version of **4** to **7a** was monitored by integrating the aromatic multiplets at δ 7.84 and 6.80 due to **4** and those at δ 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 μL, 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 ± 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 μL, 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 δ −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 μL, 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 δ −0.38 due to **5** and at δ 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 $N(CH_3)_4^+[cis\text{-}(CO)_4Mn(COCH_3)(COC_6H_5)]^-$

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Abstract: Decomposition of $N(CH_3)_4^+[cis\text{-}(CO)_4Mn(COCH_3)(COC_6H_5)]^-$ (**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 $N(CH_3)_4^+[cis\text{-}(CO)_4Mn(^{13}COCH_3)(COC_6H_5)]^-$ (**1A**) gave 42.7% ^{13}C-labeled acetophenone. Decomposition of 90% ^{13}C-benzoyl labeled $N(CH_3)_4^+[cis\text{-}(CO)_4Mn(COCH_3)(^{13}COC_6H_5)]^-$ (**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 $N(CH_3)_4^+[cis\text{-}(CO)_4Mn(COCH_3)(COC_6H_5)]^-$ (**1**) and studied its thermal decomposition to acetophenone.[1] Thermolysis of a 20% ^{13}C-labeled derivative $N(CH_3)_4^+[cis\text{-}(CO)_4Mn(COCH_3)(^{13}COC_6H_5)]^-$ (**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 $N(CH_3)_4^+[fac\text{-}(^{13}CO)(CO)_3Mn(C_6H_5)(COCH_3)]^-$ (**4**), which then underwent reductive elimination to give unlabeled acetophenone (Scheme I). Both the observation of preferential

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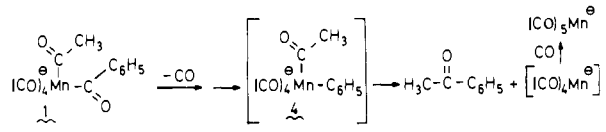
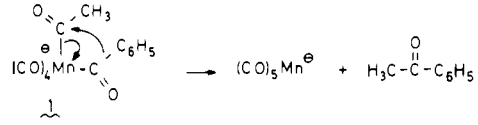
Scheme I



Scheme II



methyl migration in the analogous rhenium compound reported in the preceding paper[2] and the suggestion of Calderazzo that acetophenone could be formed by direct elimination from the bisacyl complex **1** without prior CO dissociation[3] have prompted further investigation of the mechanism of the decomposition of **1**. Here we report additional trapping and labeling studies of the decomposition of **1** that demonstrate (1) that CO dissociation from **1** precedes elimination of acetophenone, (2) that methyl migration is the kinetically preferred process for the manganese case as well as for the rhenium case, and (3) that acetophenone is primarily derived by elimination from an acetylphenylmanganese intermediate.

Results

Trapping of $Mn(CO)_4^-$ by $P(C_6H_5)_3$. In a recent review, Calderazzo suggested that the formation of acetophenone from **1** might occur by an unprecedented attack of the phenyl group of the benzoyl ligand on the carbonyl carbon of the acetyl ligand (Scheme II);[3] this process predicts the direct formation of $Mn(CO)_5^-$. Although the conversion of the analogous bisacylrhenium complex to an acylalkylrhenium complex reported in the preceding paper[2] provides an excellent precedent for loss of CO from **1** prior to the elimination of acetophenone, we felt that further tests of the mechanism outlined in Scheme I were warranted.

A fundamental difference between the mechanisms depicted in Schemes I and II is that the mechanism in Scheme I requires the formation of a coordinatively unsaturated $Mn(CO)_4^-$ intermediate prior to the formation of the eventual product $Mn(CO)_5^-$. To test for $Mn(CO)_4^-$, we have carried out the decomposition of **1** in the presence of triphenylphosphine. The ability of phosphines to trap photochemically generated $Mn(CO)_4^-$ has been established both by Ellis[4a] and by Wrighton.[4b] We have found that both $Mn(CO)_5^-$ and $Mn(CO)_4[P(C_6H_5)_3]^-$ are formed in the reaction and that the amount of $Mn(CO)_4[P(C_6H_5)_3]^-$ formed depends on the concentration of $P(C_6H_5)_3$ (Table I). The ratio of $N(CH_3)_4^+Mn(CO)_5^-$ to $N(CH_3)_4^+Mn(CO)_4[P(C_6H_5)_3]^-$ formed from **1** was determined by infrared spectroscopy. Independently synthesized samples of $N(CH_3)_4^+Mn(CO)_5^-$ and of $N(CH_3)_4^+Mn(CO)_4[P(C_6H_5)_3]^-$ were used to determine IR extinction coefficients. In a control experiment, no reaction was observed between $N(CH_3)_4^+Mn(CO)_5^-$ and $P(C_6H_5)_3$. In another control experiment, the rate of decomposition of **1** was found to be approximately the same in the presence and absence of $P(C_6H_5)_3$; this establishes that $P(C_6H_5)_3$ does not affect the rate-determining step of the decomposition of **1**. Taken together these experiments require the formation of $Mn(CO)_4^-$ as an intermediate in the decomposition of **1**.

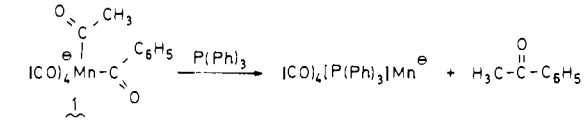


Table I. Decomposition of **1** in the Presence of $P(C_6H_5)_3$[a]

[**1**], M	$[P(C_6H_5)_3]$, M	$Mn(CO)_5^-$:$Mn(CO)_4[P(C_6H_5)_3]$[b]
0.047	0.047	32:68
0.029	0.087	21:79
0.029	0.145	13:83
0.020	0.29	4:96
0.020	0.73	0:100

[a] Half-time for decomposition in THF at ambient temperature was about 1 h. [b] Measured by infrared spectroscopy.

^{13}C-Labeling Studies. The mechanism shown in Scheme I was proposed to explain the nearly complete absence of ^{13}C label in acetophenone formed from decomposition of ^{13}C benzoyl labeled **1B.** In this mechanism, the carbonyl carbon is derived from the acetyl carbonyl carbon. To test this proposal, we prepared the 90% ^{13}C acetyl labeled complex $N(CH_3)_4^+[cis\text{-}(CO)_4Mn(^{13}COCH_3)(COC_6H_5)]^-$ (**1**) by addition of C_6H_5Li to $(CO)_5Mn^{13}COCH_3$. We were surprised to find that the acetophenone obtained on thermal decomposition of **1A** was only 42.7 ± 0.7% ^{13}C labeled. That is, slightly more than one-half of the label was lost in conversion to acetophenone.

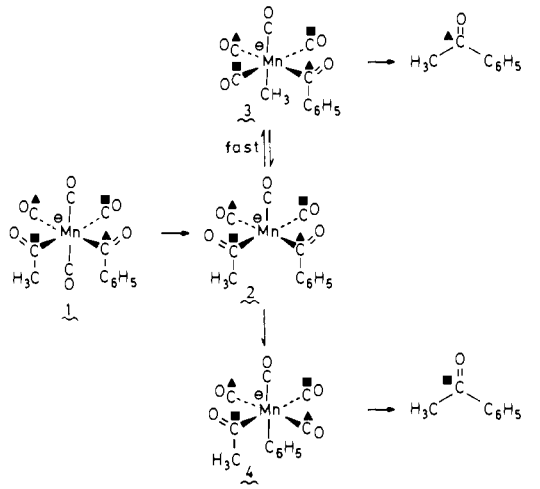
This surprising result prompted us to reinvestigate the thermal decomposition of ^{13}C benzoyl labeled $N(CH_3)_4^+[cis\text{-}(CO)_4Mn(COCH_3)(^{13}COC_6H_5)]$ (**1B**) using 90% ^{13}C label. The acetophenone obtained from decomposition of **1B** had 6.0 ± 0.7% excess ^{13}C label. This is very similar to the result we obtained earlier for 20% labeled **1B** which gave 0.0 ± 0.4 and 0.7 ± 0.4% excess ^{13}C labeled acetophenone.

Discussion

Any mechanism for the reductive elimination of acetophenone from **1** must include the following four features. First, loss of CO from **1** to give a coordinatively unsaturated intermediate **2** is required to explain the formation of $Mn(CO)_4^-$ intermediate which was trapped by $P(C_6H_5)_3$ as $Mn(CO)_4[P(C_6H_5)_3]^-$ and to account for the fact that about half of the acetophenone formed derives its carbonyl unit from neither the acetyl nor the benzoyl carbonyl of **1**. Second, to account for the incorporation of carbonyl ligands into the final acetophenone product, reversible formation of acylalkylmanganese intermediates is needed. In the related rhenium system reported in the preceding paper, stable acylalkylrhenium complexes were isolable intermediates on the pathway to acetophenone.[2] Third, for benzoylmethyl intermediate **3**, migration of methyl from manganese back to coordinated CO to regenerate the five-coordinate bisacyl intermediate **2** must be faster than reductive elimination of acetophenone. This is required to explain the loss of more than 50% of the ^{13}C acetyl labeled in the conversion of **1A** to acetophenone. Fourth, the majority of acetophenone must be formed by reductive elimination from acetylphenyl intermediate **4**. This is required to explain the formation of less labeled acetophenone (6.0%) from 90% benzoyl labeled **1B** than would have been obtained even from random scrambling of the label among five carbonyl carbons of **2**.

A mechanism which incorporates these four features and which provides an attractive explanation for our labeling results is shown in Scheme III. Decomposition of **1** is initiated by loss of a carbonyl ligand which is cis to each of the acyl ligands. The loss of an apical CO is not required by our experiments but is suggested since reaction of ^{13}CO with $(CO)_5MnCH_3$ leads to stereospecific formation of cis-labeled material[5a,b] and since phosphine and phosphite exchange of the rhenium analogue of **1** leads to the exclusive formation of a *fac* substitution product.[2]

Scheme III



The coordinatively unsaturated intermediate **2** is suggested to be conformationally rigid. Flood has confirmed by ^{13}C NMR that reaction of $(CO)_4(cis\text{-}^{13}CO)MnCH_3$ with CO gives a 2:1 ratio of $(CO)_4(cis\text{-}^{13}CO)MnCOCH_3$:$(CO)_4(trans\text{-}^{13}CO)MnCOCH_3$, which establishes that this carbonylation proceeds through a rigid five-coordinate intermediate;[5b] a fluxional intermediate would have given a 3:1 ratio. Hoffmann has carried out extended Hückel calculations of the CO insertion reaction and has concluded that the five-coordinate intermediate $(CO)_4MnCOCH_3$ is square pyramidal and nonfluxional.[6] Other reported examples of rigid five-coordinate d^6 intermediates are $Mo(CO)_3(diphos)$[7] and $Mo(CO)_3(norbornadiene)$.[8] Examples of fluxional five-coordinate d^6 intermediates are $(CO)_4MnBr$[9] and $(CO)_4CrC\text{-}OCH_2CH_2C(CH_3)_2$.[10]

Migration of methyl from the acetyl ligand of **2** to manganese is expected to lead to the cis isomer of the methylbenzoyl intermediate **3** since the related rhenium compounds were found to be cis isomers. In intermediate **3**, the former carbonyl of the acetyl group (marked in Scheme III) and the CO which was initially trans to the acetyl group of **1** are now equivalent. Stereospecific migration of methyl back to one of the two equivalent CO's (marked in Scheme III) which are cis to both the methyl and benzoyl ligands of **3** regenerates intermediate **2** but has scrambled the initial ^{13}C label of the acetyl carbon equally between the acetyl carbonyl ligand and the CO trans to the acetyl unit. The scrambling of the acetyl CO label by equilibration of **2** and **3** occurs much faster from any reductive elimination of acetophenone and accounts for the fact that less than half of the ^{13}C acetyl label is incorporated into acetophenone.

In a slower reaction than the interconversion of **2** and **3**, intermediate **3** can undergo reductive elimination of acetophenone; this process explains the 6.0% ^{13}C label incorporation into acetophenone observed in the decomposition of benzoyl-labeled **1B** and the fact that somewhat less than half of the label from acetyl-labeled **1A** is incorporated into acetophenone.

Migration of phenyl from the benzoyl ligand of **2** to manganese gives the *cis*-acetylphenyl intermediate **4**; this process is suggested to be slower than the interconversion of **2** and **3** so that all the **4** formed has the acetyl label scrambled between the acetyl ligand and the CO trans to it. For the analogous rhenium compounds described in the preceding paper,[2] methyl migration to rhenium in the analogue of **2** occurred 28-29 times faster than phenyl migration. Reductive elimination of acetophenone from **4** is more rapid than phenyl migration back to a CO ligand to regenerate **2** (see below). The large majority of reductive elimination occurs from intermediate **4**; this accounts for the low incorporation of ^{13}C in acetophenone formed from benzoyl-labeled **1B** and the slightly less than half incorporation of ^{13}C label in acetophenone from decomposition of acetyl-labeled **1A**.

In the mechanism described above, the rate at which **3** produces **2** by methyl migration is much *faster* than the rate of reductive elimination of acetophenone from **3**; however, the rate at which **4** produces **2** by phenyl migration is much *slower* than the rate of reductive elimination of acetophenone from **4**. Even if the reductive elimination of acetophenone from **3** and **4** proceeded with similar rate constants, the suggested relative rates would not be surprising since methyl migration from the rhenium analogue of **3** to coordinated CO to regenerate the analogue of **2** was found to be 1450 times faster than phenyl migration from the rhenium analogue of **4**.

If we assume that equilibration of **2** and **3** is rapid and that the relative proportions of labeled products are determined by the relative rates of reductive elimination from **3** and of irreversible phenyl migration from **2** to give **4** and eventually acetophenone, the observation that 90% acetyl labeled **1A** gives 42.7 ± 0.7% labeled acetophenone requires the formation of 5.2% of the acetophenone by elimination from **3** and 94.8% by elimination from **4**. Similarly the observation of 6.0 ± 0.7% labeled acetophenone from benzoyl-labeled **1B** requires the formation of 6.7% of the acetophenone by elimination from **3** and 93.3% by elimination from **4**. The close agreement between the calculated partitioning from the two experiments supports the assumption that reductive elimination from **4** is faster than the conversion of **4** back to **2**.

On the other hand, if one assumes that the stereospecific equilibrations of **2**, **3**, and **4** are all fast relative to reductive elimination of acetophenone from **3** and **4**, the experiment with labeled **1A** again requires that 5.2% of the acetophenone be formed from **3** and 94.8% from **4** while the experiment with labeled **1B** now requires that 13.3% of the acetophenone be formed from **3** and 86.7% from **4**. The discrepancy between these two calculations indicates that the assumption of rapid equilibration of **2** and **4** is not a good one. While some back-reaction of **4** to regenerate **2** may occur prior to reductive elimination, we feel that this is not an important process.

It should be stressed that our favored mechanism makes two untested assumptions. First, we assumed that the loss of half of the label from acetyl-labeled **1A** was due to the complete equilibration of two carbonyls via intermediates **2** and **3**. Alternative explanations invoking less than complete equilibration between more than two CO sites in **2** and **3** are certainly possible. Second, we made a related assumption that the coordinatively unsaturated bisacyl intermediate **2** was conformationally rigid and did not scramble CO's. These assumptions cannot be easily tested in the manganese system but we intend to study the ^{13}CO exchange and label scrambling reactions of the rhenium analogues of **1**, **1A**, and **1B** to test the implications of the mechanism shown in Scheme III.

Experimental Section

General. All reactions were performed in flame- or oven-dried glassware under a nitrogen atmosphere. Ether and tetrahydrofuran (THF) were distilled from sodium and benzophenone under a nitrogen atmosphere. NMR spectra were taken using a JEOLCO MH-100 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 267 spectrophotometer, a Beckman Acculab 7 spectrophotometer, and a Digilab Fourier transform interferometer. Mass spectra were taken on an AEI-902 mass spectrometer at 70 eV. Preparative gas chromatography was carried out on a Varian 90P gas chromatograph with thermal conductivity detector. Melting points were recorded on a Thomas-Hoover capillary melting point apparatus and are uncorrected. $^{13}CO_2$ (90%) was obtained from Mound Laboratory, Monsanto Research Corp. $CH_3{}^{13}CO_2Na$ (90%) was obtained from KOR Isotopes.

$N(CH_3)_4{}^+Mn(CO)_5{}^-$. $Mn_2(CO)_{10}$ (2.00 g, 5.13 mmol) was reduced to $NaMn(CO)_5$ by stirring over 50 g of 1% Na-Hg amalgam (22

mmol of Na) in 25 mL of THF for 2 h. The THF solution was added to 50% aqueous $N(CH_3)_4^+Cl^-$ (10 g, 46 mmol). The mixture was stirred for a few minutes and was then centrifuged to separate finely divided mercury. The THF layer was decanted and concentrated to a volume of about 10 mL on a vacuum line. When ether (40 mL) was distilled into the THF solution, a bright yellow, microcrystalline solid formed. The solid was washed with ether and dried under vacuum to give $N(CH_3)_4^+Mn(CO_5^-$ (1.35 g, 49%). IR (THF): ν_{CO} 1899 (s), 1867 (s) cm^{-1}. A 0.0208 M solution of $N(CH_3)_4^+Mn(CO)_5^-$ in THF had an absorbance of 0.757 at 1899 cm^{-1} in a 0.094-mm cell giving an extinction coefficient of 3870 M^{-1} cm^{-1}. There was no significant absorption at 1941 cm^{-1}.

$N(CH_3)_4^+Mn(CO)_5^-$ was characterized by conversion to the triphenyltin derivative $(CO)_5MnSn(C_6H_5)_3$. $NMe_4^+Mn(CO)_5^-$ (0.69 g, 2.56 mmol) was dissolved in 5 mL of degassed acetone, and $(C_6H_5)_3SnCl$ (0.99 g, 2.56 mmol) in 8 mL of degassed acetone was added. After the mixture was stirred at room temperature for 30 min, 70 mL of H_2O was added, and the white precipitate was collected by filtration and dried in vacuo to give $(CO)_5MnSn(C_6H_5)_3$ (1.30 g, 93%), mp 147–148 °C (lit.[11] mp 148–150 °C).

$N(CH_3)_4^+Mn(CO)_4[P(C_6H_5)_3]^-$. Method A. $Mn_2(CO)_8[P(C_6H_5)_3]_2$[12] (0.71 g, 0.83 mmol) was reduced to $NaMn(CO)_4[P(C_6H_5)_3]$ by stirring over 13 g of 1% Na–Hg amalgam (5.7 mmol of Na) in 25 mL of THF for 3 h. The supernatant orange-brown THF solution was added to solid $N(CH_3)_4^+Cl^-$ (0.53 g, 4.8 mmol) stirred for 18 h, filtered, and concentrated to a volume of about 8 mL on a vacuum line. When ether (40 mL) was distilled into the THF solution, an orange-crystalline solid formed. The solid was washed with ether and dried under vacuum to give $N(CH_3)_4^+Mn(CO)_4[P(C_6H_5)_3]^-$ (0.43 g, 52%), which was weighed and stored in a glovebox. IR (THF): ν_{CO} 1941(s), 1848 (m), 1820 (vs), 1802 (s) cm^{-1}. A 0.0242 M solution of $N(CH_3)_4^+Mn(CO)_4[P(C_6H_5)_3]^-$ in THF had an absorbance of 0.462 and 1941 cm^{-1} in a 0.094-mm cell, giving an extinction coefficient of 2030 M^{-1} cm^{-1}. The extinction coefficient at 1899 cm^{-1} was 170 M^{-1} cm^{-1}.

$N(CH_3)_4^+Mn(CO)_4[P(C_6H_5)_3]^-$ was also prepared by treatment of $HMn(CO)_4[P(C_6H_5)_3]$[13] with $N(CH_3)_4^+OH^-$ in THF.

$N(CH_3)_4^+Mn(CO)_4[P(C_6H_5)_3]^-$ was characterized by conversion of $CH_3Mn(CO)_4[P(C_6H_5)_3]$. Addition of CH_3I (25 μL, 0.40 mmol) to a solution of $N(CH_3)_4^+Mn(CO)_4[P(C_6H_5)_3]^-$ (181 mg, 0.36 mmol) in 10 mL of acetone at 0 °C produced a white precipitate. After the mixture was stirred for 30 min, 10 mL of H_2O was added and the precipitate was collected by filtration. Recrystallization from acetone–H_2O gave pale yellow crystals of $CH_3Mn(CO)_4[P(C_6H_5)_3]$ (113 mg, 70%), mp 107–108 °C (lit.[13] 110 °C). NMR (acetone-d_6): δ 7.52 (15 H, m), −0.49 (3 H, d, J = 8 Hz). IR (THF): ν_{CO} 2051 (m), 1979 (m, sh), 1967 (s), 1935 (m) cm^{-1}.

$CH_3{}^{13}COCl$. Following a procedure of Tanabe,[14] sodium acetate-*1*-^{13}C (1.0 g, 11.8 mmol) and phthaloyl dichloride (6 mL, 42 mmol) were heated to 120 °C for 30 min. The flask was heated to 180 °C, the receiving flask was cooled to 0 °C, and acetyl-*1*-^{13}C chloride (0.81 g, 88%) was collected over a 2-h period. NMR ($CDCl_3$): δ 2.67 (s).

$(CO)_5Mn{}^{13}COCH_3$. $Mn_2(CO)_{10}$ (1.00 g, 2.56 mmol) was reduced to $NaMn(CO)_5$ by stirring over 27 g of 1% Na–Hg amalgam (12 mmol of Na) in 15 mL of THF for 3 h. The supernatant THF solution was decanted from the residual amalgam and treated with $CH_3{}^{13}COCl$ (0.41 g, 5.20 mmol) at ambient temperature for 30 min. Solvent was evaporated and the residue was dissolved in CH_2Cl_2 and H_2O. The organic layer was separated and dried ($MgSO_4$), and solvent was evaporated to give $(CO)_5Mn{}^{13}COCH_3$ (0.79 g, 65%) as a yellow solid, mp 52–53 °C (lit.[15] mp 54–55 °C).

$N(CH_3)_4^+[cis\text{-}(CO)_4Mn(^{13}COCH_3)(COC_6H_5)]^-$ (1A). C_6H_5Li in ether (2.2 mL, 0.89 M, 1.96 mmol) was added to $CH_3{}^{13}COMn(CO)_5$ (390 mg, 1.63 mmol) in 10 mL of THF at −78 °C. Solvent was evaporated at room temperature and aqueous $N(CH_3)_4^+Cl^-$ (15 mL, 1.0 M, 15 mmol) was added at 0 °C. The resulting precipitate was collected, dried, and recrystallized from THF-ether to give **1A** (365 mg, 57%), mp 81–82 °C.

$C_6H_5{}^{13}CO_2H$ (0.88 g, 90% yield) was prepared from C_6H_5MgBr (11.6 mL, 0.69 M, 8.0 mmol) and $^{13}CO_2$ (8.0 mmol, 90% ^{13}C) on a vacuum line.

$C_6H_5{}^{13}COCl$. A mixture of $C_6H_5{}^{13}CO_2H$ (0.88 g, 7.2 mmol) and $SOCl_2$ (1.5 mL, 21 mmol) was refluxed for 3 h. Excess $SOCl_2$ was removed by distillation at atmospheric pressure, and $C_6H_5{}^{13}COCl$ (777 mg, 77%) was distilled at aspirator pressure, bp 105 °C (20 mm).

$(CO)_5Mn(^{13}COC_6H_5)$. $Mn_2(CO)_{10}$ (1.10 g, 2.82 mmol) was reduced to $NaMn(CO)_5$ by stirring over 24 g of 1% Na–Hg amalgam (10.4 mmol of Na) in 15 mL of THF for 3 h. The THF solution was decanted from residual amalgam and treated with $C_6H_5{}^{13}COCl$ (0.77 g, 5.5 mmol). The solution was stirred for 30 min and solvent was removed on a rotary evaporator. The residue was dissolved in CH_2Cl_2 and H_2O, and the CH_2Cl_2 layer was dried ($MgSO_4$) and concentrated to a minimum volume of solution. Hexane was added, and the solution was cooled to −20 °C to give yellow crystals of $(CO)_5Mn{}^{13}COC_6H_5$ (521 mg, 31%) in two crops, mp 90–91 °C (lit.[15] mp 95–96 °C).

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