

can undergo intramolecular C-H insertion to afford 1,3-disilacyclobutanes. To our knowledge, even the suggestion of any of these conclusions is unprecedented.

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- (9) Discussion of the mechanistic origin of *trans*-stilbene in this reaction will be deferred until the full paper. The yield is based on an assumed 1:1 stoichiometry. We have not yet isolated and identified the products containing silicon and oxygen.
- (10) The yields of **9** and **11** are based on the amount of naphthalene produced in the decomposition.
- (11) Evidence for the generation of a disilacyclopropane in solution from an intramolecular Grignard closure has been reported by D. Seyferth and D. P. Duncan, *J. Organomet. Chem.*, **111**, C21 (1976).
- (12) The obvious problem of the observed relative yields of **3** and **4** and the expected migratory aptitudes of Me and H in **2** can be explained by an equilibrium between **2** and **13**.
- (13) The silyl hydride quartet in the spectrum of **9** (δ 3.43, $J = 6$ Hz) also disappeared in this experiment as required.
- (14) Based on reacted **14**, as measured by Me₃SiCl production (47%), the yield of **15** is 83%. However, no **14** was observed by GC in this remarkably clean pyrolysis.
- (15) SCF-MO calculations for the Si₂H₄ system presented by Dr. Lawrence C. Snyder at the Pauling Award Symposium, Nov 5, 1977, Eugene, Ore., suggest that this should be exothermic. We thank Dr. Snyder for copies of his slides.
- (16) We are aware that our results for **5** are in striking contrast to those by reported by H. Sakurai,¹⁷ where **5** was found to undergo essentially quantitative dimerization to the corresponding disilene. We must withhold comment on this apparent dichotomous behavior until we can compare the reaction conditions.
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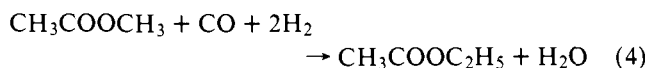
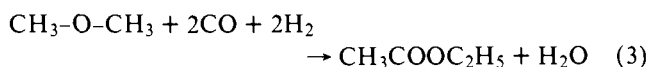
Simultaneous Carbonylation and Homologation of Dimethyl Ether and Homologation of Methyl Acetate to Ethyl Acetate in the Presence of Ruthenium Catalysts

Sir:

Many cobalt, rhodium, and iridium compounds in conjunction with iodide promoters have been reported to catalyze the homologation of methanol to ethanol¹ or the carbonylation of methanol to acetic acid.^{1,2} Ruthenium and osmium halides have been also used as promoters for cobalt/iodide catalysts in the homologation of methanol.³ It is also known that non-cyclic ethers and esters may undergo carbonylation to give esters (eq 1)¹ and anhydrides (eq 2),^{1,4} respectively, in low yields (10–50%).



We wish to report a new possibility of homologation of dimethyl ether and methyl acetate to ethyl acetate (eq 3 and 4).



In the course of studying the homologation of methanol in the presence of some ruthenium catalytic systems with iodide promoters,⁵ we found that dimethyl ether and methyl acetate, which, together with ethanol, were the predominant products of the reaction (see Table I, run 1), could be further carbonylated.⁶ The catalytic system used was based on ruthenium precursors such as tris(acetylacetonato)ruthenium(III) or diiodotetracarboxylruthenium(II) with iodide promoters (CH₃I, HI, or NaI).

The nature of the products (see Table I) was verified mass spectrometrically while the quantitative data were obtained by GC analysis.⁷

The homologation of dimethyl ether and methyl acetate to ethyl acetate has a selectivity as high as 80%. The reaction can be carried out in toluene or dioxane, the highest yields being observed in acetic acid or, better, acetic anhydride which reduces the hydrolysis of the esters. Even the simple carbonylation of dimethyl ether to methyl acetate according to eq 1 proceeds with the Ru/I catalytic system, especially in hydrocarbons (see Table I, run 2). However, this reaction does not occur with carbon monoxide alone (200 °C (230 atm); RuI₂(CO)₄/HI, 1/10) and a low hydrogen partial pressure of at least 3–5 atm is necessary to initiate the reaction.

Under the reaction conditions, besides simple (eq 1) and reductive carbonylation (eq 3 and 4), hydrolysis, esterification, and transesterification of the products can take place. Starting from dimethyl ether the selectivity to ethyl acetate can be enhanced by using appropriate ratios among the reagents and sufficiently long reaction times to convert the methyl acetate formed. Moreover, the reductive carbonylation increases with respect to the carbonylation alone by increasing the H₂/CO ratio (see Table II). It is also interesting to note that the dimethyl ether homologation, following essentially eq 3 or eq 1 + 4, takes place only when CH₃I is used as promoter. In this case, both new acetyl and ethyl groups were formed (see Table I, runs 3 and 6). In the presence of NaI (see Table I, runs 4 and 7) no formation of new acetyl groups was observed; only a large reductive carbonylation of the methyl to ethyl groups took place, and the acetyl groups of the products clearly originated from acetic acid used as solvent.

The essential requirement of the catalytic system, besides the specific presence of an iodide promoter, was the presence of an acid component such as HI, initially added or formed during the reaction from CH₃I, or an organic one such as acetic acid. The presence of an acid seems to be essential since in the absence of a proton supplier the carbonylation reaction did not proceed.

Contrary to what observed for the rhodium/iodide catalyst,² methyl iodide seems not to be involved in the homologation reaction in the presence of ruthenium catalysts. In fact pure CH₃I was not carbonylated or homologated under our reaction conditions but only partially hydrogenated to methane and HI. On the other hand, HI was a promoter more active than CH₃I when used at the same I/Ru ratio.

Some insight into the ruthenium species involved in the catalytic cycle came from the study of the metallic complexes present in the final reaction mixture. Thus, the diethyl ether solution of the catalyst, recovered from the reaction after separation of the excess of NaI, contained a product, not separable in a pure form, in which the Ru/I/Na/CO ratio was 1/3.1/0.99/3.05.⁸ The IR spectrum of the product showed ν (CO) absorptions at 2114 (s) and 2045 (s) cm⁻¹ (KBr) compared with the IR absorptions at 2112 (s) and 2051 (vs) cm⁻¹ (KBr), reported in the literature for Cs[RuI₃(CO)₃].⁹ Reaction of the ether solution with triphenylphosphine gave pure RuI₂(CO)₂(PPh₃)₂ as reported by Cleare and Griffith⁹

Table I. Carbonylation and Homologation of Dimethyl Ether and Homologation of Methanol and Methyl Acetate^a

run	catalyst (molar ratio)	reagents (mmol)	H ₂ /CO, initial (final)	time, h	convn (%)	selectivity, % ^b						ethyl groups produced, mmol		
						C ₁	C ₂	AcOMe	AcOH	AcOEt	hydro-carbon		heavy products	acetyl groups produced (+) or disappeared (-), mmol
1	RuI ₂ (CO) ₄ /CH ₃ I/NaI (1/1.2/10)	MeOH (550)	1 (1.75)	2	95	14	43	7.5	20.2	3.3	12	+66	258	
2	Ru(Acac) ₃ /CH ₃ I (1/10)	Me ₂ O (123) PhMe (235)	0.5 (0.77)	28	Me ₂ O (78)	1.8	2.0	34.7	14	20	22.8	4.7	+80.2	24
3	Ru(Acac) ₃ /CH ₃ I (1/8.5)	Me ₂ O (260) AcOH (530)	1 (0.5)	12	Me ₂ O (96) AcOH (25)	1.5	4.5	37	35	18	4	+109	160	
4	Ru(Acac) ₃ /NaI (1/10)	Me ₂ O (100) AcOH (430)	0.5 (0.55)	28	Me ₂ O (70) AcOH (30)	0.2	3	12	79	4.5	1.3	-7	150	
5	Ru(Acac) ₃ /CH ₃ I (1/12)	AcOMe (223) AcOH (218)	0.22 (0.19)	8	AcOMe (23) AcOH (-)	2.1	1.8		38	49.2	5.7	3.2	+2	21
6	Ru(Acac) ₃ /CH ₃ I (1/10)	Me ₂ O (100) AcOMe (194) AcOH (250)	0.22 (0.2)	14	MeO (58) AcOMe (-) AcOH (8)	5.4	3.6	18	64	7.5	1.5	+35	45	
7	Ru(Acac) ₃ /NaI (1/5)	Me ₂ O (95) AcOMe (94) AcOH (142)	1 (1.55)	20	Me ₂ O (16) AcOMe (61) AcOH (5)	0.4	2.0		73	23	1.6	-15	52	

^a Reaction conditions: *T*, 200 °C; *P* at room temperature, 150 atm; catalyst concentration, 1.5 × 10⁻² mol/L; CO/H₂ (1/1) was fed during the reaction to maintain the pressure to an approximately constant value. ^b Calculated as [(product, moles) × (no. of methyl groups)]/[Σ (reagents converted, mol) × (no. of methyl groups)]; C₁, MeOH, Me₂O, 1/2 MeOEt; C₂, EtOH, Et₂O, 1/2 MeOEt; hydrocarbon, CH₄ + C₂H₆; heavy products, *n*-PrOH, EtCOOH, and their C₄ or C₅ esters.

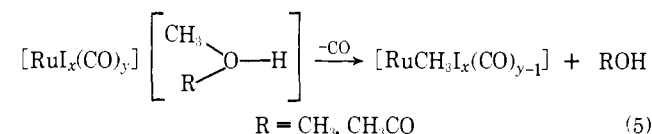
Table II. Influence of H₂/CO Ratio on Carbonylation and Homologation of Dimethyl Ether^a

Run	<i>P</i> _{CO} , atm	<i>P</i> _{H₂} , atm	H ₂ /CO, initial (final)	conv (%)	selectivity, % ^b	
					AcOMe	AcOEt
7	20	75	3.75 (1.1)	Me ₂ O (49) AcOH (15)	29	52
8	20	20	1.0 (0.65)	Me ₂ O (33.5) AcOH (4.3)	34	37
9	20	10	0.5 (0.18)	Me ₂ O (30.0) AcOH (1.0)	62	17

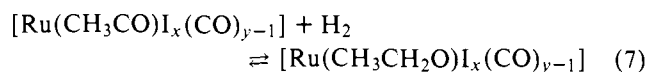
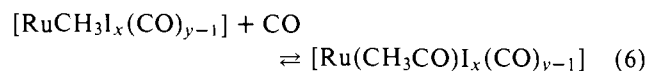
^a Reaction conditions: Me₂O/AcOMe/AcOH, initial, 1/2/3; *T*, 200 °C; time, 3 h; catalyst concentration, 1.5 × 10⁻² mol of Ru(Acac)₃/1; CH₃I/Ru, 8.5; CO/H₂ fed, 1/1. ^b See Table I.

for [RuI₃(CO)₃]⁻

These results, the observed necessity of a proton supplier and the strong promoting effect of NaI, suggest that the catalytically active species may consist of a protonated dimethyl ether or methyl acetate form as a counterion of an anionic ruthenium iodocarbonyl derivative of type [RuI_x(CO)_y]⁻. From this, a methylruthenium intermediate can be formed (eq 5) as sug-



gested by Mizoroki and Nakayama¹⁰ and Wender^{1b} for the cobalt-catalyzed methanol carbonylation and homologation, respectively. Then CO insertion into the metal-carbon bond (eq 6),¹¹ followed by hydrogenation of the resulting CH₃CORu⁻ moiety, could yield an ethoxy derivative CH₃CH₂ORu⁻ (eq 7).



Ethanol arising from successive hydrogenation of the ethoxy intermediate^{1b} or methanol from eq 5 could produce acetic esters, e.g., by alcoholysis of the acyl intermediate.

No supporting evidence presently exists on the successive steps involved to complete the catalytic cycle. However, it is important to note that, contrary to what was observed in the homologation of methanol in the presence of cobalt catalysts^{1,12} even with ruthenium promoters,³ no acetaldehyde or its derivatives (acetals and C₄ products) were found under our experimental conditions. This feature seems to be peculiar for

the ruthenium/carbonyl iodide catalytic systems and it is probably responsible for the selectivity of the reaction.

The formation of methane and ethane as by-products may arise either from the hydrogenation of the alkylruthenium intermediate or from decarbonylation of the alkoxy intermediate. An indirect evidence of this latter possibility was gathered by the selective formation of ethane in the course of similar experiments with propionic anhydride without added HI or CH₃I. In fact, the ethane can only derive through a decarbonylation reaction of a *n*-propoxyruthenium derivative proceeding according to the mechanism proposed by Chatt.¹³

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Equilibrium Isotope Effect on Hydrogen Distribution between Carbon- and Metal-Bound Sites. A Neutron Diffraction Study of Partially Deuterated Decacarbonyldihydridomethylenetriosmium

Sir:

Neutron diffraction studies allow accurate location of light atoms in transition metal compounds, as recently reported examples have shown.^{2,3} As part of a program involving the use of neutron diffraction to define carefully the geometries of small hydrocarbon moieties bound to one or more metal atoms, we now report results for a partially deuterated sample of $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{CH}_2$.⁴ Because of the differences in sign and magnitude between the neutron scattering lengths of hydrogen and deuterium,⁵ we have been able to determine the abundance of H and D at each site in the partially deuterated molecule. These population data, supported by analogous data from solution NMR spectra, reflect an equilibrium isotope effect on the H/D distribution that favors the incorporation of deuterium in the methylene group and, conversely, hydrogen in the osmium hydride positions. This effect is readily interpreted in terms of vibrational zero point energies and is general for any case involving exchange of hydrogen and deuterium between carbon- and metal-bound sites.

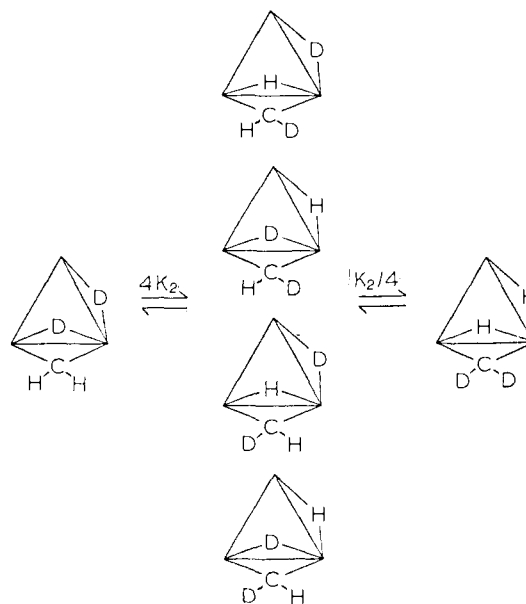
The combination of $\text{D}_2\text{Os}_3(\text{CO})_{10}$ and CH_2N_2 provides " $\text{Os}_3(\text{CO})_{10}\text{CH}_2\text{D}_2$ ", a mixture in solution of hydridomethyl and dihydridomethylene tautomers.⁴ A dichloromethane solution of this mixture in an NMR tube held at -2°C yielded a crystal which was used for neutron data collection. The crystal had dimensions of $2.0 \times 2.0 \times 0.55$ mm and weighed 5 mg, which is relatively small for neutron diffraction, after being dried under vacuum. A smaller crystal of $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{CH}_2$ (undeuterated) with dimensions $0.24 \times 0.17 \times 0.06$ mm was used for X-ray diffraction measurements.

The details of the procedure used for the measurement of the X-ray⁶ and neutron⁷ diffraction data have been described previously. A total of 2258 reflections to $2\theta = 55^\circ$ ($\lambda = 0.71069$ Å) were measured on a full-circle Picker X-ray diffractometer at Illinois and 731 reflections to $2\theta = 60^\circ$ ($\lambda = 1.142$ (1) Å) were determined at room temperature on an Electronics and Alloy four-circle diffractometer at the CP-5 reactor at Argonne National Laboratory. Based on the Laue symmetry and the systematic absences, the two possible space groups are $Pnma$ (D_{2h}^{10} , No. 62)⁸ or the nonstandard $Pn2_1a$ ($Pna2_1$, C_{2v}^9 , No. 33).⁸ The lattice parameters of $a = 18.692$ (4), $b = 10.250$ (5), and $c = 8.918$ (8) Å were determined by least-squares refinement of 12 reflections in the range $20^\circ < 2\theta < 40^\circ$ using Mo $K\alpha$ X-radiation. The structure was solved by the conventional heavy-atom method in the space group $Pnma$ using the X-ray data and independently by direct methods (MULTAN) using the neutron diffraction data. However, attempted refinement of the structure in the space group $Pnma$ was un-

successful owing to the disorder imposed by the mirror plane and subsequent refinement was based on an ordered structure in the space group $Pn2_1a$. Full-matrix least-squares refinement of the neutron data, including hydrogen and deuterium atoms, converged and yielded discrepancy indices of $R(F_o) = 0.089$, $R(F_o^2) = 0.075$, and $R_w(F_o^2) = 0.097$. The molecular structure is shown in Figure 1. The hydrogen atom scattering amplitudes were treated as variables in the least-squares refinement, which resulted in derived scattering amplitudes of $b_{\text{H}(1)} = 0.23$ (1), $b_{\text{H}(2)} = 0.24$ (1), and $b_{\text{H}(3)} = -0.06$ (1). The atom at the site of H(4) was not located⁹ on a final difference Fourier, and, therefore, its scattering length is estimated to be 0.00 ± 0.03 . The percentage of ^1H in each of the hydrogen sites is 42 (1) for H(1), 41 (1) for H(2), 70 (1) for H(3), and 64 (3) for H(4) based on the above scattering amplitudes.

The methylene carbon atom is equidistant from Os(1) and Os(2) even though these latter two atoms are chemically nonequivalent. The geometry of the CH_2 ligand ($\angle\text{H-C-H} = 106$ (1) $^\circ$) suggests that the CH_2 fragment is best described in terms of sp^3 hybridization. This situation is in contrast to that for heterocyclopropanes in which the exocyclic H-C-H angles are 114° or greater.¹⁰ The X-ray structures of two related molecules, $\text{Ru}_2(\text{CH}_2)_3(\text{PMe}_3)_6$ ¹¹ and $\text{Cp}_2\text{Rh}_2(\text{CO})_2(\text{CH}_2)$ ¹² have been reported. A point of interest in these systems, all of which contain methylene ligands bridging two metal atoms bonded by a metal-metal single bond, is that the M-C-M angle is nearly constant at $80 \pm 2^\circ$.

The solution ^1H NMR spectrum of " $\text{Os}_3(\text{CO})_{10}\text{CH}_2\text{D}_2$ " also shows a preference for H over D in the metal hydride sites of both the methylene and the methyl tautomers. For the methylene isomer no difference in intensity between the two hydride sites or between the two methylene sites could be established after repeated integration. The methylene/hydride intensity ratio was 0.75 (10). If a single parameter K_2 is defined as the equilibrium constant for a pairwise H/D interchange in the methylene isomer, then the possible configurations for a dideuterated (d_2) species are related as shown. A similar set



of monodeuterated (d_1) configurations also will contribute to the observed intensities. For the methyl isomer at each level of deuteration there are only two configurations, which are related by the equilibrium constant K_1 . The best set of parameters was determined by minimizing the difference between experimental and calculated intensities, with K_1 , K_2 , K_{eq} (relating the methyl and methylene tautomers), d_1 , and d_2 as variables.¹³ The results were $K_1 = 1.74$ (23), $K_2 = 1.58$ (21),