Please read the attached JACS communication and answer the following questions about the paper. You have 2 hours for this closed book exam.

1. (10 pts) Describe what the Fischer Tropsch reaction is.

2. (40 pts) Electron-count complexes 1, 2, 3 & 4 consistent with the way that the authors have drawn the structures in Scheme 1. Clearly show the oxidation state on each metal and the electron count on each metal center. Discuss any unusual features.
3. **(10 pts)** The Os-Rh bond distance in 4 could be considered to be a bit on the long side for a covalent bond. Similarly the Rh(0)/Os(+3) oxidation assignments needed to get a covalent Ru-Os bond (as the authors indicated in Scheme 1) could also be considered to be too far apart to give a stable complex. There is another way to electron count 4 that will give what might be considered to be a more consistent structure. Show this way of electron counting and briefly discuss. Are there any other advantages to this alternate method of electron counting?

4. **(10 pts)** In going from 1 to 3, at which metal does the carbene fragment (:CH₂) initially coordinate? Why? How does this play a role in the formation of intermediates A, D, and complex 4?
5. **(10 pts)** Complex 4 has an $\eta^1$-allyl. Could it have an $\eta^3$-allyl coordinated to the Rh center? Discuss. Why doesn’t it form the $\eta^3$-allyl complex as the final stable product (it is proposed as an intermediate in Fig. 1).

6. **(20 pts)** Sketch out and clearly label what is mechanistically occurring in each step in Scheme 2. Assume that CH$_2$N$_2$ initially reacts like it was :CH$_2$. 
Selective Coupling of Methylene Units in a Rh/Os Complex To Give Either C3 or C4 Fragments

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Despite the industrial successes of the Fischer-Tropsch (FT) reaction1 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),4 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 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)(dpmm)]2[BF4] (1) (dpmm = PPh2C(PPh2)2) reacts with excess diazomethane at ambient temperature yielding essentially quantitatively [RhOs-(η3-CH2=CH(CH2)=CH2)(CO)(dpmm)][BF4] (2), 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 η2-allyl complex [RhOs(η2-CH2=CH2)(CO)(dpmm)]2 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.6

The η1 bonding mode of the allyl ligand is established by NMR spectroscopy for which the 1H NMR spectrum shows 3JH 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 being bound to Os by selective 1H-{31P} experiments. Labeling studies using either CD3N2 or 1CH3N2 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 methyl 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)(η-C3H7)(dpmm)][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 3JH 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 a new compound [RhOs(C6H5)(CO)(dpmm)][BF4] (4)12 results, in which the condensation of four methylene units has occurred forming an osmacyclopane moiety. The X-ray structure of 4 confirms the formulation shown in Scheme 1, and a perspective view of the cation is shown in Figure 1. All parameters within the osmacyclopane 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 dpmm and osmacyclopane groups. However, in this spectrum none of these can be unequivocally identified as

(10) Spectroscopic data for 3: 1H NMR (400 MHz, CD2Cl2) δ 3.75 (m, 2H, dpmm), 2.80 (m, 2H, dpmm), 2.25 (m, 2H); 13C(1H) NMR (125 MHz, CD2Cl2) δ 210.5 (m, 5JCH=CH=CH2 = 23 or 26 Hz (coupling to Rh and C could not be differentiated), CO), 195.0 (dt, 1JCH=CH2 = 57 Hz, CO), 176.6 (s, CO), 176.3 (br, CO), 32.8 (d, 1JCH=CH=CH2 = 15 Hz, CH3); 31P{1H} NMR δ 33.7 (dm, 1JPP = 157 Hz), −28.8 (m); IR 2043, 1970, 1798 cm−1. Anal. Calcd. for RhOsP3O3Cl2: 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, 2H), 1.06 (m, 2H), 2.09 (br, 2H), 1.18 (br, 2H), 3.80 (m, 2H, dpmm), 3.93 (m, 2H, dpmm); 13C(1H) NMR (125 MHz, CD2Cl2) δ 4.36 (d, 1JCH=CH2 = 31 Hz, C3); 32.0 (t, 1JCH=CH2 = 34 Hz, C3); 33.4 (t, 1JCH=CH2 = 31 Hz, C3); 182.4 (dt, 1JCH=CH2 = 9 Hz, CO). 158.4 (dd, 1JCH=CH2 = 81 Hz, 1JPP = 5 Hz, JCH=CH2 = 17 Hz, CO)), 191.1 (m, CO); 31P{1H} NMR δ 22.2 (dm, 1JPP = 106 Hz), −6.7 (m); IR 1970, 1850 cm−1. Labeling of carbons in the C6H5 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) = 2.201(1); Os—C(7) = 2.30(1); Rh—C(7) = 2.46(1); Rh—H/TB = 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 13CH3N2, the 1H NMR resonance at δ 1.18 is confirmed as due to the agostic methyl group by the smaller average 1JCH value of 112 Hz (the others have 1JCH = 130 Hz). Apparently, both hydrogens of this methyl group are alternating between an agostic and a terminal C—H bond giving the reduced average value for 1JCH. Assuming a value of 1JCH = 130 Hz for the terminal bond, the value for the agostic C—H bond is calculated at 94 Hz, consistent with previous reports.16 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 [Rh(Os)(CO)(μ-C5D5)(dpmm)]2- [BF4] (3-D2) and [Rh(Os)(CO)(μ-13CH3C5H5)(dpmm)][BF4] (3-13C) with CH2N2 have been monitored. The reaction of CH2N2 with 3-13C yields in 2 which the allyl group is 13C enriched in a 2:1:1 proportion at the α, β, and γ positions, with no 13C 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 3-13C or 3-D2, the 13C 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 dpmm 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 (13). Crystal data for 4: monoclinic, P21/c; a = 17.1806(12) Å, b = 12.1815(7) Å, c = 26.533(2) Å, β = 103.17(1°); V = 5406.76(6) Å3; Z = 4; Dcalc = 1.583 g cm−3; μ(Mo Kα) = 28.25 cm−1; T = 80 °C; δ(Mo Kα) = 0.71073 Å; 9864 independent reflections measured, 4930 observed (I > 2σ(I)); 641 variables; R(F) = 0.0075 (observed data), wR(F) = 0.1809 (all data). Data collected on a Bruker P4/R/SMART 1000 CCD system using φ rotations and ω scans (0.3° frames, 20 s exposures) 99.4% coverage to 2θ = 50.74°.


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 CH3 insertion into the Rh—C 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 13C-bound to Os and is free to rotate about the Os—olefin bond. Similar scrambling of an ethylene-bridged species via an 13C2H4 intermediate has been proposed.16 Subsequent insertions to give 4 in which the only positions shown have 13C labeling then must proceed via selective CH3 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 CH2 insertion yielding an allyl hydride (E). The sequence C —> D —> E is not unlike that proposed by Petit and co-workers,17 for the reaction of [Fe2(CO)3(μ-CH3)] with ethylene, in which a C2H4-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 13C2H4 compound 2 occurs through an 13C-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 1:2:1:1 integration of these carbons in the 13C NMR experiment. The sequence shown in Scheme 2 also explains the deuteration scrambling observed when 3-D2 is used, with the labeled methylene shown in the sequence leading to 4 referring to either CD2 or 13CH3. 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 13C-labeling experiment.

The selective coupling of methylene groups to 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—C bond to form 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 (CH2)n units, or other hydrocarbyl fragments, are possible.

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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.

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(15) Although 13C scrambling should result in 50% enrichment at both positions in C (Scheme 2), with 50:50 labeling at the indicated sites in 4 and 25:75:25 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.

