Table I. Stability Constants of Alkali Metal Ion Complexes of the Crown Ethers Relative to that of $Tl^+$[a]

| Crown | Solvent[b] | $Na^+$ | $K^+$ | $Rb^+$ | $Cs^+$ |
|---|---|---|---|---|---|
| DBC[c] | Methanol | 13.9 | 44.4 | 5.32 | 1.21 |
| | DMF | 6.29 | 15.5 | 2.82 | 0.752 |
| 18-Crown-6 | Methanol | 0.749 | 25.4 | 3.45 | 0.654 |
| | DMF | 0.054 | 2.33 | 1.44 | 1.00 |

[a] The uncertainty in the stability constant ratio is ±10%. [b] The anion in methanol is acetate; in DMF it is perchlorate. [c] Dibenzo-18-crown-6.

Table II. Chemical Shifts of $Tl^+$–Crown Ether Complexes and of Solvated $Tl^+$

| Crown | Solvent[a] | Calcd complexed ion shift | Calcd solvated ion shift | Exptl solvated ion shift |
|---|---|---|---|---|
| DBC[b] | Methanol | −35 | 497 | 512 |
| | DMF | −110 | 120 | 124 |
| 18-Crown-6 | Methanol | −70 | 500 | 512 |
| | DMF | −180 | 122 | 124 |

[a] Anion in methanol is acetate; in DMF it is perchlorate. [b] Dibenzo-18-crown-6.

$$P = (\delta - \delta_l)/(\delta_f - \delta_l) \quad (2)$$

$\delta$ is the chemical shift at the concentration of ionophore for which $P$ is being calculated, $\delta_l$ is the chemical shift of the $Tl^+$–ionophore complex, and $\delta_f$ is the shift of the free or uncomplexed $Tl^+$. The values of $\delta_l$ and $\delta_f$ are adjusted until the variance between the experimental chemical shifts and the chemical shifts calculated using the average stability constant ratio is minimized.

As an illustration of the method, the stability constants of alkali metal ion complexes of dibenzo-18-crown-6 (DBC) and 18-crown-6 relative to the stability constant of the $Tl^+$ complex are shown in Table I. The relative stability constants measured in methanol agree within experimental error with the relative values determined by Frensdorff using ion-selective potentiometry.[11] The selectivity sequence for DBC towards the alkali ions and $Tl^+$ in methanol is $K^+ > Na^+ > Rb^+ > Cs^+, Tl^+$. The same sequence is found in DMF which solvates better.[10] The selectivity sequence for 18-crown-6 in methanol is $K^+ > Rb^+ > Na^+, Cs^+, Tl^+$. The large difference in ionic radii between $Na^+$ and $Cs^+$ makes this sequence an excellent one to demonstrate solvent effects. When the selectivity sequence is determined in DMF, the more strongly solvated $Na^+$ has a significantly smaller relative stability constant than $Cs^+$ and the sequence becomes $K^+ > Rb^+ > Cs^+, Tl^+ > Na^+$.

The decrease in the relative stability constant of $Na^+$ over $Cs^+$ for 18-crown-6 with a change in solvent indicates that if a solvent of sufficient solvating ability were used for the determination of the DBC selectivity sequence, a decrease in the stability constant of $Na^+$ over $Rb^+$ should be found. This decrease was found in DMSO where the relative stability constants of the $Na^+$ and $Rb^+$ complexes of DBC are 5.60 ± 1.11 and 5.15 ± 0.59, respectively.

The calculated chemical shifts of the solvated ion and fully complexed ion are shown in Table II and compared to the measured shift of the solvated ion. The observed solvent dependence of the complexed ion shift occurs because the crown ether only occupies the equatorial coordination sites of the cation,[12,13] and an axial solvent or anion interaction can exist. The complexed ion shifts are in the proper region for ether type interactions (−80 to −170 ppm.). The $Tl^+$ shift is −80 ppm in THF, −130 ppm in dioxane, and −170 ppm in dimethoxyethane.[10]

The two major advantages of the Tl chemical shift method are the ability to measure solvation effects on the ion selectivity in a variety of solvents and the potential of determining the nature of the ligands comprising the binding site. The main disadvantage of this method as compared to the fluorescence method is the higher concentration of $Tl^+$ and therefore also of ligand that is necessary for measuring the relative stability constants.

**Acknowledgment.** We are grateful to the National Science Foundation for support of this work.

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## On the Mechanism of a Rhodium-Complex-Catalyzed Carbonylation of Methanol to Acetic Acid

*Sir:*

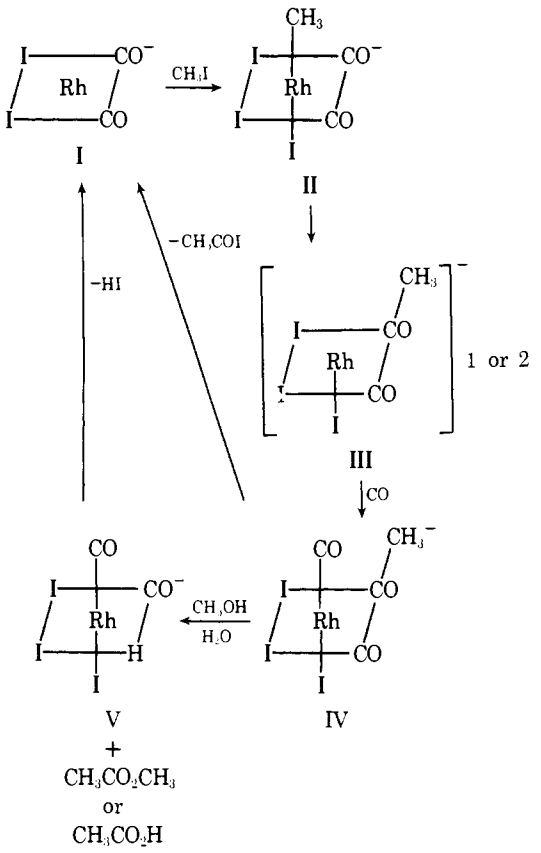
Many rhodium compounds in conjunction with various forms of iodide have been reported[1] to catalyze the carbonylation of methanol to acetic acid. While it has been speculated[1b] on the basis of reaction rates and product distribution that various sources of rhodium and iodide may form the same active catalytic species, no direct evidence has been provided as to the specific nature of reactive intermediates either with any given catalyst precursor or with a variety of catalyst precursors. This work represents an attempt to define the various rhodium species present in the catalytic cycle when one particular compound, namely a rhodium(III) halide, is charged to the reaction as the catalyst precursor.[2] We present a pathway for the reaction which is consistent with the observed[1b] independence of the overall reaction rate on carbon monoxide pressure and methanol concentration.

It has been recognized[1b] that formation of a rhodium(I) species capable of oxidative addition of methyl iodide is an important part of any catalytic cycle for synthesis of acetic acid. The catalyst precursors chosen for study in this work, the rhodium(III) halides, react with carbon monoxide in hydroxylic media with excess halide to give the rhodium(I) species, $[Rh(CO)_2X_2]^-$.[3,4]

With this complex as the starting point we propose the reaction pathway illustrated in Scheme I.

The oxidative addition of alkyl halides to $d^8$ and $d^{10}$ complexes has been extensively studied recently.[5,6] Generally, addition simply results in formation of a metal-alkyl $\sigma$-bond. We find that when a solution containing $[Rh(CO)_2X_2]^-$ ions (with a variety of cations) reacts with excess methyl iodide at room temperature, the infrared

Scheme I




spectrum of the reaction solution shows that the carbonyl stretching modes at 2064 and 1989 $cm^{-1}$ (for the $Rh(CO)_2I_2^-$ ion) are replaced by bands at 2062 and 1711 $cm^{-1}$, as the reaction proceeds. The band at 1711 $cm^{-1}$ can only be reasonably explained as an acetyl frequency and formation of intermediate III is being observed. It seems reasonable to assume that compound II is formed as an intermediate but this dicarbonyl species is unstable and isomerizes to III.

$[Rh(CO)_2Cl]_2$ (0.20 g) and $(CH_3)_3(C_6H_5)NI$ (0.28 g) were heated together at 40 °C in a mixture of methyl iodide (2 ml) and nitromethane (2 ml) for 20 min. Upon cooling the reaction solution to 0 °C, orange-brown crystals formed and were filtered off and air-dried. Anal. Calcd for $C_{12}H_{17}I_3NO_2Rh$ (i.e., $[(CH_3)_3(C_6H_5)N][RhI_3(CO)(COCH_3)]$): C, 20.85; H, 2.61; I, 55.12; O, 4.63. Found: C, 21.03; H, 2.42; I, 54.89; O, 4.79. (Note that halide exchange is complete on the rhodium in the time of this reaction.) The infrared spectrum of this material in the carbonyl region is identical with the species observed in the solution reaction of $CH_3I$ with the $Rh(CO)_2I_2^-$ ion.

The structure of this material has been determined by x-ray diffraction methods and reported elsewhere.[7] The structural study showed that the intermediate III anion is dimerized through a weak Rh-I bridge.

The reversibility of the conversion of I to III has been demonstrated by the vacuum distillation of $[(C_6H_5)_4As]_2[Rh_2I_6(CO)_2(CH_2CO)_2]$ at 200 °C. The residue was extracted with $CH_3NO_2$ and the resulting solution showed the CO stretching frequencies of $[Rh(CO)_2I_2]^-$.

On bubbling carbon monoxide through solutions of the rhodium acetyl complex III dissolved in a variety of solvents ($CH_3OH$, $CHCl_3$, $CH_3NO_2$, $C_6H_5NO_2$, $C_6H_5Cl$, $CH_2Cl_2$) at room temperature, very rapid formation of a new species is observed with CO stretching frequencies at 2141 (w) and 2084 (vs) $cm^{-1}$ and an acetyl frequency at 1708 (s) $cm^{-1}$. This species decomposes slowly at room temperature giving $[Rh(CO)_2I_2]^-$.

The observations that the initial formation of an acetyl complex (i.e., intermediate III) occurs in the absence of CO and that III reacts with CO at 1 atm pressure provide an explanation for the lack of a rate dependence[1b] on the CO partial pressure.

The scheme outlined above contains two elimination steps, one via solvolysis and formation of a rhodium-hydride species V, being analogous to the mechanism for carboxylation of alkyl halides by cobalt catalysts proposed by Heck and Breslow.[8] However, it is found that the carbonylation (CO partial pressure ~3 atm) of anhydrous methyl iodide at 80 °C with $[(C_6H_5)_4As][Rh(CO)_2X_2]$ (X = Cl, Br, or I) as catalysts (for several hours) gives significant quantities of acetyl iodide (identified by NMR, infrared, and reaction with methanol). Reductive elimination of an acyl halide by carbonylation of a rhodium(III) phosphine acyl complex has been reported[9] recently. In connection with this step of the reaction, no oxidative addition between $Rh(CO)_2X_2^-$ species and acetyl chloride or bromide can be observed over periods of 24 h at 50 °C.

Thus, the step IV → I by reductive elimination of acetyl iodide is the favored final step in the reaction sequence. Although no supporting evidence presently exists, a solvolytic mechanism may become important at high temperatures in hydroxylic solvents.

Kinetic data presented elsewhere[1b] show that the reaction is first order in both rhodium and methyl iodide concentrations, strongly suggesting that the methyl iodide addition step is rate determining.

In order to confirm the mechanism proposed above for the carbonylation reaction, some direct spectroscopic observations on reaction solutions were attempted as follows by use of the high pressure, high temperature spectrophotometric cell developed by D. E. Morris and H. B. Tinker of these laboratories.[10] The following were charged to a thick-walled glass reactor: $RhCl_3 \cdot 3H_2O$ (0.15 g), heptanoic acid[11] (45 ml), methanol (2.5 ml), methyl iodide (1.0 ml), and water (1.0 ml). The reactor was heated to 100 °C and 6 atm of CO introduced. After 30 min the solution, which was yellow, was fed into the high pressure, high temperature spectrophotometric cell and the infrared spectrum observed at 100 °C and 6 atm of pressure. The spectrum contained two strong bands at 1996 and 2067 $cm^{-1}$, characteristic of the $[Rh(CO)_2I_2]^-$ ion in this medium. GC analysis of the reaction solution at this point showed that methyl acetate and acetic acid were present. This observation indicates that under these conditions with this catalyst system, the rate determining step in the catalytic cycle is probably oxidative addition of methyl iodide to the $[Rh(CO)_2I_2]^-$ ion.

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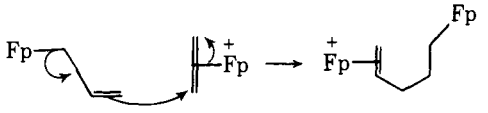
## Metal Assisted Carbon–Carbon Bond Formation. Synthesis of Hydroazulene Complexes

*Sir:*

Synthetic methods for the construction of hydroazulenes, especially those which provide for the stereospecific introduction of groups into the five- and seven-membered rings, are of particular importance for the synthesis of the large number of sesquiterpenes with this skeleton.[1] Of the several approaches at present available, few provide direct access to substituted hydroazulenes and convenient avenues for their subsequent elaboration.[2]

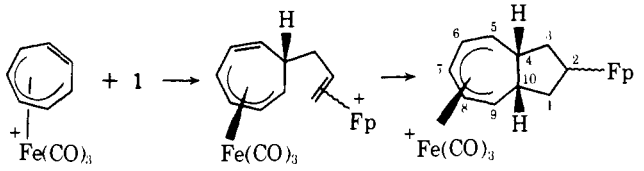
We report here a novel and efficient synthesis of hydroazulene-iron complexes, which either directly or in the course of demetalation provides ready access to hydroazulenes of diverse substitutional pattern and type.

We recently described a new carbon–carbon bond synthesis based on the condensation of metal activated olefin components.[3] This is exemplified in terms of the simplest donor (**1**) and acceptor components by eq 1. (The symbol Fp is used to designate the radical $\eta^5$-$C_5H_5Fe(CO)_2$.)



1 2 3

We now find that tropyliumiron tricarbonyl (**4**)[4] reacts rapidly with **1**, in two successive condensations, to give the dinuclear hydroazulene complex (**6**)[5] as a mixture of $C_2$-

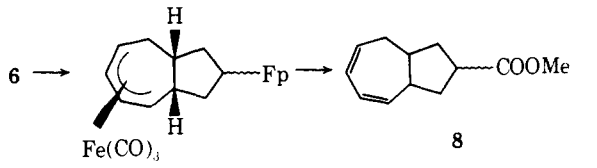


4 5 6

epimers in 75% yield: NMR ($CD_3NO_2$) $\tau$ 2.61 (t, 1, $H_7$), 4.1 (m, 2, $H_{6,8}$), 5.0 (br m, 2, $H_{5,9}$), 5.15, 5.18 (two s, 5, Cp), 6.3 (br m, 2, $H_{4,10}$), 7–8.5 (br m, 5, $H_{1,2,3}$).[6] The reaction, in 1,2-dichloroethane solution, is complete within 3 h at 55 °C. At lower temperatures the formation of the intermediate **5** may be detected in the NMR spectrum by the appearance of two resonances at $\tau$ 4.35 and 4.36, characteristic of the cyclopentadienyl protons in the Fp(olefin) cation.

The structure of the condensation product (**6**) was confirmed by reduction with $NaBH_4$ in aqueous acetonitrile to **7** (78%), oxidation with $Ce(NH_4)_2(NO_3)_6$ in methanol tetrahydrofuran to the unsaturated ester **8** (61%),[7] and dehydrogenation by brief heating in xylene in the presence of dichlorodicyanoquinone to methyl azulene-2-carboxylate (**9**), mp 107–109 (lit.[8] mp 108–109).

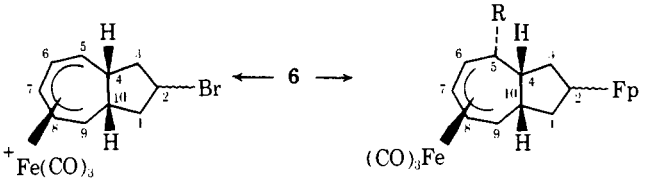
The stereochemistry assigned to **6** is based on ample precedent for initial alkylation of **4** trans to the $Fe(CO)_3$ group[9] followed by preferential cis closure of the $C_5$-ring.[10]



7 8

The potential synthetic utility of the new condensation reaction is illustrated by alternative transformations of **6** which allow for the introduction of diverse substituents at $C_5$ and of halogen at $C_2$. Furthermore, the use of donor components other than **1** provides a means for the introduction of substituents at $C_1$ and of unsaturation into the cyclopentane ring.

Thus, **6** reacts with lithium dimethylmalonate to give **10**, mp 129–133 °C (58%): ir 2050, 2000, 1970, 1937, 1765, 1740; NMR ($CS_2$) $\tau$ 4.73 (m, 2, $H_{7,8}$), 5.29 (s, 5, Cp), 6.34, 6.36, 6.41 (s, 3, OMe), 6.85 (m, 2, $H_5$, $CH(COOMe)_2$), 7.5 (m, 4, $H_{6,9,4,10}$), 8.0–8.8 (m, 5, $H_{1,2,3}$).

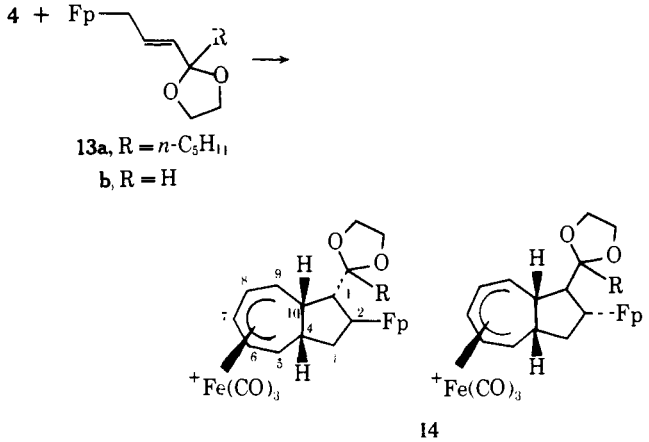


12 10, R = $CH(COOMe)_2$
11, R = OMe

The complex cation **6** also reacts with methanol in the presence of $K_2CO_3$ to give **11**, >150 °C dec (41%); NMR ($CS_2$) $\tau$ 4.68 (m, 2, $C_{7,8}$), 5.38, 5.39 (2s, 5, Cp), 6.13 (dt, 1, $J$ = 5.5, 2 Hz, $H_5$), 6.74, 6.79 (s, 3, OMe), 7.4–8.8 (br m, 8, $H_{1,2,3,4,6,9,10}$).

Oxidation demetalation of **6**, employing bromine in methylene chloride, is complete within 5 min at −78 °C, and leads to the selective replacement of the Fp group by halogen, yielding **12** (62%): NMR ($CD_3NO_2$) $\tau$ 2.50 (m, 1, $H_7$), 3.88 (m, 2, $H_{6,8}$), 4.98 (m, 2, $H_{5,9}$), 6.0–6.3 (m, 3, $H_{2,4,10}$), 7.2–8.8 (m, 4, $H_{1,3}$).

With 1-substituted ($\eta^1$-allyl)Fp complexes, which are readily available from the parent complex,[11] reaction with **4** affords 1-substituted hydroazulene complexes. The reaction of **13a** in 1,2-dichloroethane solution is essentially complete in 10 min at room temperature and yields **14a** (41%) as a mixture of trans 1,2-disubstituted complexes;[12] NMR ($CD_3NO_2$) $\tau$ 2.50 (t, 1, $J$ = 7 Hz, $H_7$), 3.97 (dd, 2, $J$ = 9,7 Hz, $H_{6,8}$), 4.9 (m, 2, $H_{5,9}$), 5.18 (s, 5, Cp), 5.96 (m, 4, $OCH_2CH_2O$), 5.9–6.8 (m, 2, $H_{4,10}$) 7.7–9.0 (m, 15, $H_{1,2,3}$ + $C_5H_{11}$). The reaction of **13b** with **4** is equally facile, affording **14b** in 73% yield: NMR ($CD_3NO_2$) $\tau$ 2.6 (m, 1,



13a, R = $n$-$C_5H_{11}$
b, R = H

14