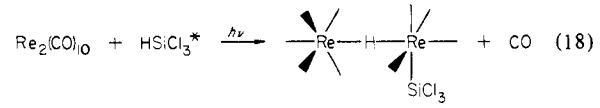
$HRe_3(CO)_{14}$ along with $Re_4(CO)_{12}(OH)_4$.

Though a similar progression of steps from IV to $HRe(CO)_4L$ and $Re_4(CO)_{12}(OH)_4$ has not been proposed in related systems, a few reactions are known that may model the individual reaction steps. A transformation similar to V → VI is found in the photochemical reaction of $Re_2(CO)_{10}$ with $HSiCl_{3-x}R_x$ (R = Me, Ph; x = 0, 1).[36] The structure of the product, $HRe_2(CO)_9SiCl_{3-x}R_x$, is as shown in eq 18; there is little direct bonding between the two



Re atoms. This structure is similar to several known polynuclear carbonyl hydrides, e.g., $HMnRe_2(CO)_{14}$ (∠Re–H–Re = 164°)[37] and $HCr_2(CO)_{10}^-$ (∠Cr–H–Cr = 180°).[38]

In a study of the substitution of $HM_2(CO)_{10}^-$ (M = Cr, Mo, W) by phosphorus ligands to yield $M(CO)_4L_2$, Darensbourg and co-workers suggested the initial steps outlined in eq 19.[39] Elim-

$$(CO)_5M\text{–}H\text{–}M(CO)_5^- \xrightarrow{-CO,\ +L} L(CO)_4M\text{–}H\text{–}M(CO)_5^- \rightarrow L(CO)_4M + HM(CO)_5^- \quad (19)$$

ination of the 18-electron hydride from $L(CO)_4M\text{–}H\text{–}M(CO)_5^-$ is analogous to the transformation from VI to VII in the reaction proposed for the dirhenium–water system.

Elimination of a metal carbonyl hydride from $HOs_3(CO)_{10}(OH)$ by the mechanism proposed in Figure 5 is not likely; the bridging $Os(CO)_4$ group would keep the trinuclear framework intact. Other examples of relatively stable polynuclear (μ-hydrido)(μ-hydroxo)metal carbonyl compounds[40] substantiate this conclusion. Elimination of a metal carbonyl hydride is therefore a process particular to dinuclear compounds or, more generally, to ones containing terminally bound metal carbonyl fragments. In another paper we describe some reactions of disubstituted dirhenium carbonyl compounds involving nitrogen bases, in which reaction pathways of the sort described here are clearly evident.[41]

Registry No. $Re_2(CO)_{10}$, 14285-68-8; H_2O, 7732-18-5; THF, 109-99-9; *eq*-$Re_2(CO)_9(OH_2)$, 83214-31-7; $HRe(CO)_5$, 16457-30-0; $Re_4(CO)_{12}(OH)_4$, 56553-73-2; *eq*-$Re_2(CO)_9(CH_3CN)$, 67486-88-8; $Re(CO)_3(CH_3CN)_3^+BF_4^-$, 64012-16-4; $Re_2(CO)_8(phen)$, 60166-20-3; *dieq*-$Re_2(CO)_8(CH_3CN)_2$, 83214-32-8; acetonitrile, 75-05-8; toluene, 108-88-3.

Supplementary Material Available: A derivation of the expression for the disappearance quantum yield, Φ_d, for $Re_2(CO)_{10}$ under photosubstitution conditions (3 pages). Ordering information is available on any current masthead page.

(36) Hoyano, J. K.; Graham, W. A. G. *Inorg. Chem.* **1972**, *11*, 1265.
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(39) Darensbourg, M. Y.; Walker, N.; Burch, R. R., Jr. *Inorg. Chem.* **1978**, *17*, 52.
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Stereochemistry and Detailed Mechanism of the Conversion of ^{13}C-Labeled *cis*-Acetylbenzoyltetracarbonylrhenate(I) to *cis*-Acetylphenyltetracarbonylrhenate(I)

Charles P. Casey* and Laima M. Baltusis

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received February 8, 1982*

Abstract: Decarbonylation of $N(CH_3)_4^+[cis\text{-}(CO)_4Re(COCH_3)(^{13}COC_6H_5)]^-$, **5B**, gives $N(CH_3)_4^+[fac\text{-}(CO)_3(^{13}CO)Re(COCH_3)(C_6H_5)]^-$, **6C**, stereospecifically at low conversion. Decarbonylation of $N(CH_3)_4^+[cis\text{-}(CO)_4Re(^{13}COCH_3)(COC_6H_5)]^-$, **5A**, gives mainly a 1:1 mixture of $N(CH_3)_4^+[(CO)_4Re(^{13}COCH_3)(C_6H_5)]^-$, **6A**, and $N(CH_3)_4^+[mer\text{-}(CO)_3(^{13}CO)Re(COCH_3)(C_6H_5)]^-$, **6-TA**, in which the ^{13}CO label is trans to the acetyl ligand. $N(CH_3)_4^+[fac\text{-}(CO)_3(^{13}CO)Re(COCH_3)(COC_6H_5)]^-$, **5C**, was prepared stereospecifically by reaction of $N(CH_3)_4^+[cis\text{-}(CO)_4Re(COC_6H_5)(CH_3)]^-$, **7**, with ^{13}CO. Decarbonylation of **5C** gives mainly $N(CH_3)_4^+[mer\text{-}(CO)_3(^{13}CO)Re(COCH_3)(C_6H_5)]$, **6-TP**, in which the ^{13}CO label is trans to the phenyl group. In addition to the stereospecific decarbonylation products obtained from **5A** and **5C**, some ^{13}CO scrambled products were also observed from **5A** (20% loss of stereochemistry) and from **5C** (52% loss of stereochemistry). At long reaction times, statistical scrambling of ^{13}CO in **6** was observed for materials obtained from decarbonylation of **5A–C**. These results are explained in terms of a mechanism involving the five-coordinate intermediate $[(CO)_3Re(COCH_3)(COC_6H_5)]^-$, **9**, which undergoes reversible methyl migration much more rapidly than it undergoes phenyl migration to give stable product **6**. Scrambling of ^{13}CO label in intermediate **9** occurs at a rate similar to the rate of phenyl migration of **9**, which gives **6**.

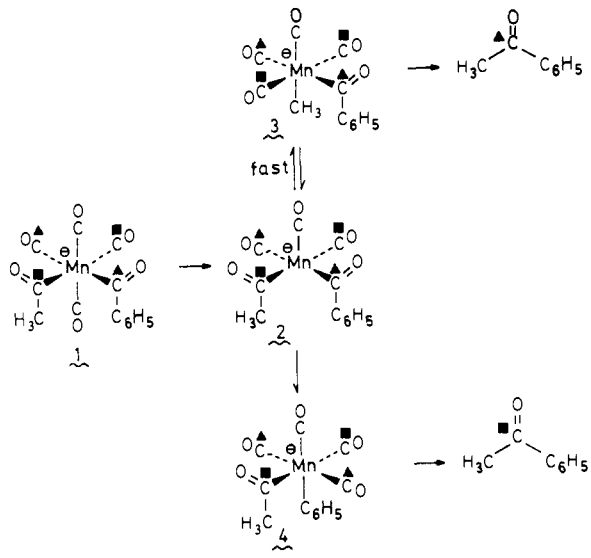
Introduction

The interconversions of acylmetal complexes and alkylmetal complexes are extremely common in organometallic chemistry[1] and are an essential step in many catalytic processes.[2] Several years ago in an effort to learn more about the detailed mechanism of this process, we synthesized *cis*-acetylbenzoyltetracarbonylmanganate(I) (**1**),[3] the first diacylmetal anion,[4] and attempted to determine the relative migratory aptitudes of phenyl and methyl

(1) Calderazzo, F. *Angew Chem., Int. Ed. Engl.* **1977**, *16*, 299. Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87. Flood, T. C. *Top. Stereochem.* **1980**, *12*, 37.
(2) Pruett, R. L. *Adv. Organomet. Chem.* **1979**, *17*, 1. Forster, D. *Ibid.* **1979**, *17*, 255. Tsuji, J.; Ohno, K. *Synthesis* **1969**, 157. Rathke, J. W.; Feder, H. M. *J. Am. Chem. Soc.* **1978**, *100*, 3623. Pruett, R. L. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 239.
(3) Casey, C. P.; Bunnell, C. A. *J. Chem. Soc., Chem. Commun.* **1974**, 733; *J. Am. Chem. Soc.* **1976**, *98*, 436.
(4) Lukehart has demonstrated that these and related diacylmetal anions can serve as chelating "metalloacac" ligands for preparation of complexes with aluminum(III) and other metals: Lukehart, C. M.; Torrence, G. P.; Zeile, J. V. *J. Am. Chem. Soc.* **1975**, *97*, 6903. Lukehart, C. M.; Zeile, J. V. *Ibid.* **1978**, *100*, 2774 and references cited therein.

0002-7863/82/1504-6347$01.25/0

Scheme I



groups by examining decomposition products from a labeled derivative of **1**. We prepared 20% [^{13}C]benzoyl-labeled **1B** by reaction of CH_3Li with $(CO)_5Mn^{13}COC_6H_5$. Thermal decomposition of **1B** at 40 °C gave acetophenone with less than 0.7 ± 0.4% ^{13}C. At that time, we incorrectly interpreted this result as arising from loss of CO from **1B**, preferential phenyl migration to manganese to produce an unobserved alkylacyl intermediate [*fac*-(^{13}CO)$(CO)_3Mn(C_6H_5)(COCH_3)]^-$, which then underwent reductive elimination to give unlabeled acetophenone.

Subsequently, we observed preferential methyl migration over phenyl migration in the related rhenium compound **5** and reinvestigated the decomposition of the diacylmanganese compound **1**.[5] We prepared 90% [^{13}C]benzoyl-labeled **1B** and (in agreement with our previous labeling studies) found that it underwent thermal decomposition to give acetophenone with only 6.0 ± 0.7% excess ^{13}C label. More interestingly, the 90% [^{13}C]acetyl-labeled material **1A** decomposed to give acetophenone with 42.7 ± 0.7% ^{13}C label (i.e., slightly more than half of the label was lost in conversion to acetophenone).

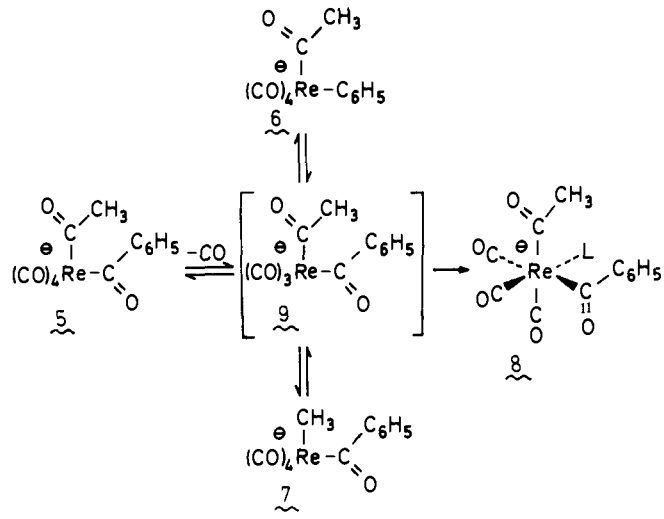
To explain these labeling results, we proposed the mechanism shown in Scheme I.[5] Decomposition was proposed to proceed via initial loss of CO from a site cis to both acyl ligands to produce a rigid five-coordinate intermediate **2**. Rapid and reversible methyl migration from the acetyl ligand to manganese (**2** ⇄ **3**) was proposed as a mechanism for scrambling ^{13}CO label between the acetyl carbonyl and the CO trans to the acetyl ligand. A slower migration of phenyl from the benzoyl ligand of intermediate **2** to manganese produces phenylacetylmanganese compound **4**. Finally, reductive elimination of acetophenone occurs predominantly from **4**.

While the above mechanistic scheme accounted in detail for the observed labeling results, several untested assumptions were made in this proposed mechanism. First, the loss of CO from **1** was assumed to occur from a site cis to both the benzoyl and the acetyl ligands. Second, the complete equilibration of ^{13}C label between the acetyl carbonyl and the CO trans to it was assumed to occur via a stereospecific interconversion of **2** and **3**. Third, we assumed that the coordinatively unsaturated diacyl intermediate **2** was conformationally rigid and did not scramble CO's. These assumptions cannot easily be tested in the manganese system but can be studied by using the analogous more stable diacylrhenium compound **5**. Here we report the synthesis of three different ^{13}C-labeled derivatives of **5** and the stereochemistry of their conversion to phenylacetylrhenium compound **6**.

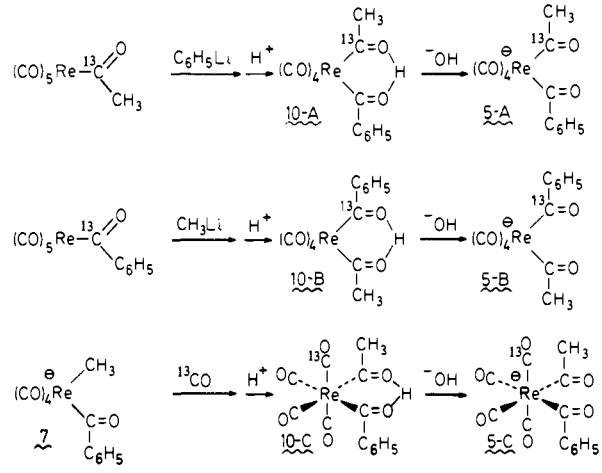
$N(CH_3)_4^+[cis\text{-}(CO)_4Re(COCH_3)(COC_6H_5)]^-$ (**5**) is similar to manganese compound **1**, but it is substantially more thermally stable.[6] **5** decarbonylates at 68.6 °C with a half-life of 81 min

(5) Casey, C. P.; Scheck, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 2728.

Scheme II



Scheme III



to give an equilibrium 15:1 mixture[7] of phenylacetyl compound **6** and methylbenzoyl compound **7** (Scheme II). Thus the alkylacetylmetal compounds proposed as an intermediate in the thermal decomposition of manganese compound **1** to acetophenone can be isolated in the case of the decomposition of the analogous rhenium compound **5**. Phenylacetylrhenium compound **6** and methylbenzoylrhenium compound **7** equilibrate with one another much faster than they are formed from **5**; the half-life for equilibration is about 110 min at only 36 °C.[6] Thus the predominant formation of phenyl migration product **6** from **5** is a measure of the greater thermodynamic stability of **6** compared with **7** and not a reflection of kinetic migratory aptitudes.

Information concerning the relative migratory aptitudes of methyl and phenyl in this system was obtained indirectly from kinetic studies of phosphine substitution reactions.[6] Triethylphosphine reacts with **7** to give $N(CH_3)_4^+[fac\text{-}(CO)_3[P(CH_2CH_3)_3]Re(COCH_3)(COC_6H_5)]^-$ (**8**) at a rate that is independent of phosphine concentration and 28 times faster than the rate of isomerization of **7** to **6**. This observation was taken as evidence that the coordinatively unsaturated intermediate **9** formed from **7** is efficiently trapped by $P(CH_2CH_3)_3$ but reverts to **7** by a retro methyl migration 28 times faster than it undergoes phenyl

(6) Casey, C. P.; Scheck, D. M. *J. Organomet. Chem.* **1977**, *142*, C12. Casey, C. P., Scheck, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 2723.

(7) In the course of this study, we have accurately determined the 270-MHz ^{1}H NMR spectra of equilibrium mixtures of **6**:**7** and find that the ratio of isomers is 15:1, not 50:1 as we had previously estimated.[6]

(8) The synthesis and X-ray crystal structure of protonated diacetyltetracarbonylrhenate has been reported: Lukehart, C. M.; Zeile, J. V. *J. Am. Chem. Soc.* **1976**, *98*, 2365.

migration to give the thermodynamically favored **6**.

Results

Synthesis of ^{13}C-Labeled Analogues of 5. To study the stereochemistry of the conversion of diacylrhenium compound **5** to phenylacetylrhenium compound **6**, we synthesized three stereospecifically labeled derivatives of **5** (Scheme III). Reaction of $(CO)_5Re^{13}COCH_3$ (prepared from $NaRe(CO)_5$ and $CH_3{}^{13}COCl$) with phenyllithium followed by acidification with HCl gave protonated diacylrhenium compound **10A**,[6] which was purified by column chromatography and then treated with $N(CH_3)_4{}^+OH^-$ to give crystalline $N(CH_3)_4{}^+[cis\text{-}(CO)_4Re(^{13}COCH_3)(COC_6H_5)]^-$ (**5A**). Similarly, benzoyl-labeled material $N(CH_3)_4{}^+[cis\text{-}(CO)_4Re(COCH_3)(^{13}COC_6H_5)]^-$ (**5B**) was prepared from $(CO)_5Re^{13}COC_6H_5$ and methyllithium and purified by chromatography of its protonated derivative **10B**.

The reactions of both **6** and **7** with CO were investigated as possible routes to ^{13}CO-labeled **5**. Reaction of phenylacetyl compound **6** with 1650 psi of CO led to carbonylation only after prolonged heating at elevated temperatures (83% conversion to **5** after 7.5 h at 70 °C). To avoid these severe reaction conditions, which might have led to some scrambling of ^{13}CO label, we studied the carbonylation of methylbenzoyl compound **7**, which had undergone reaction with $P(CH_2CH_3)_3$ 1450 times faster than **6** to produce the same phosphine-substituted diacyl compound **8**. The reaction of a 2:1 mixture of **7**:**6** with 400 psi of 90% ^{13}CO for 2 h at 30 °C gave a mixture containing 59% carbonylation product **5**, 4% unreacted methylbenzoyl compound **7**, and 37% **6**, which is unreactive toward CO under these conditions. The mixture was treated with HCl to produce **10C**, which was separated by chromatography and then treated with $N(CH_3)_4{}^+OH^-$ in CH_2Cl_2 to produce pure $N(CH_3)_4{}^+[fac\text{-}(CO)_3(^{13}CO)Re(COCH_3)(COC_6H_5)]^-$ (**5C**). Within experimental error (±1%), all of the ^{13}CO label was incorporated into a position cis to both the acetyl and the benzoyl ligands. The stereochemical assignment of **5C** was unequivocally made on the basis of ^{13}C NMR spectra (vide infra).

This synthesis of ^{13}CO-labeled **5C** not only provided stereospecifically labeled material for studies of the decarbonylation of **5** but also established that CO reacts with the five-coordinate diacylrhenium intermediate stereospecifically at a site cis to both the acetyl and the benzoyl ligands. Moreover, the principle of microscopic reversibility requires that CO leave **5** preferentially from a position cis to both acyl ligands.

^{13}C NMR Spectra and Assignments. In order to determine the stereochemistry of the conversion of ^{13}C-labeled derivatives of **5** to a 15:1 mixture of **6**:**7**,[7] it was necessary to resolve and to assign the CO and acyl resonances in the ^{13}C NMR spectra of **5**–**7**. Furthermore, for these quantitative studies, it was also necessary to obtain good integrations of the various resonances. ^{185}Re (37%) and ^{187}Re (63%) both are spin $^5/_2$ nuclei with large quadrupole moments. The quadrupole moment of the rhenium nuclei greatly broadened the room-temperature ^{13}C resonances of carbons directly bonded to rhenium. So that the extent of quadrupolar broadening could be reduced, the ^{13}C NMR were taken at −30 °C; low temperature has often been used to reduce quadrupolar broadening.[9] ^{13}C spectra were obtained in the presence of $Cr(acac)_3$, a shiftless relaxation reagent,[10] which helped to reduce the T_1 of metal carbonyls and allowed good integrations to be obtained even when 1.5-s intervals between pulses were employed. The ^{13}C spectra of **5**–**7** are listed in Table I.

For **5**, the acetyl and the benzoyl resonances were readily assigned since the ^{13}C-labeled compounds **5A** and **5B** were available. There are three chemically different kinds of CO ligand in **5**, and separate resonances were seen for each. The two CO ligands cis to both acyl groups of **5** appeared at δ 194.6, and their intensity was twice that of the other CO resonances; this is the

Table I. ^{13}C NMR Spectra of Rhenium Compounds[a]

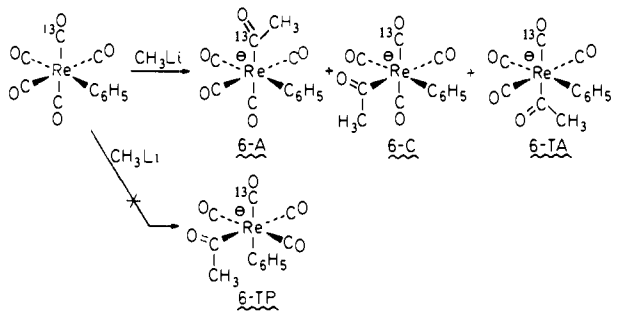
	acyl resonances		CO resonances					Ph resonances				CH₃	$N(CH_3)_4{}^+$
	COC_6H_5	$COCH_3$	OC–Re–CO	OC–Re–$COCH_3$	OC–Re–COC_6H_5	OC–ReCH₃	OC–Re–C_6H_5	ipso	para	ortho	meta		
$(CO)_5ReCOC_6H_5$	243.1		184.9		183.2			153.6	131.6	(128.9, 128.0)			
$(CO)_5ReC_6H_5$			185.1				183.7	(135.8, 124.5)		(145.9, 129.0)			
$(CO)_4Re(COCH_3)(COC_6H_5)^-$, **5**	262.4	259.4	194.6	196.3	195.4			157.5	128.5	(127.4, 125.8)		53.7	55.5
$(CO)_4Re(COCH_3)(C_6H_5)^-$, **6**		263.3	196.3	195.6			195.8	151.8	121.3	144.8	126.5	54.7	55.2
$(CO)_4Re(COC_6H_5)(CH_3)^-$, **7**	264.5		198.0		(196.4 and 195.0)			156.2	128.4	(127.3, 126.1)		−26.7	55.7

[a] Spectra taken in acetone-d_6 containing 0.09 M $Cr(acac)_3$ at −30 °C on JEOL FX-200 at 50.1 MHz except for $(CO)_5ReCOC_6H_5$, which was taken in THF-d_8.

(9) Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *80*, C31. Aime, S.; Gervasio, G.; Milone, L.; Rosenberg, E. *Transition Met. Chem.* **1976**, *1*, 177.

(10) Gansow, O. A.; Burke, A. R.; LaMar, G. N. *J. Chem. Soc., Chem. Commun.* **1972**, 456.

Scheme IV



signal that is greatly enhanced for **5C**. The resonances due to the two different CO ligands trans to the acyl groups appeared at δ 196.3 and 195.4 and were assigned on the basis of observed ^{13}C–^{13}C coupling constants. The coupling of carbons trans to one another in a metal complex is expected to be greater than carbons cis to one another.[11] In **5B**, only the higher field CO resonance is split ($J_{^{13}C-^{13}C}$ = 7 Hz) by coupling to the 90% ^{13}C-labeled benzoyl carbon atom. In **5A**, only the lower field CO resonance is split ($J_{^{13}C-^{13}C}$ = 6 Hz) by coupling to the 90% ^{13}C-labeled acetyl carbon atom. Consequently, the resonance at δ 195.4 is assigned to the CO trans to the benzoyl group, and the resonance at δ 196.3 is assigned to the CO trans to the acetyl group.

For phenylacetylrhenium compound **6**, the acetylcarbonyl ^{13}C resonance appears at δ 263.3 and is well downfield from the acyl resonances of **5**. The CO resonances of **6** appear as a 2:1:1 pattern at δ 196.3, 195.8, and 195.6. The CO resonance of **6** with relative intensity 2 was readily assigned to the two CO ligands cis to both the phenyl and acetyl groups of **6**, but the resonances due to the remaining CO ligands were difficult to assign and were not completely resolved due to their 0.2-ppm chemical shift difference. Attempts to assign the peaks by looking for nuclear Overhauser effect enhancements of the ^{13}CO carbonyl peaks upon irradiation of the methyl hydrogens, of the *o*-phenyl hydrogens, and of the *m*-phenyl hydrogens all proved inconclusive.

The assignment of the CO resonances of **6** was eventually made on the basis of a stereospecific synthesis of labeled **6**. From our earlier work we knew that reaction of CH_3Li with $(CO)_5ReC_6H_5$ produces exclusively *cis*-$(CO)_4Re(COCH_3)C_6H_5^-$ (**6**), but we did not know whether **6** was the thermodynamically favored isomer or the kinetically formed stereospecific product. That is, we could not a priori rule out the possibility that CH_3Li reacts with $(CO)_5ReC_6H_5$ to produce *trans*-$(CO)_4Re(COCH_3)C_6H_5^-$, which then isomerizes to the cis-isomer **6**. However, if the reaction of CH_3Li with $(CO)_5ReC_6H_5$ produced cis-isomer **6** stereospecifically, then the reaction of CH_3Li with *cis*-$(CO)_4(^{13}CO)ReC_6H_5$ should lead to a 1:2:1 mixture of **6A**:**6C**:**6TA** (Scheme IV). None of **6TP** with ^{13}CO trans to phenyl would be produced, and the ^{13}CO resonance absent in the product mixture could be rigorously assigned to this carbonyl group.

Decarbonylation of 90% labeled $(CO)_5Re^{13}COC_6H_5$ led to the stereospecific formation of *cis*-$(CO)_4(^{13}CO)ReC_6H_5$. Reaction of CH_3Li with *cis*-$(CO)_4(^{13}CO)ReC_6H_5$ followed by cation exchange with $N(CH_3)_4^+Cl^-$ led to the isolation of **6**. The ^{13}C NMR spectrum of this sample of **6** had major resonances at δ 263.3 for the acetyl carbonyl of **6A**, at δ 196.3 for CO cis to both phenyl and acetyl of **6C**, and at δ 195.6 now assignable to the CO trans to acetyl of **6TA** in a 1:2:1 ratio. No resonance for the CO trans to phenyl of **6TP** at δ 195.8 was visible. Since the chemical shifts of **6TA** and **6TP** differ by only 0.2 ppm, we independently confirmed that the lower field peak at δ 195.8 assigned to **6TP** was the missing resonance by diluting the labeled material by addition of natural abundance **6**. In the ^{13}C NMR of a mixture of labeled **6** and natural abundance **6**, the lower field resonance at δ 195.8 due to **6TP** was clearly present but was much smaller than the peak at δ 195.6 due to **6TA**. These observations demonstrate that the reaction of CH_3Li with $(CO)_4(^{13}CO)ReC_6H_5$ is stereospecifically cis and rigorously establish the ^{13}C chemical shift assignments of **6**.

For methylbenzoylrhenium compound **7**, the benzoyl carbonyl ^{13}C resonance appears at δ 264.5 and is downfield from the acyl resonances of **5** and **6**. The CO resonances of **7** appear as a 2:1:1 pattern at δ 198.0, 196.4, and 195.0. The resonance at δ 198.0 of intensity 2 was assigned to the two CO ligands cis to both the methyl and benzoyl groups of **7**. No attempt was made to assign the resonances of the CO's trans to methyl and benzoyl since **7** is not a major product of the decomposition of **5**.

In studying the decarbonylation of **5C** to **6**, it was crucial to be able to observe all the CO resonances of **6** (δ 196.3, 195.8, 195.6) in the presence of the very strong resonance at δ 194.6 due to the 90% enriched ^{13}CO ligand cis to both the acyl groups of **5C**, and fortunately this was readily achieved. The close proximity of the other CO resonances of **5C** (δ 196.3 and 195.4) with those of **6** did not cause problems since these sites in **5C** had only natural abundance of ^{13}C.

Stereochemistry of the Conversion of 5 to 6. Earlier we had studied the kinetics of the conversion of **5** to a mixture of **6** and **7** and found that the half-life for decarbonylation was 82 min at 68.6 °C. For studies of the decarbonylation of the labeled compounds **5A–C**, we examined the stereochemistry after ~40% conversion to **6** (1 h), after 90% conversion to **6** (5 h), and at longer times (16 and 38 h), where the stereochemical stability of **6** could be tested.

Before the labeled compounds were studied, the thermolysis of an acetone-d_6 solution of unlabeled **5** was examined at 68.5 °C in a sealed NMR tube. As expected, these studies showed that **5** was converted to a mixture of 57% **5**, 40% **6**, and 3% **7** after 1 h at 68.5 °C. After 38 h, the mixture consisted of 3% **5**, 91% **6**, and 6% **7**; the decarbonylation of **5** does not proceed to completion because an equilibrium between **5** and (**6** + CO) is set up in this closed system.[7]

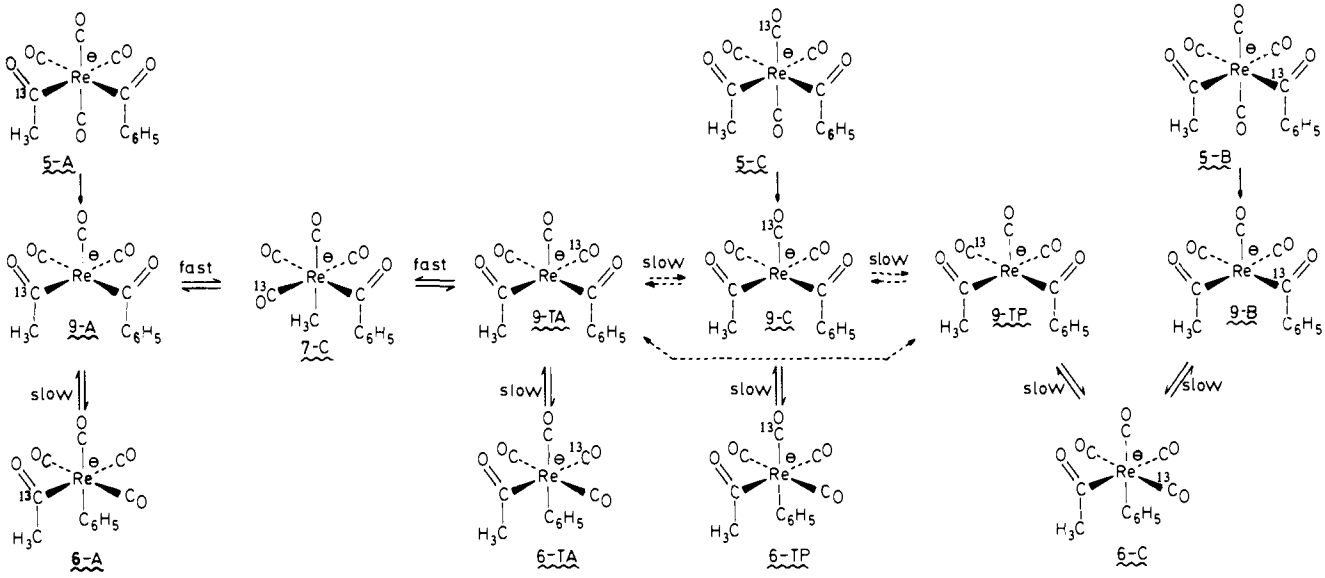
The decarbonylation of [^{13}C]benzoyl-labeled **5B** was the most stereospecific and the most straightforward of the reactions studied. After 1 h at 68.6 °C, the major peaks in the ^{13}C NMR spectrum were at δ 262.5 due to starting material **5B** (55% of total ^{13}C intensity) and at δ 196.3 due to the CO ligands cis to both the phenyl and acetyl groups of **6C** (39%). In addition we also observed small peaks at δ 264.2 assigned to [^{13}C]benzoyl-labeled **7B** (1.5%) and at δ 195.6 (sh, <0.7%) and 195.4 (0.7%) assigned to **6TP** and **6TA**, respectively. Thus, the major initial product from the decomposition of **5B** is **6C**, which results from loss of a CO from a site cis to both the acetyl and benzoyl ligands followed by migration of phenyl to this vacant site.

Thermolysis of ^{13}C-labeled **5A** at 68.6 °C for 1 h gave rise to two major new resonances. In addition to the acetyl resonance of starting material **5A** at δ 259.4 (48% of total ^{13}C intensity), new resonances of nearly equal intensity appeared at δ 263.1 (19%) due to [^{13}C]acetyl labeled **6A** and at δ 195.5 (17%) due to ^{13}CO trans to the acetyl group in **6TA**. These products are readily explained by initial loss of CO from a site cis to both acyl groups, then rapid and reversible methyl migration to the vacant site, which scrambles ^{13}CO label equally between the acetyl group and the CO trans to it, and finally phenyl migration to give the stable products **6A** and **6TA**. In addition to the resonances mentioned above, ^{13}C signals were also observed at δ 195.8 due to ^{13}CO trans to phenyl in **6TP** (5%) and at δ 196.1 for **6C** (14%). These nonstereospecific products amount to 20% of decarbonylation product **6** and arise via isomerization of the coordinatively unsaturated intermediate prior to phenyl migration (vide infra). Resonances at δ 198.1 (3%) due to the CO ligands cis to both the methyl and benzoyl groups of **7** and at δ 194.5 (2%) due to the CO ligands cis to both acyl groups of **5** were also seen.

More substantial loss of stereochemistry was observed in the thermolysis of ^{13}C-labeled **5C** at 68.6 °C for 1 h. In addition to the signal for the CO ligands cis to both acyl groups of starting material **5C** at δ 194.2 (63% of total ^{13}C intensity), a major new peak appeared at δ 195.6 (17%) due to CO trans to phenyl of **6TP**.

(11) Tachikawa, M.; Richter, S. I.; Shapley, J. R. *J. Organomet. Chem.* **1977**, *128*, C9. Aime, S.; Osella, D. *J. Chem. Soc., Chem. Commun.* **1981**, 300.

Scheme V



This product is the result of initial loss of unlabeled CO from a position cis to both acyl groups in **5C** followed by migration of phenyl to this vacant site. In addition to **6TP**, new signals were also observed at δ 196.1 due to the CO ligands cis to both the phenyl and acetyl groups of **6C** (10%), at δ 195.4 due to the CO trans to the acetyl group of **6TA** (5%), and at δ 264.1 due to the acetyl group of **6A** (3%). The nonstereospecific products **6C**, **6TA**, and **6A** amount to 52% of the decarbonylation product **6** and arise via isomerization of the coordinatively unsaturated intermediate prior to phenyl migration (vide infra).

At longer reaction times, the thermolyses of **5A**, **5B**, and **5C** all led to nearly complete loss of stereochemistry and formation of randomly labeled **6**. In the thermolysis of [^{13}C]benzoyl-labeled **5B**, the initial product was predominantly **6C** in which the ^{13}C label is cis to both the acetyl and the phenyl groups. But after 38 h at 68.6 °C, the ^{13}C NMR indicated that label had scrambled to give statistically labeled **6**. This ^{13}C NMR spectrum also showed the presence of some acetophenone from decomposition of **6** and of some **5** in equilibrium with **6**.

Similarly, in the thermolysis of [^{13}C]acetyl labeled **5A**, the initial stereospecific products were acetyl labeled **6A** (δ 263.2) and **6TA** (δ 195.6). In the ^{13}C NMR spectra taken after 5, 16, and 38 h at 68.6 °C, new peaks grew in at δ 196.3 (**6C**) at at 195.8 (**6TP**). Since the chemical shifts of **6TA** and **6TP** differ by only 0.2 ppm and since our ability to reproduce chemical shifts was about ±0.5 ppm, the observation that the new peak due to **6TP** grew in on the low-field side of the initial peak due to **6TA** was important to our assignment of resonances in this thermolysis.

In the thermolysis of **5C**, the initial stereospecific product was **6TP** (δ 195.8). At longer reaction times new peaks grew in at δ 263.2 due to **6A**, at δ 196.3 due to **6C**, and upfield of the resonance for **6TP** at δ 195.6 due to **6TA**. The observation that the new peak at δ 195.6 grew in on the upfield side of the peak for **6TP** was essential to our assignment of resonances in this thermolysis.

Discussion

The stereochemistry and mechanism of the decarbonylation of acetylbenzoylrhenium compound **5** to phenylacetylrhenium compound **6** will be discussed by making full use of Scheme V. The decarbonylation reaction begins by thermal dissociation of one of the two equivalent CO ligands cis to both the acetyl and the benzoyl ligands of **5**. The stereochemistry of CO loss was rigorously established by demonstrating that methylbenzoyl compound **7** reacts with ^{13}CO stereospecifically to introduce ^{13}CO into a position cis to both the acetyl and benzoyl ligands of **5C**. The principle of microscopic reversibility then requires selective loss of CO from this same site. The observed stereochemistry of CO dissociation is in accord with previous studies that demonstrated that acyl groups selectively activate loss of cis CO groups.[1,12]

The five-coordinate intermediate **9** generated by loss of CO from **5** has three options: (1) it can migrate methyl from the acetyl ligand to rhenium to produce **7**; (2) it can migrate phenyl from the benzoyl ligand to rhenium to produce **6**; (3) it can undergo a rearrangement to scramble the locations of labeled CO ligands. From earlier studies, we knew that methyl migration is much faster than phenyl migration,[6] but we did not know the rate of CO scrambling.

Several other aspects of Scheme V require comment here. First, previous studies of unlabeled material[6] had established that phenyl migration product **6** is thermodynamically favored over the more rapidly formed methyl migration product **7**. Second, the equilibration of **7** and **6** occurs via five-coordinate intermediate **9** and is more rapid than the formation of **7** and **6** from diacyl compound **5**. The formation of five-coordinate intermediate **9** from **6** by phenyl migration to CO occurs at about half the rate that **9** is generated by CO loss from **5**. The rate of formation of **9** from **7** by methyl migration to CO was about 1450 times faster than the formation of **9** from **6** by phenyl migration to CO.

For [^{13}C]benzoyl-labeled compound **5B**, we observed clean formation of stereospecifically labeled fac-isomer **6C**. This result is easily understood since the ^{13}C label is held in the benzoyl group of **9B** and neither reversible methyl migration to give **7** nor scrambling of CO ligands in **9B** leads to any change in **9B**. Migration of phenyl to rhenium converts **9B** stereospecifically to isomer **6C**.

For [^{13}C]acetyl-labeled compound **5A**, approximately 70% of the material was converted to a ~1:1 mixture of acetyl-labeled **6A** and **6TA** in which the label is trans to the acetyl ligand. These two products are readily explained by a rapid and reversible migration of methyl to rhenium in five-coordinate intermediate **9**. This rapid reversible migration proceeding through intermediate **7C** scrambles label between the acetyl group (**9A**) and the CO ligand trans to it (**9TA**) and is much faster than conversion of **9** to the thermodynamically favored phenyl migration product **6**. Phenyl migration eventually occurs and gives a 1:1 mixture of **6A** and **6TA**. Five-coordinate **9TA** has a ^{13}CO ligand trans to the acetyl ligand which can undergo CO scrambling to give either **9C** or **9TP**. CO scrambling of **9TA** occurs at a rate comparable to phenyl migration to produce **6**. The rearranged intermediates **9C** and **9TP** formed by CO scrambling of **9TA** eventually undergo phenyl migration to produce the nonstereospecific products **6C** and **6TP**.

(12) Flood, T. C.; Jensen, J. E.; Statler, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4410 and references therein.

For ^{13}CO-labeled **5C**, loss of ^{13}CO is not observable by our ^{13}C NMR analytical procedure, and only those products arising via loss of unlabeled CO from the position cis to both the acetyl and benzoyl ligands is observed. The major ^{13}C-labeled product arising from **5C** is **6TP** (48% of ^{13}C labeled **6**) in which the ^{13}CO ligand is trans to the phenyl group. This product arises from phenyl migration to rhenium in **9C**. Rapid reversible migration of methyl from the acetyl group to rhenium and on to the CO initially trans to the acetyl group of **9C** does not alter the labeling pattern of **9C**. However, CO scrambling of **9C** can lead to **9TP**, **9TA**, and **9A** (via a rapid reversible methyl migration to **7C**). This CO scrambling followed by phenyl migration produces **6C** (10%), **6TA** (5%), and **6A** (3%). The loss of stereochemistry in the decarbonylation of **5C** (52%) was more than twice that seen for **5A** (20%). In the decomposition of **5C**, all of the ^{13}C label is on a ^{13}CO ligand which can scramble to other sites. However, in the decomposition of **5A** a rapid reversible methyl migration initially puts half the label into the acetyl ligand of **9A**, and CO scrambling of **9A** does not affect the ^{13}C labeling pattern. Thus for **5A** about half the ^{13}C label is parked in the acetyl ligand and cannot rearrange. Similarly for **5B**, nearly all of the ^{13}C label is parked in the benzoyl ligand, and **5B** decarbonylates to give **6C** with a high stereospecificity at low conversions.

When the thermolyses of **5A**, **5B**, or **5C** were followed to longer periods of time, complete statistical scrambling of ^{13}CO to all sites of **6** was observed. This is due to the fact that **6** migrates phenyl to CO to regenerate five-coordinate intermediate **9** at about half the rate that **9** is formed from **5**. Consequently, at long times, continual regeneration of intermediate **9**, which scrambles CO at a significant rate, eventually leads to scrambling of label in **6**.

Our data from the decarbonylation are in good agreement with a CO scrambling mechanism that allows an interchange of any pair of CO ligands in intermediate **9**. In the decarbonylation of **5A**, rearrangement products are derived about equally from rearrangement of **9A** to **9C**, which leads to product **6TP** (5%) and from rearrangement of **9A** to **9TP**, which leads to product **6C** (4%). Sequential rearrangement of **9A** to **9C** to **9TP** would have resulted in formation of substantially more **6TP** than **6C**.

A kinetic model for the decarbonylation of labeled **5** was constructed based on Scheme V. The model included rates of formation of intermediate **9** from **5** (1.48×10^{-4} s^{-1}), **6** (6.6×10^{-4} s^{-1}), and **7** (0.1 s^{-1}) and relative rates of methyl migration (**9** → **7**), phenyl migration (**9** → **6**), and CO scrambling (**9TA** → **9C** and **9TP**) of 28:1:1.1. With these rate parameters, a good qualitative fit of the products of decarbonylation of **5A–C** was obtained.

The significant new finding here is that CO scrambling is slow relative to methyl migration but comparable to the rate of phenyl migration. Moreover, the stereochemistry observed here for the decomposition of the diacylrhenium compound **5** now provides a confirmation of the type of mechanism we proposed earlier to explain the labeling pattern of acetophenone formed from decomposition of the labeled diacylmanganese compounds discussed in the Introduction.[5]

A pattern is beginning to emerge concerning the fluxional behavior of five-coordinate d^6 metal complexes. The rates of isomerization of the intermediate, of ligand capture of a vacant coordination site, and of migration of a group from an acyl ligand to the metal are all very rapid and of the same order of magnitude. Fluxional five-coordinate d^6 intermediates in which rearrangement is more rapid than addition of an external ligand include $(CO)_4MnBr$,[13] $(CO)_4ReBr$,[13] $Cr(CO)_5$,[14] $Mo(CO)_5$,[15] $(phen)Cr(CO)_3$,[16] $W(CO)_4(alkene)$,[17] $Mo(CO)_4P(C_6H_5)_3$ (vacant site trans to phosphine),[18] and $(CO)_4Cr{=}\overline{CCH_2CH_2CH_2O}$.[19] Rigid five-coordinate d^6 intermediates in which ligand capture is more rapid than rearrangement include $(CO)_4Mo(alkene)$,[20] $Mo(CO)_4PR_3$ (vacant site cis to phosphine),[20] and $(CO)_4Mo{=}C(OCH_3)C_6H_5$.[19] Flood has recently reported that $(CO)_4MnC(OCH_3)$ undergoes ligand capture more rapidly than rearrangement in THF but that these relative rates are reversed in HMPA.[12] Our results indicate that methyl migration from an acetyl ligand to a five-coordinate metal complex is substantially more rapid than rearrangement of the metal complex but phenyl migration and rearrangement occur at very similar rates.

Experimental Section

General Practices. $(CO)_5ReCOC_6H_5$, $(CO)_5ReCOCH_3$, and $(CO)_5ReCH_3$ were prepared by the method of Hieber[21] and purified by column chromatography (silica gel, hexane). $N(CH_3)_4^+[(CO)_4Re(COCH_3)(COC_6H_5)]^-$ (**5**), $N(CH_3)_4^+[(CO)_4Re(C_6H_5)(COCH_3)]^-$ (**6**), and $N(CH_3)_4^+[(CO)_4Re(CH_3)(COC_6H_5)]^-$ (**7**) were prepared as previously described.[5]

All ^1H NMR spectra were taken in acetone-d_6 on a Bruker WH-270 or a JEOL FX200 spectrometer. Infrared spectra were obtained on a Beckman IR 4230 spectrometer.

$(CO)_5Re^{13}COCH_3$. $CH_3{}^{13}COCl$ (1.5 mL, 1.6 g, 21 mmol), prepared from sodium acetate-*1*-^{13}C (90% ^{13}C, Merck) and phthaloyl chloride,[6,22] was added to a THF solution of $NaRe(CO)_5$ prepared from $Re_2(CO)_{10}$ (3.0 g, 4.6 mmol) and 1% Na–Hg amalgam. The resulting $(CO)_5Re^{13}COCH_3$ (3.1 g, 91% yield) was purified by vacuum sublimation at 50 °C.

$N(CH_3)_4^+[(CO)_4Re(^{13}COCH_3)(COC_6H_5)]^-$ (5A). C_6H_5Li (13.0 mL, 0.99 M in ether, 12.9 mmol) was added to a solution of $(CO)_5Re(^{13}COCH_3)$ (3.1 g, 8.3 mmol) in 30 mL of THF at −78 °C. After 1 h at −78 °C, HCl (5.0 mL, 4.4 M in ether, 22 mmol) was added. Solvent was evaporated, and the residue was purified by column chromatography (silica gel, 2:1 hexane:chloroform) to give $(CO)_4Re(COC_6H_5)(^{13}COCH_3)H$ (**10A**) (0.59 g, 16% yield). **10A** was dissolved in 15 mL of CH_2Cl_2, and $N(CH_3)_4^+OH^-$ (0.5 mL, 2.76 M in CH_3OH, 1.38 mmol, Aldrich) was added. Solvent was evaporated under vacuum, the residue was dissolved in THF and filtered, THF was evaporated under vacuum, and the resulting orange solid was washed with ether and dried under vacuum to give **5A** (0.38 g, 55% from **10-A**): ^1H NMR (acetone-d_6, 200 MHz) δ 7.4 (m, 2 H), 7.2 (m, 3 H), 3.38 (s, 12 H), 2.25 (d, $J_{^{13}CH}$ = 4.4 Hz, 3 H, $^{13}COCH_3$); ^{13}C NMR (acetone-d_6, 0.09 M Cr(acac)$_3$, −30 °C, 50.1 MHz) δ 262.4 (COC_6H_5), 259.5 ($COCH_3$, ~90× enhanced), 195.5 (d, $J_{^{13}C^{13}C}$ = 6 Hz, CO trans to $^{13}COCH_3$), 194.5 (CO trans to COC_6H_5), 193.6 (CO's cis to both acyl groups), 157.3 (ipso), 128.5 (para), 127.5 and 125.8 (ortho and meta), 55.4 ($N(CH_3)_4^+$), 53.6 (d, $J_{^{13}C-^{13}C}$ = 19 Hz, $^{13}CH_3{}^{13}CO$); IR (THF) 2062 (m), 1963 (s), 1942 (s), 1912 (s), 1540 (m) cm^{-1}.

$(CO)_5Re^{13}COC_6H_5$. $C_6H_5{}^{13}COCl$ (3.1 g, 22.4 mmol), prepared from $C_6H_5{}^{13}CO_2H$ (90% ^{13}C, Merck) and $SOCl_2$, was added to a THF solution of $NaRe(CO)_5$ prepared from $Re_2(CO)_{10}$ (4.0 g, 6.1 mmol) and 0.9% Na–Hg amalgam. Solvent was evaporated, and the residue was sublimed at 85 °C (10^{-3} mmHg) to give 3.6 g of crude product. Sublimation at 25 °C (10^{-3} mmHg) removed $(CO)_5ReC_6H_5$ and left $(CO)_5Re^{13}COC_6H_5$ (2.60 g, 49% yield, containing about 10% *cis*-$(CO)_4(^{13}CO)ReC_6H_5$): ^1H NMR (acetone-d_6, 270 MHz) δ 7.53 (m, 2 H), 7.44 (m, 3 H), multiplets due to $(CO)_5ReC_6H_5$ at δ 7.7 and 7.0); ^{13}C NMR (THF-d_8, 0.09 M Cr(aca)$_3$, −30 °C, 50.1 MHz) δ 243.1 ($^{13}COC_6H_5$, ~90× enhanced), 184.9 (cis CO's), 183.2 (trans CO), 153.6 (d, $J_{^{13}C-^{13}C}$ = 31 Hz, ipso), 131.6 (para), 128.9 and 128.0 (ortho and meta), peak at 185.3 due to *cis*-$(CO)_4(^{13}CO)ReC_6H_5$.

$N(CH_3)_4^+[(CO)_4Re(COCH_3)(^{13}COC_6H_5)]^-$ (5B). CH_3Li (5.0 mL, 1.6 M in ether, 8.0 mmol) was added to a solution of $(CO)_5Re(^{13}COC_6H_5)$ (2.79 g, 6.4 mmol, 90% ^{13}C) in 30 mL THF at −78 °C. After 1 h at −78 °C, HCl (2.0 mL, 5.8 M in ether, 11.6 mmol) was added. Workup similar to that used for **5A** gave $(CO)_4Re(COCH_3)(^{13}COC_6H_5)H$ (**10B**) (1.55 g, 53% yield), which was then treated with $N(CH_3)_4^+OH^-$ as described for **5A** to give **5B** (0.90 g, 51% yield from **10B**): ^1H NMR (acetone-d_6, 270 MHz) δ 7.4 (m, 2 H), 7.2 (m, 3 H), 3.41 (s, 12 H), 2.25 (s, 3 H); ^{13}C NMR (acetone-d_6, 0.09 M Cr(acac)$_3$, −30 °C, 50.1 MHz) δ 262.3 ($^{13}COC_6H_5$, ~90× enhanced), 259.7 ($COCH_3$), 196.1 (CO trans to $COCH_3$), 195.1 (d, $J_{^{13}C-^{13}C}$ = 7 Hz, CO trans to $^{13}COC_6H_5$), 194.3 (CO's cis to both acyl groups), 156.9 (d, $J_{^{13}C-^{13}C}$ = 26 Hz, ipso), 128.5

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(para), 127.4 and 125.7 (ortho and para), 55.3 ($N(CH_3)_4^+$), 53.6 ($CO\text{-}CH_3$).

$N(CH_3)_4^+$[*fac*-$(CO)_3(^{13}CO)Re(COCH_3)(COC_6H_5)]^-$ (5C). A solution of a 2:1 mixture (0.90 g, 1.83 mmol) of $N(CH_3)_4^+[(CO)_4Re(CH_3)(COC_6H_5)]^-$ (**7**): $N(CH_3)_4^+[(CO)_4Re(C_6H_5)(COCH_3)]^-$ (**6**) in 10 mL of acetone was placed in a 22-mL stainless steel Parr bomb and degassed by three freeze–pump–thaw cycles on a vacuum line. ^{13}CO (90% ^{13}C, Mound Laboratory) was condensed into the bomb at −196 °C. The bomb was sealed and warmed to 30 °C, where the gauge pressure was 400 psi. After 2 h at 30 °C, the ^{13}CO was vented and recovered for further use.

^1H NMR of the crude reaction mixture indicated that it consisted of 59% **5** in addition to 4% unreacted **7** and 37% unreacted **6**. The mixture was reacted with HCl (0.8 mL, 4.2 M in ether, 3.4 mmol) to convert **5C** to **10C**, which was isolated by column chromatography as for **10A**. Purified **10C** (0.44 g, 0.98 mmol) was then treated with $N(CH_3)_4^+OH^-$ (0.4 mL, 2.76 M in CH_3OH, 1.1 mmol) to give pure **5C** (0.24 g, 38% yield based on **7**): ^1H NMR (acetone-d_6, 270 MHz) δ 7.44 (m, 2 H), 7.23 (m, 3 H), 3.40 (m, 12 H), 2.25 (s, 3 H). ^{13}C NMR (acetone-d_6, 0.09 M $Cr(acac)_3$, −30 °C, 50.1 MHz) δ 262.9 (COC_6H_5), 260.5 ($COCH_3$), 196.1 (CO trans to $COCH_3$), 194.2 (CO's cis to both acyl groups, ~90× enhanced), 157.0 (ipso), 128.5 (para), 127.3 and 125.5 (ortho and meta), 55.1 ($N(CH_3)_4^+$), 53.4 ($COCH_3$), a peak expected at 195.0 due to CO trans to COC_6H_5 was not observed due to the proximity of the intense peak at 194.2; IR (Nujol) 2070 (sh), 2060 (m), 2045 (m), 1970 (s), 1955 (sh), 1942 (s), 1920 (s), 1903 (s), 1560 (m), 1535 (m) cm^{-1}.

***cis*-$(CO)_4(^{13}CO)ReC_6H_5$.** A solution of $(CO)_5Re^{13}COC_6H_5$ (2.0 g, 4.63 mmol) in 75 mL of acetone was heated at 96 °C for 1.8 h in a sealed Fischer–Porter bottle. Solvent was evaporated, and the residue was chromatographed (silica gel, hexane) to give *cis*-$(CO)_4(^{13}CO)ReC_6H_5$ (1.65 g, 88% yield): ^1H NMR (acetone-d_6, 270 MHz) δ 7.5 (m, 2 H), 7.0 (m, 3 H); ^{13}C NMR (acetone-d_6, 0.09 M $Cr(acac)_3$, −30 °C, 50.1 MHz) δ 185.1 (cis CO's, ~90× enhanced), 183.7 (s, trans CO), 145.9 and 129.0 (ortho and meta), 135.8 and 124.5 (ipso and para).

Reaction of *cis*-$(CO)_4(^{13}CO)ReC_6H_5$ with CH_3Li. CH_3Li (12 mL, 0.9 M, 10.8 mmol) was added to a solution of *cis*-$(CO)_4(^{13}CO)ReC_6H_5$ (2.25 g, 5.5 mmol) in 30 mL of THF at −78 °C. The solution was stirred for 1 h at −78 °C and warmed to room temperature. Several milliliters of H_2O were added to quench excess CH_3Li, and the solvent was evaporated under vacuum. An aqueous solution of $N(CH_3)_4^+Cl^-$ (25 mL, 1 M, 25 mmol) and 25 mL of CH_2Cl_2 was added to the residue. The CH_2Cl_2 layer was separated, and solvent was removed under vacuum. The residue was dissolved in THF and filtered. THF was removed under vacuum, and the resulting yellow solid was washed with ether and dried under vacuum to give $N(CH_3)_4^+[(CO)_4Re(C_6H_5)COCH_3]^-$ (**6**, 1.47 g, 54% yield): ^1H NMR (acetone-d_6, 200 MHz) δ 7.78 (m, 2 H), 6.77 (m, 3 H), 3.36 (s, 12 H), 2.23 (s, 3 H). In the ^{13}C NMR (acetone-d_6, 0.09 M $Cr(acac)_3$, −30 °C, 50.1 MHz), three major peaks were observed in a 1:2:1 ratio at δ 263.6 ($COCH_3$), 196.1 (CO's cis to both acyl groups), 195.4 (CO trans to $COCH_3$). In the ^{13}C NMR spectrum of a 1:4.3 mixture of this material and unlabeled **6**, an additional peak appeared at δ 195.6 (CO trans to C_6H_5), which was approximately $^1/_3$ the magnitude of the peak at 195.4.

Decarbonylation of 5. Acetone-d_6 solutions of **5**, **5A**, **5B**, and **5C** (~0.4 M) that also contained 0.09 M $Cr(acac)_3$ were heated at 68.5 ± 0.2 °C in an oil bath and monitored by ^{13}C NMR at 1, 5, 16, and 38 h. Details of ^{13}C NMR spectra are presented in the Results section.

^{13}C NMR. ^{13}C NMR spectra were obtained on a JEOL FX-200 spectrometer operating at 50.10 MHz. Spectra of ~0.4 M solutions of rhenium compounds were taken in acetone-d_6 containing $Cr(acac)_3$. Chemical shifts were measured relative to the acetone carbonyl resonance at δ 206.0. The samples were prepared by vacuum transfer of acetone-d_6 into 5-mm NMR tubes containing the rhenium compound and $Cr(acac)_3$ and were sealed under vacuum. All spectra were taken at −30 °C to reduce quadrupolar broadening due to rhenium. Experimental parameters used during data acquisition included a 90° pulse angle, 1.5-s delay between pulses, and broad-band proton decoupling. Integration of the spectra of ^{13}C natural abundance samples of **5–7** were in agreement (±10%) with expected peak ratios. Estimation of relative peak areas for overlapping peaks was made by comparison of observed spectra with computer-simulated spectra calculated as a sum of Lorentzian peaks. The rate of decarbonylation of labeled **5** in the presence of $Cr(acac)_3$ as measured by ^{13}C NMR was within experimental error of the decarbonylation rate in the absence of $Cr(acac)_3$ as measured by ^1H NMR.

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Registry No. 5, 65583-15-5; **5A**, 83207-73-2; **5B**, 83207-75-4; **5C**, 83207-77-6; **6**, 65583-15-5; **6A**, 83207-79-8; **6C**, 83207-81-2; **6TA**, 83247-86-3; **6TP**, 83247-88-5; **7**, 65583-19-9; **10A**, 83214-24-8; **10B**, 83207-82-3; **10C**, 83207-83-4; $(CO)_5Re^{13}CoCH_3$, 83207-84-5; $(CO)_5Re^{13}COC_6H_5$, 83214-26-0; *cis*-$(CO)_4(^{13}CO)ReC_6H_5$, 83207-85-6; $CH_3{}^{13}COCl$, 1520-57-6; C_6H_5Li, 591-51-5; CH_3Li, 917-54-4; ^{13}CO, 1641-69-6; $C_6H_5{}^{13}COCl$, 52947-05-4; $NaRe(CO)_5$, 33634-75-2; $(CO)_5ReCOC_6H_5$, 56650-82-9; $(CO)_5ReC_6H_5$, 23625-72-1.

Crytalline-State Reaction of Cobaloxime Complexes by X-ray Exposure. 2. An Order-to-Order Racemization in the Crystal of [(*S*)-1-Cyanoethyl](pyridine)-bis(dimethylglyoximato)cobalt(III)

Yuji Ohashi,*[1a] Kazunori Yanagi,[1a] Toshiharu Kurihara,[1a] Yoshio Sasada,[1a] and Yoshiaki Ohgo[1b]

Contribution from the Laboratory of Chemistry for Natural Products, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan, and Niigata College of Pharmacy, 5829 Kamishinei-cho, Niigata 950-21, Japan. *Received March 1, 1982*

Abstract: Crystals of [(*S*)-1-cyanoethyl](pyridine)bis(dimethylglyoximato)cobalt(III) undergo racemization in the crystalline state on exposure to X-rays. The reaction follows approximate first-order kinetics. The rate constants are 2.83×10^{-6} s^{-1} at 293 K and 5.06×10^{-5} s^{-1} in the early stages at 353 K. The crystal contains two crystallographically independent molecules in the $P2_1$ cell that are related by a pseudoinversion. On exposure to X-rays, the cyanoethyl group in one of the molecules in the asymmetric unit changes its configuration so that a crystallographic inversion center appears. The space group of the crystal becomes $P2_1/n$, and the volume of the unit cell decreases. The methyl group of the reacting cyanoethyl group makes unusually short contacts with a neighboring molecule in the initial stage. The steric repulsion from such short contacts is probably a driving force for the racemization of the crystal on X-ray exposure.

In a previous paper[2] we described the crystalline-state reaction of [(*R*)-1-cyanoethyl][(*S*)-α-methylbenzylamine]bis(dimethylglyoximato)cobalt(III) (**1**; hereafter bis(dimethylglyoximato)cobalt and the complex are abbreviated to cobaloxime and the *R–S* cyano

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