

Carbon Chain Growth by Sequential Reactions of CO and CO₂ with [W(CO)₆] and an Aluminium(I) Reductant

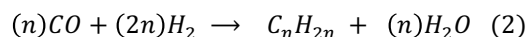
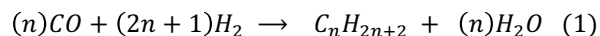
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Supporting Information Placeholder

ABSTRACT: The formation of carbon chains by the coupling of CO_x (X = 1 or 2) units on transition metals is a fundamental step relevant to Fischer-Tropsch catalysis. Fischer-Tropsch catalysis produces energy dense liquid hydrocarbons from synthesis gas (CO and H₂) and has been a mainstay of the energy economy since its discovery nearly a century ago. Despite detailed studies aimed at elucidating the steps of catalysis, experimental evidence for chain growth (C_n → C_{n+1}; n ≥ 2) from the coupling of CO units on metal complexes is, to the best of our knowledge, unprecedented. In this paper, we show that carbon chains can be grown from sequential reactions of CO or CO₂ with a transition metal carbonyl complex. By exploiting the cooperative effect of transition and main group metals, we document the first example of chain propagation from sequential coupling of CO units (C₁ → C₃ → C₄), along with the first example of incorporation of CO₂ into the growing carbon chain.

Chemical methods to convert CO and CO₂ to liquid hydrocarbons are of paramount societal, environmental, and economic importance. One such method applied on vast industrial scales is the Fischer-Tropsch (F-T) process.^{1,2} The F-T process converts mixtures of CO and H₂ to short-chain hydrocarbons under modest temperatures and pressures and can be considered as a controlled polymerisation and hydrogenation of CO. The primary reaction products are short to medium chain alkanes (Eq. 1) and alkenes (Eq. 2) that form alongside smaller amounts of hydrocarbon oxygenates.



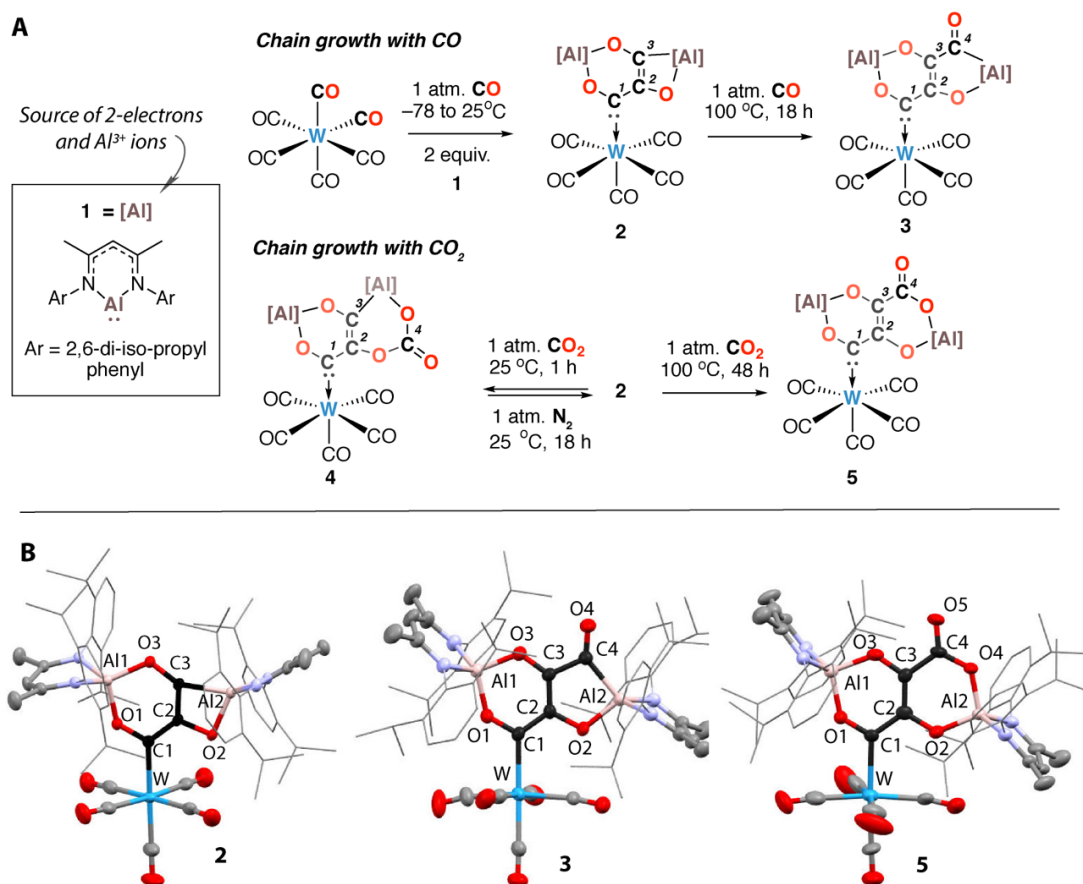
Modern variants of F-T processes are used in the liquefaction of methane, coal and biomass.^{3,4} More recently, as a step toward the remediation of anthropogenic CO₂, there has been increasing interest in F-T processes that incorporate CO₂ rich gas-feeds.^{5,6}

Although F-T technology is nearly a century old, little is known about the fundamental reactions involved in chain growth. Heterogeneous catalysts are typically comprised of a transition metal (e.g. Co, Fe, Ru or Ni), a chemical promoter (e.g. K₂O), and a chemically innocent structural material (e.g. SiO₂, Al₂O₃ or MgO). Surface bound transition metal carbonyls have been identified as reaction intermediates and growth of the carbon chain occurs in an environment rich in electropositive main group ions.^{7,8}

One approach used to gain insight into F-T catalysis has been to use homogeneous complexes to model the heterogeneous reactions. Studies centred on the reaction of CO with metal complexes have provided some notable results. Coupling of CO to form C₂ units has been observed to occur by double insertion of CO into transition metal–element bonds,^{9–11} or by reductive coupling of two metal-bound CO ligands.^{12–14} The homologation of CO to form either open-chain or cyclic C₃, C₄, C₅ and C₆ units has been reported for a series of actinide,^{15–20} lanthanide,^{21–23} and transition metal hydride complexes.²⁴ Despite advances in this area, there are clear limitations of the homogeneous models. Chain growth in which an isolable C_n isomer is converted to a C_{n+1} isomer (n ≥ 2) has yet to be experimentally verified. Very few of the models exploit the cooperative behaviour of main group and transition metal elements known to be important in commercial F-T catalysts,²³ and none show that CO₂ can be incorporated into growing chains.

Here we report carbon chain growth from C₁ to C₃ to C₄ by sequential reactions of CO and CO₂ with a transition metal carbonyl complex in the presence of the aluminium(I) complex **1** (Fig. 1). This latter species acts as a surrogate for both H₂ and the promoters in F-T catalysis, providing both reducing equivalents (2 electrons) and electropositive main group ions. Mechanistic analysis shows that, the Al³⁺ ions not only coordinate to and stabilise the growing carbon chain, but also act as a reactive site for chain propagation. These experiments provide unprecedented insight into chain growth reactions relevant to F-T catalysis and shed new light on the potential roles of main group promoters.

Figure 1. (a) Carbon chain growth by sequential reactions of CO and CO₂ with [W(CO)₆] and **1**. (b) Solid-state structures of **2**, **3** and **5** (50% probability displacement ellipsoid).



Warming a frozen suspension of [W(CO)₆] and 2 equiv. of **1** under 1 atm. of CO from -78 °C to 25 °C in benzene solvent leads to the formation of the C₃ homologated product **2** (Fig. 1). Heating an isolated and purified sample of **2** under 1 atm. of CO for a further 18 h at 100 °C leads to the formation of **3** a chain growth product (Fig. 1). Chain growth of the C₃ to a C₄ fragment could also be achieved upon reaction of **2** with 1 atm. of CO₂. While the reaction of CO₂ with **2** at 25 °C initially forms **4**, this kinetic product is not stable. The isolation and structural characterisation (supporting information, Fig. S9) of **4** is amenable through its low solubility in benzene solution, and this product crystallises directly from the reaction mixture. Upon dissolution of isolated samples of **4** in either C₆D₆ or d₈-THF at 25 °C under an atmosphere of N₂, complex **2** and CO₂ are reformed. At higher temperatures, **4** rearranges to the thermodynamic product **5** (Fig. 1). These experiments represent the first example of defined chain growth from reactions of CO with a transition metal carbonyl complex and the first example in which chain growth in F-T models occurs by insertion of CO₂ into an existing carbon chain.

No reaction occurs between **1** and CO in the absence of [W(CO)₆] and mixing of **1** and [W(CO)₆] in the absence of CO leads to mixtures that contain **2** (see supporting information for further details).

Complexes **2-5** have been crystallographically characterised and all contain a {W(CO)₃} fragment coordinated to either a C₃ or C₄ chain comprised of CO or CO/CO₂ units stitched together to form carbon-carbon bonds. The bond lengths and angles of the main group fragments of **2-5** are consistent with assignment of an aluminium +3 oxidation state (supporting information, Table S1) and support electron transfer from aluminium to the carbon chain to form either {C₃O₃}⁴⁺, {C₄O₄}⁴⁺ or {C₄O₃}⁴⁺ units. The chain acts as a ligand for two Al³⁺ centres forming both C,O-chelates and O,O-chelates. Chain growth occurs with the ring expansion of the bicyclic structure with **2**, **3** and **4/5** containing [4,6], [5,6] and [6,6] *ortho*-fused rings respectively. In all cases the origin of carbon chain, C1, is bound to tungsten as a carbene ligand. The W-C1 bond lengths are similar across the series and range from 2.196(3) – 2.24(1) Å, suggesting variation of the chain length has little effect on the nature of the tungsten-carbene interaction (supporting information, Table S2).

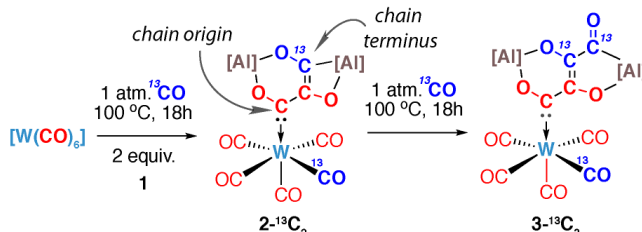
Bond lengths and angles within the growing carbon chain of **2-5** may be compared. The carbon atoms of the chain are close to sp²-hybridised with the sum of the bond angles approaching 360°. The carbon-carbon bond lengths are consistent with a framework that contains alternating single and double bonds (supporting information, Fig. S10). For example, the C1-C2 and C2-C3 bond lengths in **2** are 1.437(4)

and 1.379(4) Å respectively while those in **3** are 1.458(5) and 1.396(5) Å respectively. Both are shorter than the C3–C4 bond length of 1.507(6) Å. Comparison of these data against C–C and C=C distances for sp^2 -hybridised carbon atoms reveals some deviation from the idealised bond lengths and suggests that the localised resonance structure is at best a first approximation. Nevertheless, the carbon–oxygen bond lengths are also consistent with this assignment and range from approximately 1.3 – 1.4 Å for the single bonds of **2–5** but are considerably shorter for the C4–O4 and C4–O5 carbonyl units of **3** and **5** taking values of 1.233(5) and 1.20(1) Å respectively. There is a notable exception to the trends discussed above. The C2–O2 length of the four-membered ring of **2** is longer than expected at 1.409(3) Å. In combination with the long Al2–C3 bond length of 1.982(3) Å and acute C3–Al2–O bond angle of 74.1(1)°, suggests that the four-membered metallacycle of **2** contains significant ring strain.

The isolation and characterisation of a series of intermediates in carbon chain growth processes relevant to F-T chemistry offers an unprecedented opportunity to study the mechanism of carbon–carbon bond formation. A series of isotopic labelling experiments were conducted with ^{13}CO and $^{13}\text{CO}_2$ gases (Figure 2). These reactions showed that the first two carbon units of the chain, C1 and C2, are derived from the transition metal carbonyl fragment, while the second two units, C3 and C4, originate from either gaseous CO or CO_2 . Hence, reaction of **1** with $[\text{W}(^{12}\text{CO})_6]$ in the presence of ^{13}CO forms labelled samples of **2**- $^{13}\text{C}_2$ with isotopic enrichment at the chain terminus (C3) and the *cis*-position of the transition metal complex as evidenced by ^{13}C NMR spectroscopy. Isotopic enrichment of the transition metal carbonyl fragment is consistent with a mechanism in which following initiation of chain growth, any coordination sites which ^{12}CO vacates are occupied by external ^{13}CO . Reaction of **2**- $^{13}\text{C}_2$ with ^{13}CO

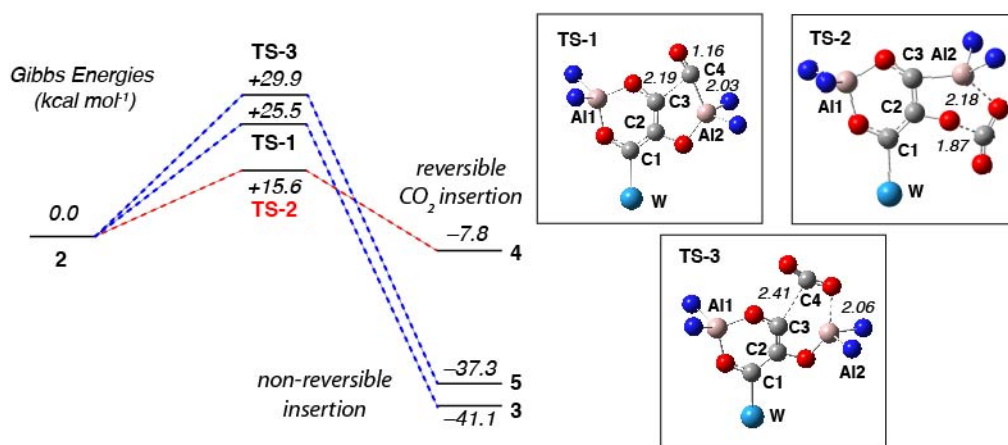
forms **3**- $^{13}\text{C}_3$ with ^{13}C enrichment at the C4 position. The source of each carbon atom in the chain was unambiguously confirmed by performing a series of reactions with $[\text{W}(^{13}\text{CO})_6]$ and **1** in the presence of ^{12}CO and further experiments showed that $^{13}\text{CO}_2$ also reacts at the chain terminus of **2** (supporting information, Fig S2-7).

Figure 2. Isotopic labelling experiments.



The mechanistic insight gained from these experiments was further supported by density functional theory (DFT) calculations. The formation of **3** by insertion of CO into the Al–C bond of the strained four-membered ring of **2** is calculated to proceed by a moderate energy transition state **TS-1** ($\Delta G^\ddagger = +25.5$ kcal mol $^{-1}$) and is highly exergonic ($\Delta G^\circ = -41.1$ kcal mol $^{-1}$). The aluminium ion is essential for carbon–carbon bond formation. **TS-1** involves the direct coordination of CO to aluminium through a donor-acceptor interaction. The precedent for the insertion of CO into Al–C bonds is limited to either the reaction of $[\text{Al}(\text{tBu})_3]$ or a strained metallocyclopropene complex.^{25, 26} Similarly, the formation of **4** ($\Delta G^\ddagger = +15.6$ kcal mol $^{-1}$, $\Delta G^\circ = -7.8$ kcal mol $^{-1}$) and **5** ($\Delta G^\ddagger = +29.9$ kcal mol $^{-1}$, $\Delta G^\circ = -37.3$ kcal mol $^{-1}$) were calculated to occur by the formation of **TS-2** and **TS-3** respectively. The coordination of the oxygen atom of CO_2 to aluminium appears crucial the formation of both **TS-2** and **TS-3**. The calculations are consistent with the reversible formation of **4** and its ultimate conversion to the more thermodynamically stable product **5** (Figure 3).²⁷

Figure 3. DFT calculations on the reaction of **2** with CO and CO_2 . Inserts – truncated transition states for chain growth by insertion of CO (**TS-1**) or CO_2 (**TS-2** and **TS-3**) with annotated bond distances (Å).



These calculations show that chain growth through insertion reactions of either CO or CO₂ into the Al–C and Al–O bonds of **2** are feasible under the experimental conditions. The relief of ring strain undoubtedly provides a thermodynamic driving force for chain growth at the terminus. Our work establishes not only that chain growth is possible from reactions of CO or CO/CO₂ with a transition metal carbonyl complex, but that Al³⁺ ions can act as both structural supports and reactive sites for chain propagation.

ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic data for **2–5** are available from the Cambridge Crystallographic Data Centre (CCDC 1860655–1860658) and as a .cif file, full details of the experiments and calculations are available as a .pdf. This material is available free of charge via the internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

The authors declare no financial conflicts.

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- A plausible alternative pathway to form **3**, involving migratory insertion of CO at the tungsten centre of **2** was identified. Not only is this pathway inconsistent with the isotopic labelling experiments, the key transition state ($\Delta G^\ddagger = 43 \text{ kcal mol}^{-1}$) was calculated to be considerably higher in energy than **TS-1** precluding its involvement in chain growth.

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