Selective Coupling of Methylene Units in a Rh/Os Complex To Give Either C₃ or C₄ Fragments

Steven J. Trepanier, Brian T. Sterenberg, Robert McDonald,[‡] and Martin Cowie*
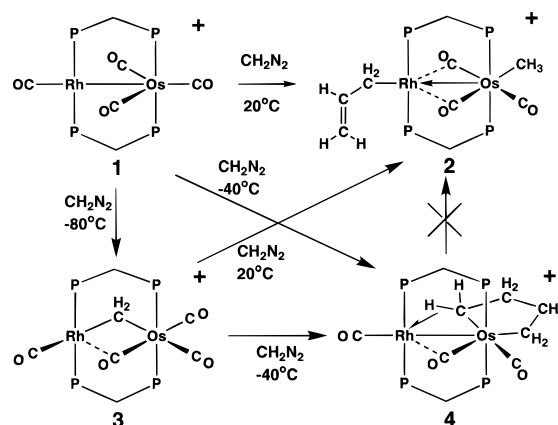
Department of Chemistry, University of Alberta Edmonton, AB, Canada T6G 2G2

Despite the industrial successes of the Fischer−Tropsch (FT) reaction[1] since its discovery over 75 years ago,[2] the process is still not well understood and its lack of selectivity continues to be a drawback. Although there is general agreement that the reaction is a result of the stepwise polymerization of methylene groups,[3] a number of mechanisms have been proposed, the most prominent of which involve the following: the direct polymerization of methylene units (Fischer and Tropsch),[2] the coupling of methylene and alkyl fragments (Pettit, Biloen, et al.),[4] and the coupling of methylene and vinyl groups (Maitlis et al.).[5] The observation that even within the closely related group 8 and 9 transition-metal catalysts the different metals give substantially different products and product distributions[6] suggested to us that some control over product distributions might be achieved by the use of *combinations* of these metals. In this communication we report results of model studies on a diphosphine-bridged RhOs complex, in which the facile coupling of methylene units (originating from diazomethane) occurs, yielding selectively either C₃ or C₄ fragments bound to the metals.

The mixed-metal complex [RhOs(CO)₄(dppm)₂][BF₄] (**1**)[7] (dppm = Ph₂PCH₂PPh₂) reacts with excess diazomethane at ambient temperature yielding essentially quantitatively [RhOs-(η¹-CH₂CH=CH₂)(CH₃)(CO)₃(dppm)₂][BF₄] (**2**),[8] in which the allyl group is η¹-bound to Rh and the methyl group is bound to Os (see Scheme 1). Compound **2** (as the triflate salt) has been prepared independently by the reaction of the η³-allyl complex [RhOs(η³-C₃H₅)(CO)₃(dppm)₂][9] with methyl triflate and has very similar spectral parameters to a number of related vinyl/methyl species, one of which was characterized by an X-ray structure.[9] The η¹ bonding mode of the allyl ligand is established by NMR spectroscopy for which the ¹H NMR spectrum shows ³¹P coupling of the Rh-bound phosphines to only the α-hydrogens, and the ¹³C{¹H} NMR spectrum also shows Rh coupling (23.5 Hz) to only the α-carbon. In addition, the methyl group is identified as

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‡ Faculty Service Officer, Structure Determination Laboratory.

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(8) Spectroscopic data for **2**: ¹H NMR (400 MHz, CD₂Cl₂) δ 5.16 (ddt, ³J_{HH} = 16, 10, 7 Hz, 1H), 3.70 (d, ³J_{HH} = 10 Hz, 1H), 3.33 (m, 2H, dppm), 3.23 (m, 2H, dppm), 2.90, (d, ³J_{HH} = 16 Hz, 1H), 2.60 (dm, ³J_{HH} = 7 Hz, 2H), −0.26 (t, ³J_{PH} = 7 Hz, 3H); ¹³C{¹H} NMR (natural abundance) δ 232.6 (dt, ¹J_{RhC} = 27 Hz, CO), 203.5 (dt ¹J_{RhC} = 12 Hz, CO), 179.0 (t, CO), 140.0 (s, CH), 111.0 (s, CH₂), 44.3 (d, ¹J_{RhC} = 24 Hz, CH₂), −17.7 (t, CH₃); ³¹P-{¹H} NMR δ 27.2 (dm, ¹J_{RhP} = 148 Hz), −5.0 (m); IR 2031, 1799 cm⁻¹. Anal. Calcd for RhOsP₄F₄BO₃C₅₇H₅₂: C, 51.99; H, 3.98. Found: C, 51.46; H, 3.35.

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Scheme 1

being bound to Os by selective ¹H{³¹P} experiments. Labeling studies using either CD₂N₂ or ¹³CH₂N₂ in the above reaction establish that the allyl group results from condensation of three methylene groups with concomitant transfer of a hydrogen to a fourth methylene unit, generating the methyl group.

In an attempt to learn more about this unprecedented conversion of methylene groups to an allyl and a methyl ligand we attempted to observe intermediates in this transformation by carrying out the reaction at low temperatures. At −80 °C the above reaction yields the methylene-bridged [RhOs(CO)₄(μ-CH₂)(dppm)₂][BF₄] (**3**),[10] which can be isolated in high yield. The ¹³C{¹H} NMR spectrum shows three terminal carbonyls (one on Rh, two on Os) and one in a semibridging interaction, as shown in Scheme 1. The methylene group is shown to be bridging the metals by the coupling of all four ³¹P nuclei to these protons in the ¹H NMR and by the coupling of ca. 15 Hz of this carbon to Rh in the ¹³C{¹H} NMR spectrum. Reacting **3** at ambient temperature with excess diazomethane generates **2** as the sole product, suggesting that **3** is an intermediate in the formation of **2** from **1**.

If either compound **1** or **3** is reacted with excess diazomethane at between −60 and −40 °C[11] a new compound [RhOs(C₄H₈)-(CO)₃(dppm)₂][BF₄] (**4**)[12] results, in which the condensation of *four* methylene units has occurred forming an osmacyclopentane moiety. The X-ray structure of **4**[13] confirms the formulation shown in Scheme 1, and a perspective view of the cation is shown in Figure 1. All parameters within the osmacyclopentane unit are consistent with this formulation, showing normal C−C single bond lengths and undistorted angles at carbon. The methylene group nearest Rh is also involved in an agostic interaction with this metal. The ¹H NMR spectrum of **4** displays six methylene resonances of the dppm and osmacyclopentane groups. However, in this spectrum none of these can be unequivocally identified as

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(10) Spectroscopic data for **3**: ¹H NMR (400 MHz, CD₂Cl₂) δ 3.75 (m, 2H, dppm), 2.80 (m, 2H, dppm), 2.25 (m, 2H); ¹³C{¹H} NMR (¹³C enriched) δ 210.5 (dm, ¹J_{RhC} = 23 or 26 Hz (coupling to Rh and C could not be differentiated), CO), 195.0 (dt, ¹J_{RhC} = 57 Hz, CO), 176.6 (t, CO), 176.3 (br, 1CO), 32.8 (d, ¹J_{RhC} = 15 Hz, CH₂); ³¹P{¹H} NMR δ 33.7 (dm, ¹J_{RhP} = 157 Hz), −2.8 (m); IR 2043, 1970, 1798 cm⁻¹. Anal. Calcd for RhOsP₄F₄-BO₄C₅₅H₄₆: C, 51.81; H, 3.64. Found: C, 51.63; H, 3.67.

(11) At −60 °C no compound **2** is produced but the rate of formation of **4** is very slow. At −40 °C the ratio of **4:2** produced is 1:1.

(12) Spectroscopic data for **4**: ¹H NMR (400 MHz, CD₂Cl₂) δ 0.67 (m, 2H₄), 1.06 (m, 2H₅), 2.09 (br, 2H₆), 1.18 (br, 2H₇), 3.80 (m, 2H, dppm), 3.93-(m, 2H, dppm); ¹³C{¹H} NMR (¹³C enriched) δ 24.6 (d, ¹J_{CC} = 31 Hz, C₄), 36.2 (t, ¹J_{CC} = 34 Hz, C₅), 37.8 (t, ¹J_{CC} = 33 Hz, C₆), −0.3 (d, ¹J_{CC} = 30 Hz, C₇), 182.4 (dt, ²J_{PC} = 9 Hz, ²J_{CC} = 2 Hz, CO), 186.4 (ddt, ¹J_{RhC} = 81 Hz, ²J_{CC} = 5 Hz, ²J_{PC} = 17 Hz, CO), 191.1 (m, CO); ³¹P{¹H} NMR δ 22.2 (dm, ¹J_{RhP} = 106 Hz), −6.7 (m); IR 1970, 1850 cm⁻¹. Labeling of carbons in the C₄H₈ unit is as shown in Figure 1.
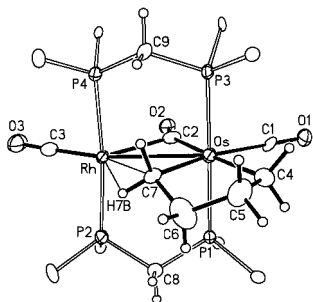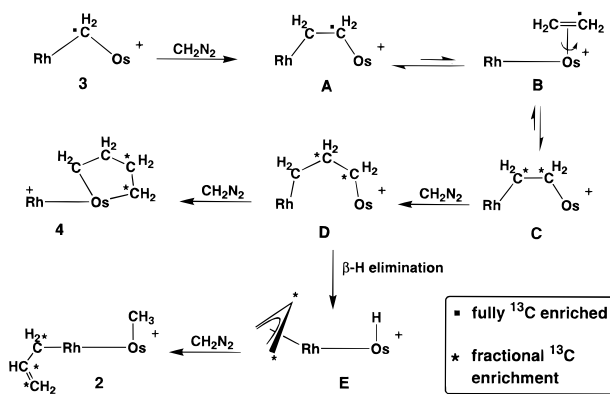
Figure 1. Perspective view of the cation of **4**; only the ipso carbons of the phenyl groups are shown. Important bond lengths (Å) and angles (deg): Rh−Os = 2.956(1); Os−C(4) = 2.20(1); Os−C(7) = 2.30(1); Rh−C(7) = 2.46(1); Rh−H7B = 1.93 (hydrogen position not refined); C(4)−C(5) = 1.45(2); C(5)−C(6) = 1.51(2); C(6)−C(7) = 1.53(1); C(4)−Os−C(7) = 79.3(4); Os−C(4)−C(5) = 113(1); C(4)−C(5)−C(6) = 112(1); C(5)−C(6)−C(7) = 112(1); Os−C(7)−C(6) = 103.8(7).

Scheme 2

that involving the agostic interaction, although the signal at δ 1.18 is broad, possibly masking small coupling to Rh. If compound **4** is generated from **1** by reaction with $^{13}CH_2N_2$, the ^1H NMR resonance at δ 1.18 is confirmed as due to the agostic methylene group by the smaller average $^1J_{CH}$ value of 112 Hz (the others have $^1J_{CH} \simeq 130$ Hz). Apparently, both hydrogens of this methylene group are alternating between an agostic and a terminal C−H bond giving the reduced average value for $^1J_{CH}$. Assuming a value of $^1J_{CH} = 130$ Hz for the terminal bond, the value for the agostic C−H bond is calculated at 94 Hz, consistent with previous reports.[14] Compounds **2** and **4** do not interconvert so are apparently derived by independent paths.

In an effort to determine mechanistic information in these transformations, the reactions of $[RhOs(CO)_4(\mu\text{-}CD_2)(dppm)_2]$-$[BF_4]$ (**3-D₂**) and $[RhOs(CO)_4(\mu\text{-}^{13}CH_2)(dppm)_2][BF_4]$ (**3-^{13}C**) with CH_2N_2 have been monitored. The reaction of CH_2N_2 with (**3-^{13}C**) yields **2** in which the allyl group is ^{13}C enriched in a 1:2:1 proportion at the α, β, and γ positions, with no ^{13}C incorporation into the methyl group. In the reaction of **3-D₂**, deuterium incorporation into all four sites of **2** is observed (vide infra). In compound **4**, synthesized from either **3-^{13}C** or **3-D₂**, the ^{13}C or deuterium label is scrambled equally between the two adjacent sites remote from Rh, with none appearing in the other sites (see structure **4**, Scheme 2). There is no evidence of deuterium incorporation into the dppm ligand of either product **2** or **4**.

Based on the labeling studies, a reaction sequence that rationalizes the selective formation of products **2** or **4** is proposed

as shown in Scheme 2 (only the metals and the fragments resulting from diazomethane are shown). Reaction of **3** with 1 equiv of diazomethane should generate the ethylene adduct **A**. Although we propose CH_2 insertion into the Rh−CH_2 bond of **3**, based on analogies with subsequent insertions (vide infra), the labeled carbon can scramble between both positions, as shown in **C**,[15] via intermediate **B** in which the ethylene is η^2-bound to Os and is free to rotate about the Os−olefin bond. Similar scrambling of an ethylene-bridged species via an η^2-C_2H_4 intermediate has been proposed.[16] Subsequent insertions to give **4** in which only the positions shown have ^{13}C labeling then must proceed via selective CH_2 insertions into the Rh−C bonds of **C** to give first **D** then **4**. This is the sequence that occurs at lower temperature. However, if the temperature is raised sufficiently (to −40 °C or above) β-H elimination in intermediate **D** competes with CH_2 insertion yielding an allyl hydride (**E**). The sequence **C → D → E** is not unlike that proposed by Pettit and co-workers,[17] for the reaction of $[Fe_2(CO)_8(\mu\text{-}CH_2)]$ with ethylene, in which a C_3H_6-bridged intermediate, analogous to **D**, undergoes β-hydride elimination to give an allyl hydride, before elimination of propylene. Reaction of the allyl hydride (**E**) with additional diazomethane presumably yields the allyl methyl product **2**. We suggest that formation of the η^1-allyl compound **2** occurs through an η^3-allyl moiety in which coordination of either end of the allyl unit (labeled or unlabeled) to Rh can occur. This results in a further 50% dilution of the label at the terminal positions, explaining the 1:2:1 integration of these carbons in the ^{13}C NMR experiment. The sequence shown in Scheme 2 also explains the deuterium scrambling observed when **3-D₂** is used, with the labeled methylene shown in the sequence leading to **4** referring to either CD_2 or $^{13}CH_3$. However, the β-hydride elimination step should generate **E** having an equal H/D population at the hydride position, resulting in subsequent deuterium incorporation into the methyl group. Deuterium incorporation into the allyl fragment occurs as explained for the ^{13}C-labeling experiment.

The *selective* coupling of methylene groups to give either allyl or metallacyclopentane fragments on a mixed-metal core demonstrates how metals having different properties can have applications in Fischer−Tropsch chemistry. In the reactions described it appears that the coordinative unsaturation at Rh, combined with the weaker Rh−C versus Os−C bonds,[18] results in selective insertions of methylene units into the Rh end of the hydrocarbyl-bridged intermediates. Currently, we are attempting to model some of the other steps shown in Scheme 2 and are attempting the reactions described above using other group 8 and 9 metal combinations to determine if additional insertions, yielding larger $(CH_2)_n$ units, or other hydrocarbyl fragments, are possible.

Supporting Information Available: Listings of crystal data, data collection, solution and refinement, complete atomic coordinates, bond distances and angles, and anisotropic parameters for compound **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

JA983626M

(13) Crystal data for **4**: monoclinic, $P2_1/n$; $a = 17.1806(12)$ Å, $b = 12.1815(7)$ Å, $c = 26.533(2)$ Å, $\beta = 103.177(1)°$; $V = 5406.7(6)$ Å^3; $Z = 4$; $D_{calc} = 1.583$ g cm^{-3}; μ(Mo Kα) = 28.28 cm^{-1}; $T = -80$ °C; λ(Mo Kα) = 0.71073 Å; 9864 independent reflections measured, 4930 observed ($I > 2\sigma(I)$); 641 variables; $R_1(F) = 0.0675$ (observed data), $wR_2(F^2) = 0.1869$ (all data). Data collected on a Bruker P4/RA/SMART 1000 CCD system using ϕ rotations and ω scans (0.3° frames, 20 s exposures) 99.4% coverage to $2\theta = 50.74°$.

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(15) Although ^{13}C scrambling should result in 50% enrichment at both positions in **C** (Scheme 2), with 50:50 labeling at the indicated sites in **4** and 25:50:25 labeling in **2**, the actual enrichment is substantially less, owing to loss of ethylene (and associated label) from the proposed adducts **A**, **B**, or **C**. Similarly, loss of deuterium label also occurs.

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