

# Preferred Kinetic Migration of Methyl and Preferred Thermodynamic Migration of Phenyl in Conversion of *cis*-Acetylbenzoyltetracarbonylrhenate(I) to *cis*-Benzoylmethyltetracarbonylrhenate(I) and *cis*-Acetylphenyltetracarbonylrhenate(I)

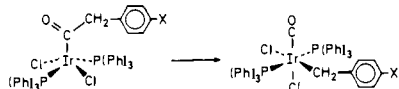
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**Abstract:** Reaction of  $\text{CH}_3\text{Li}$  with  $(\text{CO})_5\text{ReCOC}_6\text{H}_5$  or reaction of  $\text{C}_6\text{H}_5\text{Li}$  with  $(\text{CO})_5\text{ReCOCH}_3$  produce  $\text{N}(\text{CH}_3)_4^+[\text{cis}-(\text{CO})_4\text{Re}(\text{COCH}_3)(\text{COC}_6\text{H}_5)]^-$  (**2**). Thermolysis of **2** at  $69^\circ\text{C}$  produces a 98:2 mixture of  $\text{N}(\text{CH}_3)_4^+[\text{cis}-(\text{CO})_4\text{Re}(\text{C}_6\text{H}_5)(\text{COCH}_3)]^-$  (**4**) and  $\text{N}(\text{CH}_3)_4^+[\text{cis}-(\text{CO})_4\text{Re}(\text{CH}_3)(\text{COC}_6\text{H}_5)]^-$  (**5**), which equilibrate under these conditions. Reaction of **2**, **4**, or **5** with  $\text{P}(\text{CH}_2\text{CH}_3)_3$  gives  $\text{N}(\text{CH}_3)_4^+[\text{fac}-(\text{CO})_3\{\text{P}(\text{CH}_2\text{CH}_3)_3\text{Re}(\text{COCH}_3)(\text{COC}_6\text{H}_5)\}]^-$  (**7a**). The rate of phosphine addition to **5** to give **7a** is 28 times faster than the isomerization of **5** to **4**. This implies that methyl migration to rhenium occurs 28–29 times faster than phenyl migration to rhenium in the five-coordinate bisacyl intermediate  $[(\text{CO})_3\text{Re}(\text{COCH}_3)(\text{COC}_6\text{H}_5)]^-$  (**6**).

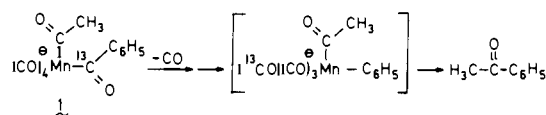
## Introduction

The interconversions of acyl metal complexes and alkyl metal complexes are extremely common in organometallic chemistry<sup>1</sup> and are an essential step in the hydroformylation reaction,<sup>2</sup> the carbonylation of methanol to acetic acid,<sup>3</sup> the decarbonylation of acid chlorides and aldehydes,<sup>4</sup> and the hydrogenation of carbon monoxide to methanol<sup>5</sup> or ethylene glycol.<sup>6</sup> However, little is known about the relative kinetic migratory aptitudes of acyl metal compounds and the factors which influence the relative rates of migration. In rearrangement reactions of organic compounds, relative migratory aptitudes have provided important experimental evidence for the nature of the transition state of the rearrangement reaction. Since the rate-determining step in most conversions of metal acyl compounds to metal alkyl compounds is the loss of a coordinated ligand and not alkyl migration,<sup>1</sup> kinetic studies cannot normally be used to determine relative migration rates. An exception is the case of the rearrangement of five-coordinate acyliridium(III) complexes to six-coordinate (alkyl)-(carbonyl)iridium(III) complexes studied by Kubota<sup>7</sup> and by Blake.<sup>8</sup> They found that electron-donating para substituents accelerated the conversion of arylacetyl complexes to benzyl metal carbonyl complexes and assigned an electropositive nature to the migrating group on the basis of these results.<sup>7</sup>



Several years ago we began studies of the synthesis and reactions of bisacyl metal compounds since we felt that relative migratory aptitudes could best be measured by internal competition of two different acyl ligands for migration to a vacant coordination site. We found that reaction of methyl lithium with benzoylpentacarbonylmanganese(I) gave *cis*-acetylbenzoyltetracarbonylmanganate(I) (**1**), the first bisacyl metal anion.<sup>9</sup> Later, in a elegant series of studies, Lukehart demonstrated that these and related bisacyl metal anions could serve as chelating "metalloacac" ligands for preparation of complexes with aluminum(III) and other metals.<sup>10</sup> Thermal decomposition of bisacyl metal complex **1** gave acetophenone. We proposed that this reaction proceeded by loss of CO, migration of an alkyl group to manganese, and reductive elimination of acetophenone from the acylalkyl intermediate<sup>9</sup> (Scheme 1). Decomposition of **1** labeled with <sup>13</sup>C on the ben-

## Scheme 1

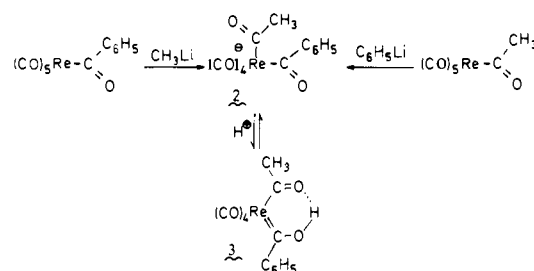


zoyl carbonyl carbon gave unlabeled acetophenone. The formation of unlabeled acetophenone was attributed to kinetically preferred phenyl migration followed by reductive elimination;<sup>9</sup> however, in this paper and the paper which follows, we present evidence that a more complex series of events leads to unlabeled acetophenone.

In attempting to extend the studies of bis(acyl)manganese compounds to a wider variety of acyl ligands, we encountered severe difficulties in isolating other stable bis(acyl)manganese anions due to the kinetic lability of the materials. Consequently, we turned our attention to the synthesis of bis(acyl)rhenium anions since acylrhenium compounds were known to be more kinetically robust than their manganese analogues.<sup>11</sup> Here we report the synthesis of acetylbenzoyltetracarbonylrhenate(I) (**2**) and its conversion to a mixture of *cis*-benzoylmethylcarbonylrhenate(I) (**3**) and the isomeric *cis*-acetylphenyltetracarbonylrhenate(I) (**4**) anions.<sup>12</sup> In addition, we report that the phenyl migration product **4** is the thermodynamically favored product but that there is a kinetic preference for the initial formation of methyl migration product **5**.

## Results

**Synthesis of  $\text{N}(\text{CH}_3)_4^+[\text{cis}-(\text{CO})_4\text{Re}(\text{COCH}_3)(\text{COC}_6\text{H}_5)]^-$  (**2**).** Addition of  $\text{CH}_3\text{Li}$  to a THF solution of  $(\text{CO})_5\text{ReCOC}_6\text{H}_5$  at  $-78^\circ\text{C}$  followed by workup with aqueous tetramethylammonium chloride gave  $\text{N}(\text{CH}_3)_4^+[\text{cis}-(\text{CO})_4\text{Re}(\text{COCH}_3)(\text{COC}_6\text{H}_5)]^-$  (**2**) in 26% yield as bright orange crystals. **2** was



also obtained in 19% yield by reaction of  $C_6H_5Li$  with  $(CO)_5ReCOCH_3$ . The highest yield and most convenient preparation of **2** involved a two-step procedure. Reaction of  $CH_3Li$  with a THF solution of  $(CO)_5ReCOC_6H_5$  followed by treatment with HCl in ether or with  $CF_3CO_2H$  led to isolation of the protonated derivative *cis*- $(CO)_4Re(COCH_3)(COC_6H_5)H$  (**3**) in 60% yield. The synthesis and X-ray crystal structure of protonated bis(acetyl)tetracarbonylrhenate has been reported by Lukehart and Zeile.<sup>13</sup> Deprotonation of **3** with tetramethylammonium hydroxide in  $CH_2Cl_2$  at 0 °C gave **2** in 90% yield.

In contrast to the bis(acyl)manganese compound **1**, whose solutions are rapidly oxidized by air,<sup>9</sup> solid rhenium salt **2** is air stable and its solutions are only slowly air oxidized over several days. The <sup>1</sup>H NMR spectrum of **2** in acetone-*d*<sub>6</sub> consists of a 2-proton multiplet at  $\delta$  7.46 assigned to the ortho aromatic protons, a 3-proton multiplet at  $\delta$  7.26 assigned to the meta and para aromatic protons, a 12-proton singlet at  $\delta$  3.44 assigned to the tetramethylammonium ion, and a 3-proton singlet at  $\delta$  2.26 assigned to the acetyl protons. The infrared spectrum in THF has four carbonyl stretching bands at 2062 (m), 1963 (s), 1945 (s), and 1912 (s)  $cm^{-1}$ , which establish the *cis* stereochemistry of the complex,<sup>14</sup> and two acyl bands at 1575 and 1545  $cm^{-1}$ .

**Thermal Decomposition of 2. Synthesis of Acylalkyl Complexes.** The decomposition of bisacyl anion **2** in acetone-*d*<sub>6</sub> at 69 °C was monitored by <sup>1</sup>H NMR, which indicated that the major product was  $N(CH_3)_4^+[cis-(CO)_4Re(C_6H_5)(COCH_3)]^-$  (**4**). New peaks characteristic of anionic phenyl metal complexes<sup>15a</sup> appeared in the aromatic region of the NMR at  $\delta$  7.84 for two ortho hydrogens and at  $\delta$  6.80 for the three meta and para hydrogens. A new acetyl resonance appeared at  $\delta$  2.24, 0.02 ppm upfield from the acetyl resonance of **2**. In addition, a very small singlet was observed at  $\delta$  -0.38 which is due to the isomeric methyl migration product  $N(CH_3)_4^+[cis-(CO)_4Re(CH_3)(COC_6H_5)]^-$  (**5**) (vide infra). The ratio of **4**:**5** was estimated by NMR to be 98:2. **4** was isolated in 41% yield from the reaction mixture. The rates of decarbonylation of bis(acyl)rhenium compound **2** ( $t_{1/2} = 82$  min at 68.6 °C) and of the monoacyl compound  $(CO)_5ReCOC_6H_5$  ( $t_{1/2} \approx 1$  h at 70 °C)<sup>15b</sup> were very similar.

The identity of these new acylalkyl metal complexes was confirmed by independent synthesis (Scheme 11). Addition of  $CH_3Li$  to  $(CO)_5ReC_6H_5$  followed by workup with aqueous  $N(CH_3)_4^+Cl^-$  gave a 53% yield of  $N(CH_3)_4^+[cis-(CO)_4Re(C_6H_5)(COCH_3)]^-$  (**4**) whose <sup>1</sup>H NMR was identical with that of the major product of the thermolysis of **2**. The infrared spectrum of **4** contains a single acyl carbonyl stretch at 1555  $cm^{-1}$  and four carbonyl stretching bands characteristic of a *cis* disubstituted tetracarbonyl metal complex.<sup>14</sup>

Addition of  $C_6H_5Li$  to  $(CO)_5ReCH_3$  followed by workup with aqueous  $N(CH_3)_4^+Cl^-$  gave a 70% yield of  $N(CH_3)_4^+[cis-(CO)_4Re(CH_3)(COC_6H_5)]^-$  (**5**). The NMR spectrum of **5** shows an upfield singlet at  $\delta$  -0.38 for the methyl bonded to rhenium and an aromatic multiplet similar to that observed for bisacyl complex **2**. The infrared spectrum of **5** contains a single acyl carbonyl stretch at 1525  $cm^{-1}$  and four carbonyl stretching bands characteristic of a *cis* disubstituted tetracarbonyl metal complex.<sup>14</sup>

The decarbonylation of bisacyl complex **2** to give acylalkyl

complexes **4** and **5** was found to be reversible. Heating a sample of **4** to 67 °C under 63 psi of carbon monoxide for 8 h gave a 72:38 mixture of **4**:**2**. Roughly the same ratio was arrived at when bisacyl complex **2** was subjected to the same conditions.

The measurement of the ratio of the two different acylalkyl isomers would provide a direct measure of the relative migratory aptitudes of phenyl and methyl from the presumed intermediate  $(CO)_3Re(COCH_3)(COC_6H_5)^-$  only if the acylalkyl products **4** and **5** were stable under the reaction conditions. However, when an independently prepared sample of either **4** or **5** was subjected to the reaction conditions (68 °C), it was found to rearrange to the same 98:2 mixture of **4**:**5**. The rate of isomerization of the benzoylmethyl complex **5** to the acetylphenyl complex **4** at 36 °C was about the same as the rate of decarbonylation of **2** to give **4** at 68.6 °C. Thus the ratio of products observed in thermolysis of **2** reflects the equilibrium constant between the two isomeric products and not the kinetic migratory aptitude.

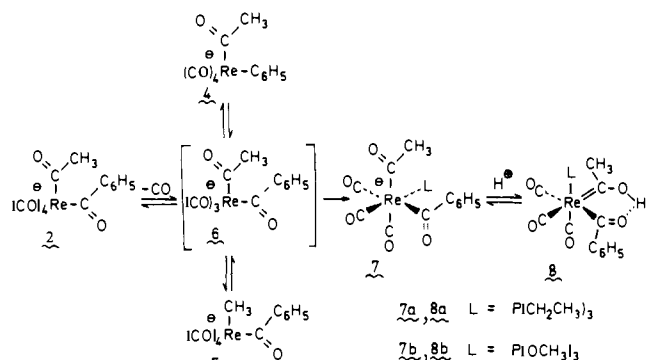
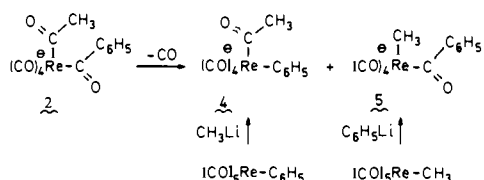
In an effort to carry out the decarbonylation of bisacyl complex **2** at lower temperatures so that equilibration of acylalkyl products **4** and **5** could be prevented, the low-temperature photolysis of **2** was studied. However, photolysis of **2** at -15 °C with a 450-W medium-pressure Hanovia lamp led only to unidentified decomposition products and no formation of **4** or **5**. Attempts to decarbonylate **2** using  $[(C_6H_5)_3P]_3RhCl$ , a reagent known to decarbonylate transition-metal acyls,<sup>16</sup> also gave no evidence for formation of **4** or **5** after 4 h at 24 °C, conditions under which substantial equilibration of **4** and **5** would have taken place. Consequently, decarbonylation of **2** with  $[(C_6H_5)_3P]_3RhCl$  at higher temperatures was not attempted.

The acylalkyl compounds **4** and **5** are fairly stable toward reductive elimination of ketone at the temperature used for decarbonylation of **2**. Formation of acetophenone can be seen only after long periods at this temperature. When a sample of bisacyl complex **2** was heated to 120 °C for 3.5 h in a sealed tube in acetone, acetophenone was found to be the major product (70%) by gas chromatography.

**Ligand Substitution and Addition Reactions.** To further investigate the mechanism of these isomerization and decarbonylation reactions, the reactions of **2**, **4**, and **5** with phosphines and phosphites were studied. The measurement of the rates of these ligand substitution and addition reactions gave kinetic information which has allowed us to quantitatively measure the relative migration rates of methyl and phenyl from a five-coordinate bis(acyl)rhenium intermediate.

Reaction of bisacyl complex **2** with excess triethylphosphine gave the phosphine substituted bisacyl complex  $N(CH_3)_4^+[fac-(CO)_3[P(CH_2CH_3)_3]Re(COCH_3)(COC_6H_5)]^-$  (**7a**), which was converted to the protonated derivative **8a** by treatment with  $CF_3CO_2H$ . The observation of three carbonyl bands of approximately equal intensity at 2015, 1933, and 1914  $cm^{-1}$  establishes the *fac* configuration of **8a**.<sup>17</sup> Similarly, reaction of **2** with  $P(OCH_3)_3$  gave **7b**, which was converted to

Scheme II



**Table I.** Rates of Decarbonylation and Ligand Substitution of **2**<sup>a,b</sup>

reaction	10 <sup>4</sup> k, s <sup>-1</sup>
<b>2</b> → <b>4</b> + <b>5</b>	1.42 ± 0.08
<b>2</b> → <b>7a</b>	1.21 ± 0.09 <sup>c</sup>
<b>2</b> → <b>7b</b>	1.49 ± 0.03 <sup>d</sup>

<sup>a</sup> In acetone-*d*<sub>6</sub> solution at 68.6 °C. <sup>b</sup> First-order rate constant ± one standard deviation. <sup>c</sup> Two equivalents of P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>; [P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>] = 0.54 M. <sup>d</sup> Three equivalents of P(OCH<sub>3</sub>)<sub>3</sub>; [P(OCH<sub>3</sub>)<sub>3</sub>] = 0.60 M.

**Table II.** Rates of P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> Addition to **4** and **5** and of Isomerization of **5** to **4**<sup>a,b</sup>

reaction	temp, °C	10 <sup>5</sup> k, s <sup>-1</sup>
<b>5</b> → <b>4</b> <sup>c</sup>	36.0 ± 0.5	10.0 ± 0.15
	21.0 ± 0.5	1.60 ± 0.03
<b>4</b> → <b>7a</b>	63.0 ± 0.2	3.88 ± 0.06
	50.0 ± 0.2	1.00 ± 0.04
	36.0 ± 0.1	0.203 ± 0.004
<b>5</b> → <b>7a</b>	21	0.0313 ± 0.0034 <sup>d</sup>
	21.0 ± 0.5	44.9 ± 8.8 <sup>e</sup>

<sup>a</sup> In acetone-*d*<sub>6</sub> solution. <sup>b</sup> First-order rate constant ± one standard deviation. <sup>c</sup> Plotted as approach to equilibrium. <sup>d</sup> Extrapolated from rates at higher temperatures: Δ*H* = 21.9 ± 0.5 kcal mol<sup>-1</sup>, Δ*S* = -13.6 eu at 309 K. <sup>e</sup> Average of six observed rates varying P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> concentration (see Table III).

protonated derivative **8b**. Three equal-intensity bands in the IR spectrum of **8b** at 2031, 1957, and 1925 cm<sup>-1</sup> are in agreement with the assigned *fac* configuration of **8b**.

The decarbonylation, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> substitution, and P(OCH<sub>3</sub>)<sub>3</sub> substitution of bisacyl complex **2** at 68.6 °C were all found to proceed at essentially the same rate (Table I). The rate of reaction of P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> with **2** to form **7a** was followed by NMR by monitoring the appearance of a new multiplet at δ 1.94 due to the methylene protons of complexed P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> in **7a**. The rate of reaction of **2** with P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> was independent of phosphine concentration and gave a linear first-order rate plot to over 80% reaction. The rate of reaction of P(OCH<sub>3</sub>)<sub>3</sub> with bisacyl complex **2** to form **7b** was followed by NMR by monitoring the growth of a new doublet at δ 3.56 due to complexed P(OCH<sub>3</sub>)<sub>3</sub> in **7b**. A first-order rate plot for the conversion of **2** to **7b** showed curvature after 30% reaction. The slowing of the formation of **7b** is due to subsequent decomposition of **7b** which dissociates P(OCH<sub>3</sub>)<sub>3</sub> and forms acetylphenyl complex **4**. When an isolated sample of **7b** was independently heated to 68.6 °C in acetone-*d*<sub>6</sub>, acetylphenyl complex **4** and P(OCH<sub>3</sub>)<sub>3</sub> were formed at a rate approximately twice as fast as the decarbonylation or phosphine substitution reactions of **2**.

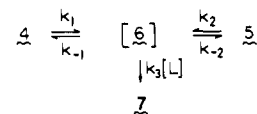
Addition of P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> to either acylalkyl complex **4** or **5** gave the same bis(acyl)phosphine substituted complex **7a** as obtained from reaction of bisacyl complex **2** with P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>. Treatment of reaction product **7a** with CF<sub>3</sub>CO<sub>2</sub>H followed by thin layer chromatography (TLC) led to the isolation of protonated derivative **8a**. Similarly addition of P(OCH<sub>3</sub>)<sub>3</sub> to **4** or **5** gave the addition product **7b** which was subsequently protonated to give **8b** which was isolated by TLC.

The rates of reaction of P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> with acylalkyl complexes **4** and **5** were measured by NMR (Table II). First-order rate plots of the reaction of **4** with P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> were linear to greater than 80% reaction. The rate of reaction of **5** with P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> did not show any significant phosphine concentration dependence over the range 0.6–1.6 M (Table III). The rate of reaction of P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> with acetylphenyl complex **4**, the more stable isomer, was slower than with benzoylmethyl complex **5** as expected for reactions proceeding through

**Table III.** Rates of Addition of P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> to **5** at 21 °C<sup>a,b</sup>

[P(CH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub> ], M	[ <b>5</b> ], M	10 <sup>4</sup> k, s <sup>-1</sup>
0.72	0.29	4.84 ± 0.31
0.99	0.29	5.52 ± 0.29
1.14	0.27	3.84 ± 0.10
1.38	0.25	3.35 ± 0.08
1.39	0.24	4.02 ± 0.11
1.62	0.23	5.35 ± 0.29

<sup>a</sup> In acetone-*d*<sub>6</sub> solution. <sup>b</sup> First-order rate constant ± one standard deviation.

**Scheme III**

a common five-coordinate bisacyl intermediate, **6**. At 21 °C, the extrapolated rate of reaction of P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> with **4** is 1450 times slower than with **5**.

We were surprised to find that the reaction of benzoylmethyl complex **5** with P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> is 28 times faster than the rate of isomerization of **5** to **4**. Both reactions are thought to proceed by initial methyl migration to give the five-coordinate bisacyl intermediate **6**. The much faster addition reaction of **5** compared with isomerization to **4** can be explained if intermediate **4** is efficiently trapped by phosphine but reverts to benzoylmethyl complex **5** by methyl migration much faster than it goes on to isomerized acetylphenyl complex **4** by phenyl migration.

**Quantitative Determination of Kinetic Migrating Preferences.** Two different procedures can be used to derive quantitative estimates of the kinetic preference for methyl migration over phenyl migration in the conversion of coordinatively unsaturated intermediate **6** to acylalkyl complexes **4** and **5** (Scheme III).

The most straightforward procedure comes from a comparison of the rate of isomerization of **5** to **4** with the rate of reaction of **5** with P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> to give phosphine substituted bisacyl complex **7a**. The rate constant for P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> addition to **5** was independent of phosphine concentration and provides evidence for efficient trapping of intermediate **6**. The rate constant for P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> addition to **5** is then simply *k*<sub>2</sub>, the rate of formation of intermediate **6** from **5**. The rate of isomerization of **5** to **4** is given by the rate of formation of intermediate **6**, *k*<sub>2</sub>, multiplied by the fraction of **6** that is converted to **4**, that is, *k*<sub>-1</sub>/(*k*<sub>-1</sub> + *k*<sub>-2</sub>). The much slower conversion of **5** to **4** compared with phosphine addition rate indicates that *k*<sub>-2</sub> must be substantially larger than *k*<sub>-1</sub> and justifies the approximation that *k*<sub>-1</sub>/(*k*<sub>-1</sub> + *k*<sub>-2</sub>) ≈ *k*<sub>-1</sub>/*k*<sub>-2</sub>. Using eq 1, the ratio of the methyl migration:phenyl migration (*k*<sub>-2</sub>:*k*<sub>-1</sub>) was calculated to be 28:1.

$$\begin{aligned} \frac{\text{rate of } \mathbf{5} \rightarrow \mathbf{7a}}{\text{rate of } \mathbf{5} \rightarrow \mathbf{4}} &= \frac{k_2}{k_2[k_{-1}/k_{-1} + k_{-2}]} \\ &\approx \frac{k_2}{k_2[k_{-1}/k_{-2}]} = \frac{k_2}{k_{-1}} \quad (1) \end{aligned}$$

The migratory aptitudes can also be calculated from the rates of phosphine addition to **4** and **5** and from the equilibrium constant for **4** and **5**. The equilibrium constant for two species **4** and **5** equilibrating via a single unstable intermediate **6** can be expressed in terms of individual rate constants for formation and destruction of the intermediate (Scheme III and eq 2).

$$K_{\text{eq}} = [\mathbf{5}]/[\mathbf{4}] = k_1 k_{-2}/k_2 k_{-1} \quad (2)$$

The ratio of methyl migration to phenyl migration from in-

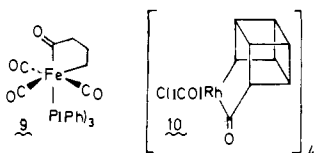
intermediate **6** ( $k_{-2}:k_{-1}$ ) is then given by the equation

$$k_{-2}/k_{-1} = (k_2/k_1)K_{\text{eq}} \quad (3)$$

Since efficient trapping of **6** by phosphine was demonstrated, the rates of reaction of **4** and **5** with  $\text{P}(\text{CH}_2\text{CH}_3)_3$  in Table II provide good measures of  $k_1$  and  $k_2$ . The measured equilibrium constant for  $[\mathbf{5}]/[\mathbf{4}]$  was 0.02. Substitution of these values into eq 3 gives a ratio of the rates of methyl migration:phenyl migration ( $k_{-2}:k_{-1}$ ) of 29:1, in excellent agreement with the results obtained by the first procedure.

## Discussion

**Acylalkyl Complexes.** The formation of acylalkylrhenium compounds **4** and **5** as stable products was somewhat unexpected since reductive elimination to form ketones from complexes of this sort is generally quite rapid. No such intermediate was seen in reactions of the analogous bis(acyl)manganese compound **1**, and attempts to prepare an acylalkylmanganese compound gave only decomposition products. A number of metal complexes such as **9**<sup>18</sup> and **10**<sup>19</sup> which have an alkyl and an acyl group tied together in a small ring have been reported.<sup>18-21</sup> The stability of these cyclic compounds



may be related to their reluctance to reductively eliminate strained rings; indeed, they are frequently prepared by insertion of the metal into a strained ring. The unusual acylalkylzirconium compound  $(\text{C}_5\text{H}_5)_2\text{ZrCH}_3(\text{COCH}_3)$ , in which the oxygen atom of the acyl unit is coordinated to zirconium, is stable to reductive elimination.<sup>22</sup> Chatt has reported difficulty in preparing  $\text{L}_2\text{M}(\text{R})(\text{COR})$  compounds of Pd and Pt by carbonylation routes and was able to obtain only an acetyl-methyl complex,  $[(\text{C}_2\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_2\text{H}_5)_2]\text{Pt}(\text{CH}_3)(\text{COCH}_3)$ , in "low yield."<sup>23</sup>

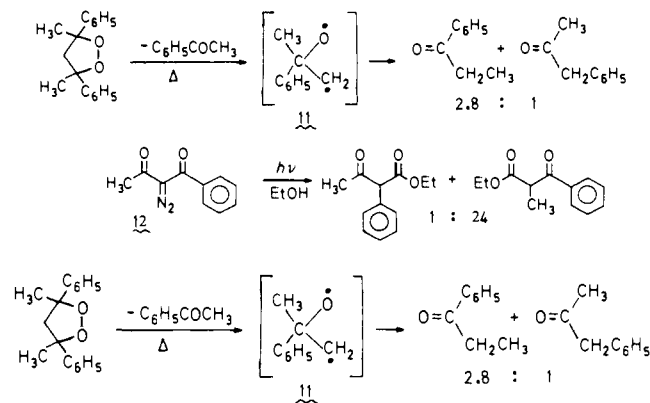
Collman has proposed acylalkyliron intermediates similar to **4** and **5** in the ketone-forming reactions of  $\text{Na}_2\text{Fe}(\text{CO})_4$ , but they have not been detected directly.<sup>24</sup> Bergman has suggested the formation of an acylalkylcobalt intermediate in the conversion of  $(\text{C}_5\text{H}_5)\text{Co}(\text{CO})(\text{CH}_3)_2$  to acetone.<sup>25</sup>

The greatly increased kinetic stability of **4** and **5** relative to their manganese analogues is probably due to the significantly stronger rhenium-carbon bonds compared with the weaker manganese-carbon bonds.<sup>26</sup>

**Thermodynamic Preference for  $\text{ReC}_6\text{H}_5$  over  $\text{ReCH}_3$ .** A substantial thermodynamic preference for phenylrhenium complex **4** by a factor of 50 over methylrhenium complex **5** was observed. For the equilibrium between  $(\text{CO})_5\text{MnCOR}$  and  $(\text{CO})_5\text{MnR} + \text{CO}$ , a preference for the phenylmanganese compound was also observed but the equilibrium constant for  $\text{R} = \text{C}_6\text{H}_5$  was only 5.5 times larger than that for  $\text{R} = \text{CH}_3$ .<sup>27</sup> Evidently there is a greater bond energy difference between  $\text{Re}-\text{C}_6\text{H}_5$  and  $\text{Re}-\text{CH}_3$  bonds than between  $\text{ReCO}-\text{C}_6\text{H}_5$  and  $\text{ReCO}-\text{CH}_3$  bonds. Phenyl-metal bonds are generally stronger than methyl-metal bonds; in  $(\text{C}_5\text{H}_5)_2\text{TiR}_2$ , a substantial difference between  $\text{Ti}-\text{C}_6\text{H}_5$  and  $\text{Ti}-\text{CH}_3$  bond strengths was noted.<sup>28</sup>

**Kinetic Preference for Methyl Migration over Phenyl Migration.** A 28-29-fold kinetic preference for methyl migration over phenyl migration from the pentacoordinate acetylbenzoyl intermediate **6** was observed. Cases in which methyl migration is preferred over phenyl migration are extremely rare. For migrations of alkyl groups to carbon centers in carbenium ion rearrangements,<sup>29</sup> in carbene rearrangements,<sup>30</sup> and in free-radical rearrangements,<sup>31</sup> strong preferences for phenyl mi-

gration are observed. For rearrangements of alkyl groups from carbon to oxygen in the Baeyer-Villiger oxidations of ketones,<sup>32</sup> phenyl migration is also preferred. In only two cases has a preference for methyl migration over phenyl migration been observed. Preferred methyl migration was seen in the rearrangement of 1-oxatrimethylene diradical **11** generated by decomposition of peresters<sup>33</sup> and peroxides<sup>34</sup> or by photolysis of epoxides.<sup>35</sup> In the photochemical Wolff rearrangement of  $\text{CH}_3\text{COCN}_2\text{COC}_6\text{H}_5$  (**12**) a 24:1 preference for



methyl migration was observed; in the thermal Wolff rearrangement of **12** a 1.65:1 preference for phenyl migration was observed.<sup>36</sup>

In the rearrangement of five-coordinate, partially fluorinated acetyliridium complexes,  $[(\text{C}_6\text{H}_5)_3\text{P}]_2(\text{Cl})_2\text{Ir}(\text{COCH}_n\text{F}_{3-n})$ , to the coordinatively saturated alkyl complexes,  $[(\text{C}_6\text{H}_5)_3\text{P}]_2(\text{Cl})_2\text{Ir}(\text{CO})(\text{CH}_n\text{F}_{3-n})$ , Blake found an inverse relationship between the rate of rearrangement and  $\Delta H^\circ$  for the reaction.<sup>8</sup> On increasing the number of fluorines the reactions became slower but more exothermic. This result is analogous to our rhenium system, in which phenyl migration is thermodynamically preferred and methyl migration is kinetically preferred.

The observed preference for methyl migration in the reactions of the bis(acyl)rhenium intermediate **6** is contrary to our earlier interpretation of the decomposition of  $(\text{CO})_4\text{Mn}(\text{COCH}_3)(^{13}\text{COC}_6\text{H}_5)^-$  (**1**) to unlabeled acetophenone.<sup>9</sup> We had interpreted this result in terms of a kinetic preference for phenyl migration to give  $(\text{CO})_3(^{13}\text{CO})\text{Mn}(\text{C}_6\text{H}_5)(\text{COCH}_3)^-$ , which then reductively eliminated unlabeled acetophenone. We have now reinvestigated this reaction and, in the accompanying paper, present new experimental results which indicate that preferential methyl migration also occurs in the manganese system.

## Experimental Section

**General.** All reactions were performed in flame-dried glassware and under a nitrogen atmosphere. Ether and tetrahydrofuran (THF) were distilled from sodium and benzophenone under a nitrogen atmosphere. Methylene chloride was distilled from  $\text{P}_2\text{O}_5$  under a nitrogen atmosphere. NMR spectra were taken using JEOLCO MH-100 and Bruker WH-270 spectrometers. Infrared spectra were recorded on a Perkin-Elmer 267 infrared spectrometer, and for the metal carbonyl region were recorded using 5 $\times$  expansion. Mass spectra were taken on an AEI-902 mass spectrometer. Preparative thin layer chromatography (preparative TLC) was performed on Merck PF-254 silica gel. Gas chromatographic analyses were performed using a Hewlett-Packard 5700A gas chromatograph and 3380A recorder-integrator. Kinetic runs were carried out in a thermostated oil bath ( $\pm 0.2^\circ\text{C}$ ) for temperatures greater than  $40^\circ\text{C}$ , in a Lauda K2/R water bath ( $\pm 0.1^\circ\text{C}$ ) at  $36^\circ\text{C}$ , and in the MH-100 NMR probe ( $\pm 0.5^\circ\text{C}$ ) for temperatures at or below  $36^\circ\text{C}$ . Melting points were recorded on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

$(\text{CO})_5\text{ReCOC}_6\text{H}_5$ ,  $(\text{CO})_5\text{ReCOCH}_3$ ,  $(\text{CO})_5\text{ReC}_6\text{H}_5$ , and  $(\text{CO})_5\text{ReCH}_3$  were prepared by the method of Hieber.<sup>37</sup>

$\text{N}(\text{CH}_3)_4^+[\text{cis}-(\text{CO})_4\text{Re}(\text{COCH}_3)(\text{COC}_6\text{H}_5)]^-$  (**2**).  $\text{CH}_3\text{Li}$  in ether (0.34 mL, 1.18 M, 0.40 mmol) was added to a stirred solution of  $(\text{CO})_5\text{ReCOCH}_3$  (146 mg, 0.34 mmol) in 5 mL of THF at  $-78^\circ\text{C}$ . The solution was stirred for 1 h at  $-78^\circ\text{C}$ , solvent was removed on a rotary evaporator, and aqueous  $\text{N}(\text{CH}_3)_4^+\text{Cl}^-$  (1.2 mL, 1.0 M, 1.2 mmol), 5 mL of  $\text{H}_2\text{O}$ , and 5 mL of  $\text{CH}_2\text{Cl}_2$  were added. The mixture was stirred for several minutes; then the  $\text{CH}_2\text{Cl}_2$  layer was transferred into another flask by syringe and dried over molecular sieves. Solvent was removed leaving an orange solid which was recrystallized from THF-ether to give orange crystals of **2** (46 mg, 26%), mp 133–134  $^\circ\text{C}$  dec, NMR and IR in Results section.

Anal. Calcd for  $\text{C}_{17}\text{H}_{20}\text{NO}_6\text{Re}$ : C, 39.23; H, 3.87; N, 2.69. Found: C, 39.31; H, 3.99; N, 2.64.

Using a similar procedure,  $\text{C}_6\text{H}_5\text{Li}$  (0.18 mL, 1.59 M, 0.28 mmol) was added to  $(\text{CO})_5\text{ReCOCH}_3$  (87 mg, 0.24 mmol), followed by aqueous  $\text{N}(\text{CH}_3)_4^+\text{Cl}^-$  to give, after recrystallization from THF-ether, orange crystals of **2** (23 mg, 19%), mp 131–133  $^\circ\text{C}$  dec.

$(\text{CO})_4\text{Re}(\text{COCH}_3)(\text{COC}_6\text{H}_5)\text{H}$  (**3**).  $\text{CH}_3\text{Li}$  in ether (0.47 mL, 2.20 M, 1.03 mmol) was added to a stirred solution of  $(\text{CO})_5\text{ReCOCH}_3$  (372 mg, 0.86 mmol) in 15 mL of THF at  $-78^\circ\text{C}$ . The solution was stirred for 1 h; then HCl in ether (2.3 mL, 0.69 M, 1.59 mmol) was added and the solution was stirred for another 10 min. Solvent was removed on a rotary evaporator, and **3** (232 mg, 60%) was isolated as a yellow solid, mp 82–83  $^\circ\text{C}$ , by preparative TLC (silica gel, 2:1 hexane- $\text{CHCl}_3$ ,  $R_f$  0.40). NMR ( $\text{CDCl}_3$ ):  $\delta$  7.45–7.80 (5 H, m,  $\text{C}_6\text{H}_5$ ), 2.91 (3 H, s,  $\text{CH}_3$ ), 17.5 (1 H, br s, enol H). IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{OH}}$  3400 (broad);  $\nu_{\text{CO}}$  2088 (m), 1996 (vs), 1960 (s)  $\text{cm}^{-1}$ . Exact mass: calcd for  $\text{C}_{13}\text{H}_9\text{O}_6\text{Re}$ , 447.9959; found, 447.9950. MS ( $m/e$ , %): 448 (<1), 433 (25), 431 (15), 377 (11), 327 (11), 321 (11), 293 (11), 271 (10).

In a similar procedure,  $\text{C}_6\text{H}_5\text{Li}$  (0.18 mL, 1.70 M, 0.31 mmol) was added to  $(\text{CO})_5\text{ReCOCH}_3$  (93 mg, 0.25 mmol), followed by HCl in ether (0.65 mL, 0.69 M, 0.45 mmol) to give **3** (35 mg, 27%).

**Reaction of 3 with  $\text{N}(\text{CH}_3)_4^+\text{OH}^-$** . **3** (176 mg, 0.40 mmol) was dissolved in 5 mL of  $\text{CH}_2\text{Cl}_2$  at  $0^\circ\text{C}$ .  $\text{N}(\text{CH}_3)_4^+\text{OH}^-$  (0.15 mL, 2.76 M in  $\text{CH}_3\text{OH}$ , 0.41 mmol) was added and the solution was stirred for several minutes. Solvent was removed on a rotary evaporator, and the residue was dissolved in 5 mL of THF and filtered. Removal of solvent gave **2** (184 mg, 90%) as an orange solid which was washed with ether and dried under vacuum, mp 133–134  $^\circ\text{C}$  dec.

**Thermolysis of 2**. An acetone- $d_6$  solution of **2** was sealed in an NMR tube under vacuum and heated to 68.6  $^\circ\text{C}$ . The reaction was monitored by integrating the aromatic multiplets due to **2** and **4**. **4** and **5** were the only products observable by NMR. **4** was isolated in 41% yield by evaporation of solvent and recrystallization from THF-ether.

**2** (46 mg, 0.88 mmol) in 0.3 mL of acetone- $d_6$  was heated to 120  $^\circ\text{C}$  for 3.5 h in a sealed tube. Gas chromatographic analysis indicated a 70% yield of acetophenone (10% OV-17, Chromosorb W, 74  $^\circ\text{C}$ ,  $n\text{-C}_{12}\text{H}_{26}$  internal standard) and a 19% yield of benzene (20% VCON 50 HB 280 $\times$ , Chromosorb P, 57  $^\circ\text{C}$ ).

**2** (51 mg, 0.098 mmol) in 0.3 mL of THF was heated to 120  $^\circ\text{C}$  for 14 h. NMR indicated the presence of acetophenone:  $\delta$  2.54 (3 H, s,  $\text{CH}_3$ ), 7.5 (3 H, m, meta and para H), and 7.95 (2 H, m, ortho H).

$\text{N}(\text{CH}_3)_4^+[\text{cis}-(\text{CO})_4\text{Re}(\text{C}_6\text{H}_5)(\text{COCH}_3)]^-$  (**4**).  $\text{CH}_3\text{Li}$  (0.96 mL, 1.16 M, 1.11 mmol) was added to a stirred solution of  $(\text{CO})_5\text{ReC}_6\text{H}_5$  (303 mg, 0.75 mmol) in 7 mL of THF at  $-78^\circ\text{C}$ . The initially colorless solution turned yellow. After the solution was stirred for 1 h, the solvent was removed and aqueous  $\text{N}(\text{CH}_3)_4^+\text{Cl}^-$  (3.0 mL, 1.0 M, 3.0 mmol), 5 mL of  $\text{H}_2\text{O}$ , and 5 mL of  $\text{CH}_2\text{Cl}_2$  were added. The mixture was stirred for several minutes; then the  $\text{CH}_2\text{Cl}_2$  layer was separated by syringe. Evaporation of solvent gave a yellow-orange oil which was recrystallized from THF-ether to give **4** (197 mg, 53%) as pale orange crystals, mp 135–137  $^\circ\text{C}$  dec. NMR (acetone- $d_6$ ):  $\delta$  7.84 (2 H, ortho H's), 6.80 (3 H, m, meta and para H's), 3.38 (12 H, s,  $\text{N}(\text{CH}_3)_4^+$ ), 2.24 (3 H, s,  $\text{CH}_3$ ). IR:  $\nu_{\text{CO}}$  2059 (m), 1950 (s, sh), 1942 (vs), 1900 (s);  $\nu_{\text{acyl}}$  1555  $\text{cm}^{-1}$ .

Anal. Calcd for  $\text{C}_{16}\text{H}_{20}\text{NO}_5\text{Re}$ : C, 39.02; H, 4.09; N, 2.84. Found: C, 38.96; H, 4.35; N, 2.83.

$\text{N}(\text{CH}_3)_4^+[\text{cis}-(\text{CO})_4\text{Re}(\text{CH}_3)(\text{COC}_6\text{H}_5)]^-$  (**5**).  $\text{C}_6\text{H}_5\text{Li}$  in ether (1.40 mL, 0.89 M, 1.25 mmol) was added to a stirred solution of  $(\text{CO})_5\text{ReCH}_3$  (396 mg, 1.16 mmol) in 13 mL of THF at  $-78^\circ\text{C}$ . The solution was stirred for 1 h; then solvent was removed on a rotary evaporator and aqueous  $\text{N}(\text{CH}_3)_4^+\text{Cl}^-$  (3.0 mL, 1.0 M, 3.0 mmol) and 5 mL of  $\text{H}_2\text{O}$  were added. The mixture was extracted with  $3 \times 5$  mL of  $\text{CH}_2\text{Cl}_2$ . Evaporation of  $\text{CH}_2\text{Cl}_2$  gave a yellow-orange oil

which was recrystallized from THF-ether to yield bright orange crystals of **5** (400 mg, 70%), mp 131–132.5  $^\circ\text{C}$  dec. NMR (acetone- $d_6$ ):  $\delta$  7.50 (2 H, m, ortho H's), 7.28 (3 H, m, meta and para H's), 3.38 (12 H, s,  $\text{N}(\text{CH}_3)_4^+$ ),  $-0.38$  (3 H, s,  $\text{CH}_3$ ). IR (THF):  $\nu_{\text{CO}}$  2045 (m), 1941 (vs), 1886 (s);  $\nu_{\text{acyl}}$  1525  $\text{cm}^{-1}$ .

**Equilibration of 2 and 4**. About 40 mg of either **2** or **4** in 3 mL of THF was placed in a Fischer-Porter bottle. The vessel was evacuated and flushed with  $\text{CO}$ , then pressurized with  $\text{CO}$  and heated to 67  $^\circ\text{C}$  (the pressure at 67  $^\circ\text{C}$  was 48 psig). At intervals of 4 h, the system was cooled to 0  $^\circ\text{C}$ , vented, and flushed with  $\text{N}_2$ , and the mixture analyzed by NMR by integrating the aromatic multiplets due to **2** and those due to **4**. After 8 h compound **2** had become a 72:28 mixture of **4:2**, and after 8 h compound **4** had become a 77:23 mixture of **4:2**.

**Equilibration of 4 and 5**. An acetone- $d_6$  solution of **5** (55 mg in 0.3 mL) was sealed in an NMR tube and monitored on an MH-100 NMR (probe temperature 21  $^\circ\text{C}$ ). The isomerization was followed by watching the disappearance of the  $\delta -0.38$  signal for the  $\text{CH}_3\text{Re}$  group of **5** and the appearance of the  $\delta 2.24$  signal for  $\text{CH}_3\text{CORe}$  group of **4**. After the system had reached equilibrium, a 270-MHz NMR spectrum was obtained and the ratio of **4:5** was determined to be 53:1 by planimetry integration of the methyl region of the spectrum. Similar analysis of an equilibrium mixture obtained from equilibration of **4** gave a ratio of **4:5** of 50:1.

**Triethylphosphine Substitution of 2**. A mixture of **2** (50 mg, 0.096 mmol) and  $\text{P}(\text{CH}_2\text{CH}_3)_3$  (53  $\mu\text{L}$ , 0.36 mmol) in 0.3 mL of acetone- $d_6$  was sealed in an NMR tube and heated to 68.6  $^\circ\text{C}$  in a constant-temperature bath. The growth of the multiplet at  $\delta 1.94$  due to the methylenes of the complexed phosphine of **7a** was used to monitor the progress of the substitution reaction.

**fac-(CO)<sub>3</sub>P(CH<sub>2</sub>CH<sub>3</sub>)Re(COCH<sub>3</sub>)(COC<sub>6</sub>H<sub>5</sub>)H (8a)**. Solvent was evaporated from the sample of **7a** obtained above, the residue was dissolved in 1 mL of  $\text{CH}_2\text{Cl}_2$  and cooled to  $-78^\circ\text{C}$ , and  $\text{CF}_3\text{CO}_2\text{H}$  (9  $\mu\text{L}$ , 0.11 mmol) was added. The protonated phosphine substituted bisacyl complex **8a** was isolated by preparative TLC (silica gel, 2:1 hexane- $\text{CHCl}_3$ ,  $R_f$  0.14) to give **8a** (38.5 mg, 74%) as a yellow solid, mp 75–76  $^\circ\text{C}$ . NMR ( $\text{CDCl}_3$ ):  $\delta$  22.05 (1 H, s, enol H), 7.85 (2 H, m, ortho H's), 7.55 (3 H, m, meta and para H's), 2.92 (3 H, s,  $\text{CH}_3$ ), 1.70 (6 H, quintet,  $J_{\text{PH}} = J_{\text{HH}} = 8$  Hz,  $\text{PCH}_2$ ), 0.85 (9 H, d of t,  $J = 16, 8$  Hz,  $\text{PCH}_2\text{CH}_3$ ). IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{CO}}$  2015 (s), 1933 (s), 1914 (s)  $\text{cm}^{-1}$ . An analytical sample was obtained by recrystallization from hexane, mp 76–76.5  $^\circ\text{C}$ .

Anal. Calcd for  $\text{C}_{18}\text{H}_{24}\text{O}_5\text{PRe}$ : C, 40.22; H, 4.50; P, 5.76; Re, 34.64. Found: C, 40.46; H, 4.65; P, 5.73; Re, 35.17.

$\text{N}(\text{CH}_3)_4^+[\text{fac}-(\text{CO})_3\text{P}(\text{OCH}_3)_3\text{Re}(\text{COCH}_3)(\text{COC}_6\text{H}_5)]^-$  (**7b**). A mixture of **2** (36 mg, 0.07 mmol) and  $\text{P}(\text{OCH}_3)_3$  (16  $\mu\text{L}$ , 0.14 mmol) in 0.3 mL of acetone- $d_6$  was sealed in an NMR tube and heated to 68.6  $^\circ\text{C}$ . Reaction was monitored by following the growth of a doublet at  $\delta 3.55$  due to complexed phosphite in **7b**. The tube was opened, solvent and excess phosphite were evaporated under a stream of  $\text{N}_2$ , and the residue was dissolved in 1 mL of THF, cooled to  $-78^\circ\text{C}$ , and acidified with  $\text{CF}_3\text{CO}_2\text{H}$  (5  $\mu\text{L}$ , 0.065 mmol). **fac-(CO)<sub>3</sub>[P(OCH<sub>3</sub>)<sub>3</sub>]Re-(COCH<sub>3</sub>)(COC<sub>6</sub>H<sub>5</sub>)H (8b)**, 8.5 mg, 20%) was isolated by preparative TLC (silica gel, 2:1 hexane- $\text{CHCl}_3$ ,  $R_f$  0.1) as a yellow solid, mp 89–90  $^\circ\text{C}$ . NMR ( $\text{CDCl}_3$ ):  $\delta$  22.24 (1 H, s, enol H), 7.70–7.40 (5 H, m,  $\text{C}_6\text{H}_5$ ), 3.48 (9 H, d,  $J = 11$  Hz,  $\text{P}(\text{OCH}_3)_3$ ), 2.88 (3 H, s,  $\text{CH}_3$ ). IR ( $\text{CHCl}_3$ ):  $\nu_{\text{CO}}$  2031 (s), 1957 (s), 1925 (s)  $\text{cm}^{-1}$ . An analytical sample was obtained by recrystallization from hexane.

Anal. Calcd for  $\text{C}_{15}\text{H}_{18}\text{O}_6\text{PRe}$ : C, 33.15; H, 3.34; P, 5.70; Re, 34.26. Found: C, 33.36; H, 3.26; P, 5.56; Re, 34.08.

Salt **7b** was prepared by adding  $\text{N}(\text{CH}_3)_4^+\text{OH}^-$  (41  $\mu\text{L}$ , 2.76 M in  $\text{CH}_3\text{OH}$ , 0.11 mmol) to **8b** (59 mg, 0.11 mmol) in 5 mL of  $\text{CH}_2\text{Cl}_2$  at  $-78^\circ\text{C}$ . Removal of solvent and recrystallization from THF-ether gave **7b** 936 (36 mg, 54%), mp 58–62  $^\circ\text{C}$ . NMR (acetone- $d_6$ ):  $\delta$  7.55 (2 H, m, ortho H's), 7.20 (3 H, m, meta and para H's), 3.55 (9 H, d,  $J = 11$  Hz,  $\text{P}(\text{OCH}_3)_3$ ), 3.45 (12 H, s,  $\text{N}(\text{CH}_3)_4^+$ ), 2.27 (3 H, s,  $\text{CH}_3$ ). IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{CO}}$  1998 (s), 1908 (s), 1891 (s)  $\text{cm}^{-1}$ .

**Thermolysis of 7b** (36 mg, 0.06 mmol) in 0.3 mL of acetone- $d_6$  was carried out in a sealed NMR tube at 68.6  $^\circ\text{C}$  for 1 h. The NMR spectrum showed, in addition to **7b**, resonances due to **4** and free  $\text{P}(\text{OCH}_3)_3$ ; the ratio of **4** and  $\text{P}(\text{OCH}_3)_3$  to **7b** was  $\sim 3:1$ . The tube was opened and solvent was evaporated under high vacuum. The infrared spectrum of the rhenium compounds showed mostly **4** with some **7b** present.

**Addition of Triethylphosphine to 4**. A mixture of **4** (38 mg, 0.08 mmol) and  $\text{P}(\text{CH}_2\text{CH}_3)_3$  (40  $\mu\text{L}$ , 0.27 mmol) in 0.3 mL of acetone- $d_6$  was sealed in an NMR tube and heated to  $36.0 \pm 0.1^\circ\text{C}$ . The con-

version of **4** to **7a** was monitored by integrating the aromatic multiplets at  $\delta$  7.84 and 6.80 due to **4** and those at  $\delta$  7.60 and 7.25 due to **7a**. Complex **8a** (20 mg, 48%, 62% based on estimated extent of reaction) was isolated in the same manner as in the substitution of **2**.

**Addition of Trimethyl Phosphite to 4.** A mixture of **4** (33 mg, 0.07 mmol) and  $P(OCH_3)_3$  (20  $\mu$ L, 0.15 mmol) in 0.3 mL of acetone- $d_6$  was sealed in an NMR tube. The reaction was carried out at  $36.0 \pm 0.1$  °C, and was monitored by integrating the aromatic multiplets due to **4** and **7b**. Complex **8b** (15 mg, 41%, 70% based on extent of reaction) was isolated in the same manner as in the substitution of **2**.

**Addition of Triethylphosphine to 5.** A mixture of **5** (45 mg, 0.09 mmol) and  $P(CH_2CH_3)_3$  (40  $\mu$ L, 0.27 mmol) in 0.3 mL of acetone- $d_6$  was sealed in an NMR tube and placed in the NMR probe at 21 °C. The conversion of **5** to **7a** was monitored by comparing the height of the methyl peak of **5** at  $\delta$  -0.38 to that of internal  $Me_4Si$ . After acidification with  $CF_3CO_2H$ , complex **8a** was isolated from the reaction mixture in 53% yield.

**Addition of Trimethyl Phosphite to 5.** A mixture of **5** (30 mg, 0.06 mmol) and  $P(OCH_3)_3$  (30  $\mu$ L, 0.25 mmol) in acetone- $d_6$  was sealed in an NMR tube and placed in the NMR probe at 15 °C. The conversion of **5** to **7b** was monitored by comparing the heights of the methyl peaks at  $\delta$  -0.38 due to **5** and at  $\delta$  2.27 due to **7b**. After acidification with  $CF_3CO_2H$ , complex **8b** was isolated from the reaction mixture in 59% yield.

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## Mechanism of Reductive Elimination of Acetophenone from $N(CH_3)_4^+[cis-(CO)_4Mn(COCH_3)(COC_6H_5)]^-$

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**Abstract:** Decomposition of  $N(CH_3)_4^+[cis-(CO)_4Mn(COCH_3)(COC_6H_5)]^-$  (**1**) in the presence of  $P(C_6H_5)_3$  gives  $N(CH_3)_4^+Mn(CO)_4[P(C_6H_5)_3]^-$  and provides evidence for a  $Mn(CO)_4^-$  intermediate. Decomposition of 90%  $^{13}C$ -acetyl labeled  $N(CH_3)_4^+[cis-(CO)_4Mn(^{13}COCH_3)(COC_6H_5)]^-$  (**1A**) gave 42.7%  $^{13}C$ -labeled acetophenone. Decomposition of 90%  $^{13}C$ -benzoyl labeled  $N(CH_3)_4^+[cis-(CO)_4Mn(COCH_3)(^{13}COC_6H_5)]^-$  (**1b**) gave 6.0%  $^{13}C$ -labeled acetophenone. These results are interpreted in terms of a mechanism involving loss of CO from **1** and formation of a five-coordinate intermediate  $Mn(CO)_3(COCH_3)(COC_6H_5)^-$  (**2**), which is in rapid equilibrium with a benzoylmethyl intermediate  $Mn(CO)_4(CH_3)(COC_6H_5)^-$  (**3**). Conversion of **2** to the acetylphenyl intermediate  $Mn(CO)_4(C_6H_5)(COCH_3)^-$  (**4**) is followed by reductive elimination to give acetophenone.

## Introduction

Several years ago, in an effort to measure relative migratory aptitudes in the conversion of acyl metal compounds to alkyl metal compounds, we synthesized  $N(CH_3)_4^+[cis-(CO)_4Mn(COCH_3)(COC_6H_5)]^-$  (**1**) and studied its thermal decomposition to acetophenone.<sup>1</sup> Thermolysis of a 20%  $^{13}C$ -labeled derivative  $N(CH_3)_4^+[cis-(CO)_4Mn(COCH_3)-$

$(^{13}COC_6H_5)]^-$  (**1B**) gave acetophenone with less than 0.7-0.4%  $^{13}C$  label. At the time, we proposed that decomposition of **1** proceeded by loss of CO, preferential migration of phenyl to manganese to produce an acylalkyl intermediate  $N(CH_3)_4^+[fac-(^{13}CO)(CO)_3Mn(C_6H_5)(COCH_3)]^-$  (**4**), which then underwent reductive elimination to give unlabeled acetophenone (Scheme 1). Both the observation of preferential