Carbon Chain Growth by Sequential Reactions of CO and CO$_2$ with a Transition Metal Carbonyl Complex

Richard Y. Kong and Mark R. Crimmin

Department of Chemistry, Imperial College London, South Kensington, London, SW7 2AZ, UK.

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 H$_2$) 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 ($C_n \rightarrow C_{n+1}$; $n \geq 2$) from the reaction of CO with metal complexes is unprecedented. In this paper, we show that carbon chains can be grown from sequential reactions of CO or CO$_2$ 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 ($C_1 \rightarrow C_3 \rightarrow C_4$), along with the first example of incorporation of CO$_2$ into the growing carbon chain.

Introduction

Chemical methods to convert CO and CO$_2$ 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 H$_2$ 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.

\[
(n)CO + (2n + 1)H_2 \rightarrow C_nH_{2n+2} + (n)H_2O \quad (1)
\]

\[
(n)CO + (2n)H_2 \rightarrow C_nH_{2n} + (n)H_2O \quad (2)
\]

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 CO$_2$, there has been increasing interest in F-T processes that incorporate CO$_2$ 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 (K₂O), and chemically innocent structural material (e.g. SiO₂, Al₂O₃ or MgO). Surface bound transition metal carbonyls have been identified as reaction intermediates and growth 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 Cₙ isomer is converted to a Cₙ₊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.

Results and Discussion

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 CO\textsubscript{2}. While the reaction of CO\textsubscript{2} with 2 at 25 \degree C initially forms 4, this kinetic product is not stable. The isolation and structural characterisation (supporting information, Fig. S8) 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 C\textsubscript{6}D\textsubscript{6} or d\textsubscript{8}-THF at 25 \degree C under an atmosphere of N\textsubscript{2}, complex 2 and CO\textsubscript{2} 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 CO\textsubscript{2} into an existing carbon chain.

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

Complexes 2-5 have been crystallographically characterised and all contain a \{W(CO)\textsubscript{5}\} fragment coordinated to either a C\textsubscript{3} or C\textsubscript{4} chain comprised of CO or CO/CO\textsubscript{2} 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 \( \{C_3O_3\}^{4-}, \{C_4O_4\}^{4-} \) or \( \{C_4O_5\}^{4-} \) units. The chain acts as a ligand for two Al\(^{3+}\) 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 sp\(^2\)-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. S9). 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 \(^{13}\)CO\(_2\) gases. 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 [W(\(^{12}\)CO)\(_6\)] in the presence of \(^{13}\)CO forms labelled samples of 2-\(^{13}\)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-\(^{13}\)C\(_2\) with \(^{13}\)CO forms 3-\(^{13}\)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 $[W^{13}\text{CO}_6]$ and 1 in the presence of $^{12}\text{CO}$ and further experiments showed that $^{13}\text{CO}_2$ also reacts at the chain terminus of 2 (supporting information, Fig S2-7).

**Figure 2.** (a) Isotopic labelling experiments. (b) 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) into the chain terminus with annotated bond distances (Å).

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 a reaction of $[\text{Al}^{i\text{Bu}}_3]^{25,26}$ 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. These calculations show that chain growth through insertion reactions of either CO or CO$_2$ 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/CO\(_2\) with a transition metal carbonyl complex, but that Al\(^{3+}\) ions can act as both structural supports and reactive sites for chain propagation.

References


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 (ΔG‡ = 43 kcal mol⁻¹) was calculated to be considerably higher in energy than TS-1 precluding its involvement in chain growth.

**Supplementary Information**

Is available in the online version of the paper.

**Acknowledgements**

We are grateful to the Royal Society for provision of a University Research Fellowship (MRC) and the ERC (FluoroFix: 677367) for generous funding. We thank Imperial College London for the award of a President’s Scholarship (RYK).

**Author contributions**

R. Y. K. contributed all experimental and computational work including the synthetic chemistry, the isotope labelling experiments, the X-ray crystallography and the DFT calculations. M.R.C directed the project. Both authors contributed intellectually to the project and to the writing of the manuscript.
Author Information

X-ray crystallographic data for 2-5 are available from the Cambridge Crystallographic Data Centre (CCDC 1860655-1860658). The authors declare no competing financial interests. Correspondence and requests for materials should be addressed to M.R.C. (m.crimmin@imperial.ac.uk).