species (**4**) is highly endothermic and thermodynamically not favoured. This is in agreement with the experimental findings of Keim et al. [11]. The C<sub>2</sub>-alcohols and aldehydes, observed in the polar solvent NMP, are not likely to be formed from the reaction sequence analogue to the Fischer–Tropsch synthesis. The formation is likely to take place via hydroformylation in the solvent under these high temperatures and pressures, which is a well-known reaction on single metal atoms.

### 3.3. Analysis of reaction pathways over di-atomic Ru-complexes

All possible reaction intermediates (subject to the outlined constraints) were investigated for mono-atomic Ru-clusters. The large amount of possible clusters over di-atomic Ru-clusters rendered this approach not feasible. Thus, complexes were chosen to mimic postulated intermediates in heterogeneous Fischer–Tropsch catalysis.

#### 3.3.1. Generation of the chain starter

Two different reaction pathways (mechanism A1 and A2 in Scheme 3) are proposed for the generation of the chain starter Ru(CO)<sub>4</sub>CH<sub>3</sub>RuH(CO)<sub>4</sub> (**4**). The change in enthalpy relative to the

change in enthalpy of the starter of the catalytic chain, Ru(CO)<sub>4</sub>( $\mu$ -CO)RuH<sub>2</sub>(CO)<sub>4</sub> (**2**),  $\Delta H_{\text{rxn}}$ , is illustrated in Fig. 3.

#### 3.3.2. Reaction pathway A1

Along reaction pathway A1 all intermediates contain bridging C-ligands. The formation of the bridging Ru-alkoxy (**3a**<sup>1</sup>) via activation of hydrogen on one Ru-centre is slightly endothermic ( $\Delta H_{\text{rxn}} = +35$  kJ/mol). The transformation of **3a**<sup>1</sup> into the bridging Ru-alkyl (**3a**<sup>2</sup>) is exothermic ( $\Delta H_{\text{rxn}} = -90$  kJ/mol), followed by a slightly endothermic tautomerisation ( $\Delta H_{\text{rxn}} = +40$  kJ/mol) to the terminal methylene ligand on one Ru and a bridging CO-ligand (**3a**<sup>3</sup>) between the two. However, the energy difference between the local minimum **3a**<sup>2</sup> and species **3a**<sup>3</sup> is relatively high and the thermodynamic feasibility is questionable. The generation of the chain initiator (**4**) requires only the activation of a H<sub>2</sub>-molecule and releases a large amount of energy ( $\Delta H_{\text{rxn}} = -170$  kJ/mol) making it thermodynamically very favoured. The energetic barriers of all these reaction steps are below typical FT activation energies of 100–120 kJ/mol, making the overall generation of the chain initiator over a di-atomic Ru-cluster along reaction pathway A1 thermodynamically feasible.

#### 3.3.3. Reaction pathway A2

In comparison to reaction pathway A1, reaction pathway A2 contain no bridging intermediates. The starter of the catalytic chain (**2**) transforms exothermically into the dihydrido-Ru species **3b**<sup>1</sup> ( $\Delta H_{\text{rxn}} = -50$  kJ/mol). The next reaction step to the Ru-enol (**3b**<sup>2</sup>) is, however, energetically more demanding with  $\Delta H_{\text{rxn}}$  of +50 kJ/mol. H<sub>2</sub>-addition to generate **3b**<sup>3</sup> is slightly endothermic ( $\Delta H_{\text{rxn}} = +5$  kJ/mol), whereas the H<sub>2</sub>O desorption step to the Ru-methylene (**3b**<sup>4</sup>) and the generation of the chain initiator (**4**) are both exothermic reactions ( $\Delta H_{\text{rxn}} = -50$  kJ/mol and  $\Delta H_{\text{rxn}} = -150$  kJ/mol). This reaction sequence does not include a local minimum as was observed for reaction pathway A1.

#### 3.3.4. Chain growth

Starting from the chain initiator **4** 3 different reaction mechanisms are proposed for the generation of the chain growth species Ru(CO)<sub>4</sub>CH<sub>2</sub>CH<sub>3</sub>RuH(CO)<sub>4</sub> (**6**). Fig. 4 shows the enthalpy of reaction relative to the enthalpy of reaction for the formation of the starting compound of the catalytic cycle **2**,  $\Delta H_{\text{rxn}}$ , for the different intermediates proposed in mechanisms B1, B2 and B3 (see Scheme 4) at a reaction temperature of 475 K.

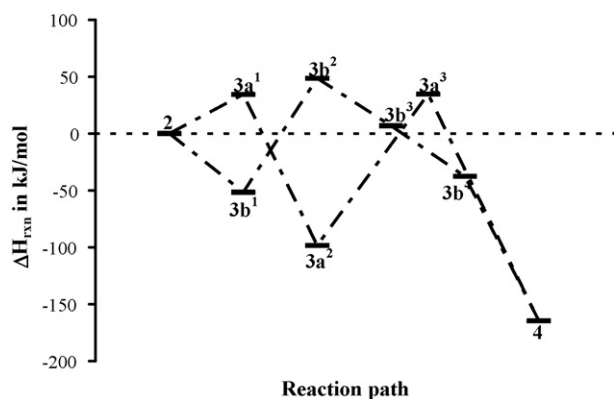


Fig. 3. Enthalpy of reaction,  $\Delta H_{\text{rxn}}$ , in kJ/mol for the different intermediates proposed along the reaction pathways A1 and A2 over diatomic Ru-cluster leading to the generation of the chain initiator at 475 K.

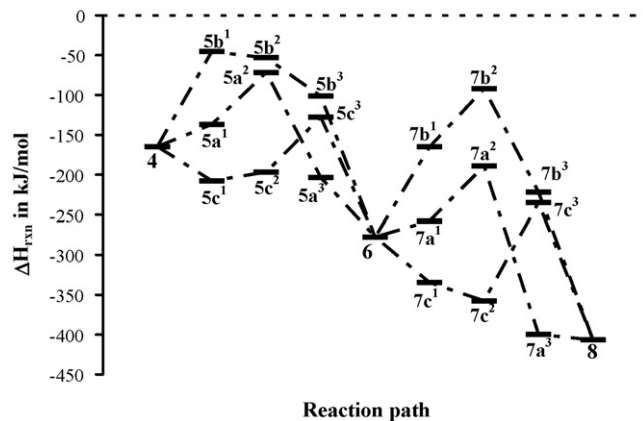


Fig. 4. Enthalpy of reaction,  $\Delta H_{\text{rxn}}$ , in kJ/mol for the different intermediates proposed along the reaction pathway over diatomic Ru-clusters for the first step of chain growth (mechanisms B1, B2 and B3) and second step of chain growth (mechanisms C1, C2 and C3) at 475 K.

### 3.3.5. Reaction pathway B1

Along reaction pathway B1 the generation of the methylene group occurs at the bridging ligand (see Scheme 4). The shift of a terminal CO-ligand from the chain initiator **4** into a bridging position forming **5a<sup>1</sup>**, is exothermic ( $\Delta H_{\text{rxn}} = -140$  kJ/mol), followed by a lower energy releasing H<sub>2</sub>-activation to the bridging Ru-enol intermediate **5a<sup>2</sup>** ( $\Delta H_{\text{rxn}} = -70$  kJ/mol). The H<sub>2</sub>-addition and H<sub>2</sub>O desorption to **5a<sup>3</sup>** releases heat, having a  $\Delta H_{\text{rxn}}$  value of  $-200$  kJ/mol. Finally, the generation of the chain growth species **6** is even more exothermic with  $\Delta H_{\text{rxn}}$  of  $-260$  kJ/mol.

### 3.3.6. Reaction pathway B2

The chain growth, as proposed along reaction pathway B2, follows a non-bridging methylene mechanism, starting from the slightly exothermic formation of the terminal Ru-enol intermediate **5b<sup>1</sup>** ( $\Delta H_{\text{rxn}} = -50$  kJ/mol). H<sub>2</sub>-activation from **5b<sup>1</sup>** to **5b<sup>2</sup>** releases a small amount of energy, having a  $\Delta H_{\text{rxn}}$  value of  $-55$  kJ/mol, followed by the H<sub>2</sub>O desorption step to the terminal Ru-methylene **5b<sup>3</sup>**, which is slightly more exothermic ( $\Delta H_{\text{rxn}} = -85$  kJ/mol). The formation of the Ru-ethyl **6** releases 260 kJ/mol (as already described for reaction pathway B1).

### 3.3.7. Reaction pathway B3

The first postulated step along reaction pathway B3, CO-adsorption and simultaneous insertion in the Ru-CH<sub>3</sub>-bond, generating **5c<sup>1</sup>** is a highly exothermic ( $\Delta H_{\text{rxn}} = -210$  kJ/mol). The reduction via H<sub>2</sub>-addition to the Ru-alkoxyl (**5c<sup>2</sup>**) is slightly less exothermic ( $\Delta H_{\text{rxn}} = -200$  kJ/mol). The transformation of the Ru-alkoxyl species to the Ru-ethylene (**5c<sup>3</sup>**) is not expected to be an elementary reaction step, due to the complexity of the reaction. The last step requires a H-shift and a CO-activation leading to the formation of the chain growth species **6** as already described for reaction pathways B1 and B2.

### 3.3.8. Further chain growth

For the second part of the chain growth, leading to the formation of the Ru-propyl species **8**, three different reaction mechanisms, respectively mechanisms C1, C2 and C3, already described for the formation of the Ru-ethyl species **6**. The enthalpies of reaction for these different reactions show the same trend, whereas these reactions are more exothermic in comparison to the first part of chain growth. The origin of this trend is the typical product distribution for FT synthesis, namely that adsorbed longer chain hydrocarbons are more stable than shorter ones.

### 3.3.9. Discussion of reaction pathways over di-atomic Ru-complexes

For the generation of the chain starter **4** both proposed reaction pathways, viz. A1 and A2, are thermodynamic feasible with a minimum required activation energy of 50 kJ/mol. All proposed intermediates have 18 valence electrons and their formation may occur via elementary reaction steps. Reaction pathway A1 is energetically slightly favoured over reaction pathway A2. However, the formation of **3a<sup>2</sup>** is in a local minimum, making mechanism A2 the preferred reaction pathway.

Reaction pathways B3 and C3 (both based on the CO-insertion mechanism [50–52]) seem to be the thermodynamic most feasible reaction pathways for hydrocarbon chain growth on a diatomic Ru-complex. However, all three proposed reaction pathways are thermodynamically feasible. The formation of all intermediates is exothermic. It has to be mentioned that with increase of chain length of the alkyl species on the Ru-complex, the stability of the compounds increases.

## 4. Conclusions

Different proposed reaction pathways to investigate the thermodynamic feasibility of FT reactions over mono- and di-atomic Ru-complexes as model catalysts were analysed in terms of the thermodynamic feasibility.

By comparing the theoretically calculated reaction enthalpies with known FT activation energies [15] it was shown that the C–O bond cleavage on a single Ru centre is thermodynamically not feasible. It requires more energy ( $>200$  kJ/mol) than the typical FT activation energy of 100–120 kJ/mol [15]. Furthermore, some of the proposed reaction steps cannot be elementary reaction steps. Therefore, it is concluded that formation of the chain initiator cannot occur on a mono-atomic Ru-centre. Thus, the Fischer–Tropsch synthesis cannot take place over a mono-atomic Ru-centre.

Calculations on different proposed reaction pathways over di-atomic Ru-clusters showed lower enthalpies, making the formation of the chain initiator thermodynamically feasible. The formation of reaction intermediates during chain growth is increasingly exothermic towards longer hydrocarbon chains. This is a known effect in product formation in the Fischer–Tropsch synthesis. Whereas all proposed reaction mechanisms, viz. the enol, the methylene and the CO-insertion mechanism, are thermodynamically feasible, the CO-insertion mechanism seems to be the most preferred one.

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