

Use of Isotope Crossover Experiments in Investigating Carbon-Carbon Bond-Forming Reactions of Binuclear Dialkylcobalt Complexes

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Our present understanding of the mechanisms of organometallic reactions stems almost completely from investigation of complexes containing only one metal.^{1a,b} Recently interest has been increasing in the synthesis, structure elucidation, and reaction mechanisms of polynuclear clusters, complexes containing more than one metal.^{1c-e} This attention derives partially from the possibility that polynuclear catalysts and reagents might be designed in such a way that the metals could interact, generating cooperative systems more selective than their mononuclear analogues. Another stimulant to this work has been the relationship of cluster complexes to larger multimetal systems, such as heterogeneous catalysts.

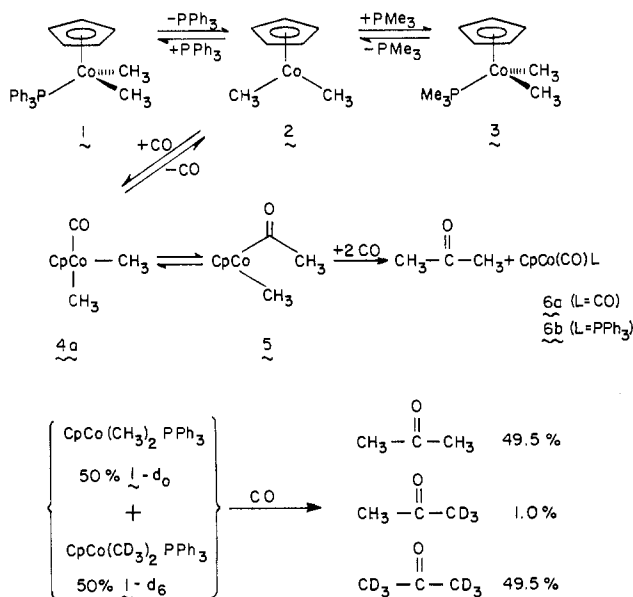
Many polynuclear clusters have been prepared and characterized, and some of these have been found to function as unique catalysts or catalyst precursors. However, very little is yet known about how chemical transformations take place at multinuclear reaction centers. Given this paucity of information, we decided a few years ago to initiate a mechanistic study of simple cluster systems containing two metal centers, in which each of the metals has a σ -bound organic ligand attached to it. We also chose to focus on reactions of these complexes in which new carbon-carbon or carbon-hydrogen bonds are formed. This Account describes our work on such a system: a binuclear alkylcobalt complex capable of transferring both alkyl groups to a molecule of carbon monoxide. In this work we have adopted as one of our highest priorities the determination of whether the cluster "holds together" during its reactions, a question that is in our opinion too often ignored in such studies. We have found that isotope crossover experiments provide a powerful tool for investigating this structural integrity question, and in this Account we outline a number of examples in which such crossover experiments have provided important, and occasionally surprising, information about the mechanisms involved in the reactions of binuclear cluster complexes. Also summarized are studies of the reactions of related mononuclear complexes which have provided information critical to understanding the chemistry of these binuclear systems.²

Reactions of (η^5 -Cyclopentadienyl)dimethyl(triphenylphosphine)cobalt

The title complex (1) is a well-characterized material³ which contains two simple alkyl groups bound to cobalt.

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Chart I



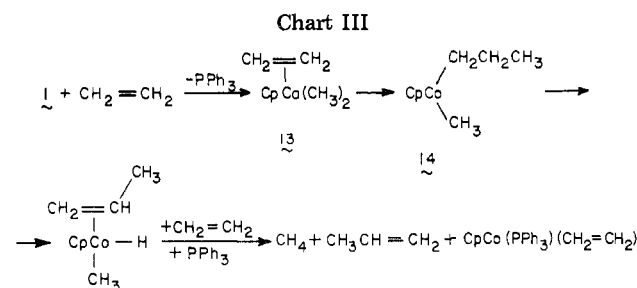
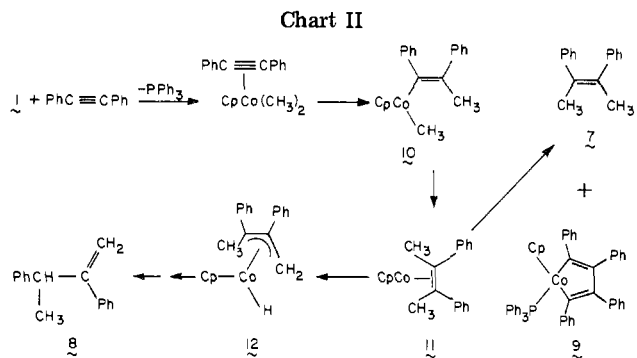
It undergoes clean C-C bond-forming reactions with a number of unsaturated organic compounds. Based on our own results in this system and carbonylations studied extensively in other organometallic complexes,⁴ the most straightforward process of this sort is the reaction of 1 with carbon monoxide. At 50 °C this leads to a quantitative yield of acetone, along with $\text{CpCo}(\text{CO})_2$

(1) (a) R. F. Heck, "Organotransition Metal Chemistry", Academic Press, New York, 1974; (b) J. K. Kochi, "Organometallic Mechanisms and Catalysis", Academic Press, New York, 1979; (c) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **85**, 451 (1976); *Science*, **196**, 839 (1977); (d) P. Chini and B. T. Heaton, *Top. Curr. Chem.*, **71**, 1 (1977); (e) H. Vahrenkamp, *Struct. Bonding (Berlin)*, **32**, 1 (1977).

(2) For recent examples of studies of reactions involving binuclear organometallic complexes, along with leading references to related work, see: (a) C. P. Kubiak and R. Eisenberg, *J. Am. Chem. Soc.*, **99**, 6129 (1977); (b) M. A. Cobb, B. Hungate, and A. Poë, *J. Chem. Soc., Dalton Trans.*, 2226 (1976); (c) J. C. Smart and C. J. Curtis, *Inorg. Chem.*, **17**, 3290 (1978); (d) P. A. Wegner, V. A. Uski, R. P. Kiester, S. Dabestani, and V. W. Day, *J. Am. Chem. Soc.*, **99**, 4846 (1977); (e) M. Y. Darensbourg, J. L. Atwood, R. R. Burch, Jr., W. E. Hunter, and N. Walker, *ibid.*, **101**, 2631 (1979); (f) J. P. Collman, R. G. Finke, P. L. Matlock, R. Wahren, and J. I. Brauman, *ibid.*, **98**, 4685 (1976); (g) J. P. Collman, R. K. Rothrock, R. G. Finke, and F. Rose-Munch, *ibid.*, **99**, 7381 (1977); (h) M. H. Chisholm, *Transition Metal Chem.*, **3**, 321 (1978); (i) J. E. Bulkowski, P. L. Burk, M. F. Ludmann, and J. A. Osborn, *J. Chem. Soc., Chem. Commun.*, 498 (1977); (k) S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter, and P. Woodward, *ibid.*, 221 (1978); (l) M. M. Olmstead, H. Hope, L. S. Benner, and A. L. Balch, *J. Am. Chem. Soc.*, **99**, 5502 (1977); (m) M. P. Brown, R. J. Puddephatt, and C. E. E. Upton, *J. Chem. Soc., Dalton Trans.*, 2490 (1976); (n) M. L. H. Green and S. J. Simpson, *J. Organometal. Chem.*, **148**, C27 (1978).

(3) (a) R. B. King, *Inorg. Chem.*, **5**, 82 (1966); (b) H. Yamazaki and N. Hagihara, *J. Organomet. Chem.*, **21**, 431 (1970).

(4) For reviews, see (a) A. Wojcicki, *Adv. Organomet. Chem.*, **11**, 87 (1973); (b) F. Calderazzo, *Angew. Chem., Int. Ed. Engl.*, **16**, 299 (1977).

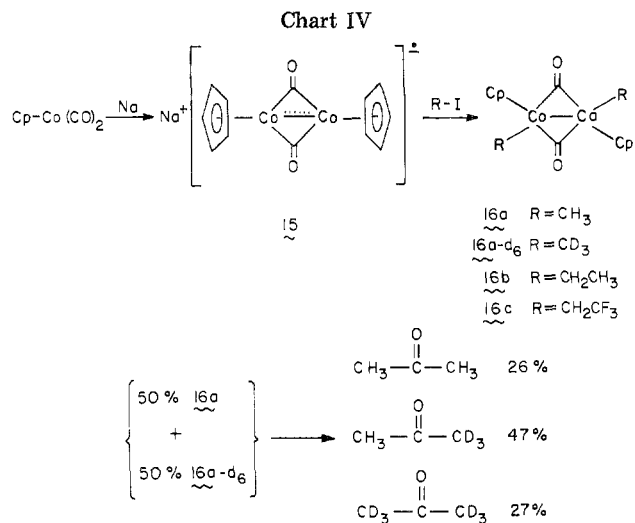


and $\text{CpCo}(\text{CO})\text{PPh}_3$ (6). The first step of this reaction, as shown in Chart I, involves replacement of phosphine by CO in the cobalt coordination sphere. Intermediate **4a** builds up to some extent and can be detected by NMR and IR spectroscopy. The next step involves migration of CH_3 to coordinated CO, leading to acyl complex **5**, and this complex undergoes reductive elimination. We believe the initial replacement reaction proceeds through 16-electron species **2**; this intermediate can be scavenged efficiently by phosphines such as $\text{P}(\text{CH}_3)_3$, which are more nucleophilic than PPh_3 . Kinetic studies show the trimethylphosphine reaction is a dissociative process, proceeding via intermediate **2**, and by analogy we assume the conversion of **1** to **4a** is dissociative as well. Carbonylation of a 50:50 mixture of 0.05 M **1** and **1-d₆**, containing completely deuterated methyl groups, leads to acetone- d_0 and acetone- d_6 containing $\leq 1\%$ acetone- d_3 , demonstrating the insertion and reductive elimination to be $\geq 98\%$ intramolecular.⁵

(5) (a) In this and the following experiments, we refer to "percent intermolecularity" as the percent of product which could have been formed in a random process generating a statistical (1:2:1) ratio of acetone- d_0 , - d_3 , and - d_6 . Equation i, where $[f_{d_3}]_p$ = fraction of d_3 acetone fraction of intermolecular product =

$$[f_{d_3}]_p \left(1 + \frac{1}{2} \left[\frac{f_{d_0}}{f_{d_6}} \right]_0 + \frac{1}{2} \left[\frac{f_{d_6}}{f_{d_0}} \right]_0 \right) \quad (\text{i})$$

product and $[f_{d_0}/f_{d_6}]_0$ = ratio of d_0 to d_6 starting material, relates the percent intermolecularity, defined in this way, to the measured percentages of the three labeled acetones. (b) Another facet of this experiment illustrates the need to carry out careful controls in order to properly interpret crossover labeling data, especially in cases where scrambling is detected. Our first experiments on the carbonylation of mixtures of **1** and **1-d₆**, carried out using relatively high concentrations of starting complex, gave substantial amounts of acetone- d_3 . Lower concentrations reduced the amount of scrambling, and the percentages shown in Chart I are those determined at a starting concentration of 0.05 M. The source of the intermolecularity was uncovered by heating complexes **1-d₀** and **1-d₆** in the absence of CO for 24 h at 60 °C (the carbonylation temperature) and an initial concentration of 0.25 M, and then diluting to 0.05 M to carry out an "intramolecular" carbonylation of the resulting mixture. This experiment gave a statistical ratio of the three labeled acetones, indicating that molecules of **1** are capable of exchanging methyl groups. The mechanism of this reaction is presently under investigation.



Complex **1** also reacts with alkynes and alkenes. Charts II and III summarize results from two reactions we have studied particularly extensively.^{6,7} Treatment of **1** with excess diphenylacetylene gives alkenes **7** and **8** and metallacycle **9**. As in the CO case, this process apparently involves initial replacement of phosphine by alkyne, followed by stereospecific cis insertion of the alkyne into one of the cobalt-methyl bonds, leading to vinyl complex **10**. Reductive elimination and scavenging of the unsaturated cobalt fragment lead to **7** and **9**, presumably via cobalt π -complex **11**. Competitive with displacement of **7** from **11** is insertion of the metal into an allylic C-H bond of the complexed alkene; this gives a π -allylcobalt hydride (**12**), which after a second reductive elimination leads ultimately to isomerized alkene **8**. In the case of ethylene, as shown in Chart III, insertion in π -complex **13** yields propyl/methyl complex **14**. β -Elimination rather than reductive elimination is the most rapid process here, and methane and propene are the organic products.

We have again used isotope labeling, in both crossover and direct analysis experiments, to provide evidence in support of the mechanisms outlined in Charts II and III. Reactions carried out with mixtures of **1** and **1-d₆** demonstrated the alkyne dialkylation to be intramolecular. The reaction of **1-d₆** with ethylene proved to be particularly important, because of a recent suggestion that such apparent insertion reactions might proceed by α -elimination mechanisms.⁸ Reaction of **1-d₆** with ethylene gave only CD_3H and $\text{CD}_3\text{CH}=\text{CH}_2$, a result which conclusively rules out the α -elimination process in this case.⁷

Thermal Decomposition of Binuclear Cobalt Dialkyls

It is becoming increasingly clear that cluster complexes can mediate many organic transformations. A crucial question in such reactions is whether the cluster is the true catalyst or reagent, or whether it fragments into smaller, transient species which are the active species.^{2,9} Our studies in the binuclear cobalt series

(6) E. R. Evitt and R. G. Bergman, *J. Am. Chem. Soc.*, **100**, 3237 (1978).

(7) E. R. Evitt and R. G. Bergman, *J. Am. Chem. Soc.*, **101**, 3973 (1979).

(8) (a) K. J. Ivin, J. J. Rooney, C. D. Stewart, M. L. H. Green, and R. Mahtab, *J. Chem. Soc., Chem. Commun.*, 604 (1978); (b) M. L. H. Green and R. Mahtab, *J. Chem. Soc., Dalton Trans.*, 262 (1979).

Table I
Selected Kinetic Data for Reactions of Mono- and Binuclear Cobalt Alkyl Complexes

reaction	conditions	rate constant, s ⁻¹
16a → acetone + clusters	THF, 33 °C	6.7 × 10 ⁻⁵
4a → acetone + clusters	THF, 35 °C	4.5 × 10 ⁻⁶
16b → 3-pentanone, C ₂ H ₅ , C ₂ H ₆ , clusters	THF, 23 °C	8.18 × 10 ⁻⁵
16c → 4c + 6 + clusters	THF, 23 °C	4.07 × 10 ⁻⁵
20, 21 → acetone + 6	THF, 0.5 atm of CO, 0 °C	5.5 × 10 ⁻⁵
20, 21 → acetone + 6	THF, 9.5 atm of CO, 0 °C	3.23 × 10 ⁻⁵
28 + PPh ₃ → 32a	C ₆ D ₆ , 0.10 M PPh ₃ , 25 °C	5.59 × 10 ⁻⁵
28 + PPh ₃ → 32a	C ₆ D ₆ , 0.93 M PPh ₃ , 28 °C	1.24 × 10 ⁻⁴

provided a means of examining this question for one system in some detail.

This study began with the largely serendipitous synthesis of a series of binuclear cobalt dialkyls. We found that chemical reduction of CpCo(CO)₂ led to the paramagnetic binuclear radical anion 15 (Chart IV), whose structure we determined by X-ray diffraction.¹⁰ Alkylation of the anion was successful with a number of primary alkyl halides. The mechanism of this process is still not clear, but it provided us with the series of neutral dialkyl complexes 16. Both thermal decomposition and carbonylation of 16a led to acetone in high yield.¹¹ The fact that this was a process initiated in a binuclear complex, and involving the formation of two new C-C bonds, greatly stimulated our interest.

Our work has focused on three complexes in the series, 16a-c. We first determined that thermal decomposition of the dimethyl complex led to acetone in 85% yield; the organometallic products of this reaction were CO-deficient cobalt carbonyl complexes which had appeared earlier¹² in the photochemical decomposition of CpCo(CO)₂. Monitoring the decomposition by NMR revealed an intermediate which built up and then disappeared during the course of the reaction.¹¹ This material was identical with the mononuclear complex CpCo(CH₃)₂CO (4a) which we had identified as the intermediate responsible for acetone formation during the carbonylation of the mononuclear complex 1. Thus it was clear that transfer of a methyl group from one cobalt atom to the other in 16a preceded ketone formation. In this case, however, crossover experiments revealed that the reaction was inter- rather than intramolecular. Carbonylation of a mixture of 16a and its methyl-labeled analogue 16a-d₆ gave an essentially statistical ratio of acetone-d₀, -d₃, and -d₆. When separate solutions of 16a and 16a-d₆ were allowed to decompose until a maximum amount of 4a was observed, and then mixed, a much smaller amount of acetone-d₃ was observed. This was consistent with our determination that carbonylation of 1 was intramolecular and demonstrated that the intermolecular component of the decomposition of 16a had to occur before complex 4a was formed.

Thermal decomposition of the diethyl complex 16b was more complex. Ketone formation, leading to 3-

(9) For some leading references to the chemistry of higher organometallic clusters, see (a) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **84**, 959 (1975); (b) G. Schmid, *Angew. Chem., Int. Ed. Engl.*, **17**, 392 (1978); (c) E. Band and E. L. Muetterties, *Chem. Rev.*, **78**, 639 (1978); (d) J. B. Keister and J. R. Shapley, *J. Am. Chem. Soc.*, **98**, 1056 (1976); (e) R. D. Adams and N. M. Golembeski, *ibid.*, **101**, 2579 (1979); (f) T. Kitamura and T. Joh, *J. Organomet. Chem.*, **65**, 235 (1974).

(10) N. E. Schore, C. S. Ilenda, and R. G. Bergman, *J. Am. Chem. Soc.*, **99**, 1781 (1977).

(11) N. E. Schore, C. Ilenda, and R. G. Bergman, *J. Am. Chem. Soc.*, **98**, 7436 (1976).

(12) K. P. C. Vollhardt, J. E. Bercaw, and R. G. Bergman, *J. Organomet. Chem.*, **97**, 283 (1975).

Chart V

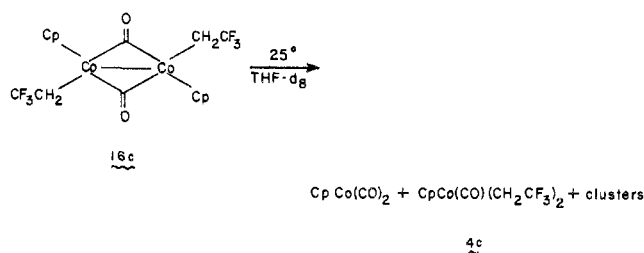
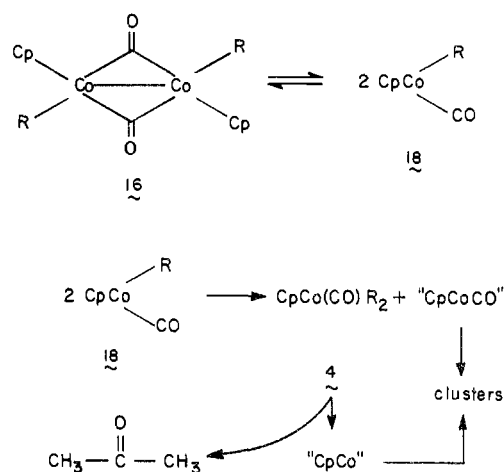


Chart VI



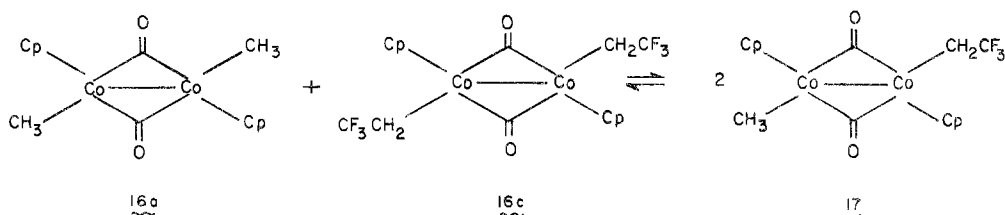
pentanone, occurred, but a competitive β -elimination reaction, leading to ethylene and ethane, was also observed. More enlightening was the decomposition of the bis(trifluoroethyl) complex 16c shown in Chart V. This led to CpCo(CO)₂, clusters, and CpCo(CO)-(CH₂CF₃)₂ (4c). Due, presumably, to the strength of the metal-carbon bonds in this complex, 4c is unusually stable. Unlike 4a, it does not undergo CO insertion/reductive elimination leading to ketone and hence may be isolated and characterized by conventional means.¹³ As in the case of 16a, the decompositions of 16b and 16c also exhibit good first-order kinetics (Table I).

The first mechanistic hypothesis we constructed to account for these observations is summarized in Chart VI. We postulated that complex 16, in analogy to other complexes with single metal-metal bonds,¹⁴ was in equilibrium with a small amount of monomeric Co(II) species 18. Transfer of a methyl group from one molecule of 18 to another directly generates the NMR-observable intermediate 4, which is isolable in the case of

(13) M. A. White and R. G. Bergman, unpublished results.

(14) See, for example, (a) H. B. Abrahamson and M. S. Wrighton, *J. Am. Chem. Soc.*, **99**, 5510 (1977); (b) J. P. Fawcett, A. Poë, and K. R. Sharma, *ibid.*, **98**, 1401 (1976); (c) E. L. Muetterties, B. A. Sosinsky, and K. I. Zamaraev, *ibid.*, **97**, 5299 (1975); (d) R. D. Adams, D. E. Collins, and F. A. Cotton, *ibid.*, **96**, 749 (1974).

Chart VII



16c. This proceeds to ketone by the route outlined earlier in Chart I. Initially we considered¹¹ a variant of this mechanism in which **18** transfers an alkyl group to another molecule of **16**, generating a chain process leading to **4a**. However, the clean first-order kinetics we have since measured for these reactions makes the nonchain mechanism seem more reasonable.

An important part of this mechanism is the first step, involving metal-metal bond cleavage. We therefore set out to obtain independent evidence for this process. Suggestive evidence that this reaction was occurring rapidly at room temperature was provided by some of the chemistry of complexes **16**. For example, **16a** reacted with NO to give $\text{CpCo}(\text{NO})\text{CH}_3$, and **16c** reacted with I_2 to give a quantitative yield of the isolable complex $\text{CpCo}(\text{CO})(\text{CH}_2\text{CF}_3)\text{I}$. More striking, however, was the NMR behavior of **16c**. This exhibited reversible broadening of its sharp proton resonances between -50 and $+10$ °C, indicating rapid equilibration of **16c** with a paramagnetic species, presumably **18c**. Once again, a crossover experiment was instrumental in confirming this conclusion: mixing **16a** and **16c** rapidly generated the unsymmetrical complex **17** (Chart VII). These results provide strong evidence that **16** and **18** are in equilibrium in solution.^{13,15} However, they do not tell us whether these Co(II) species—or, for that matter, any intermolecular pathways—are directly involved in the ketone-forming reaction. This question is addressed later in this Account.

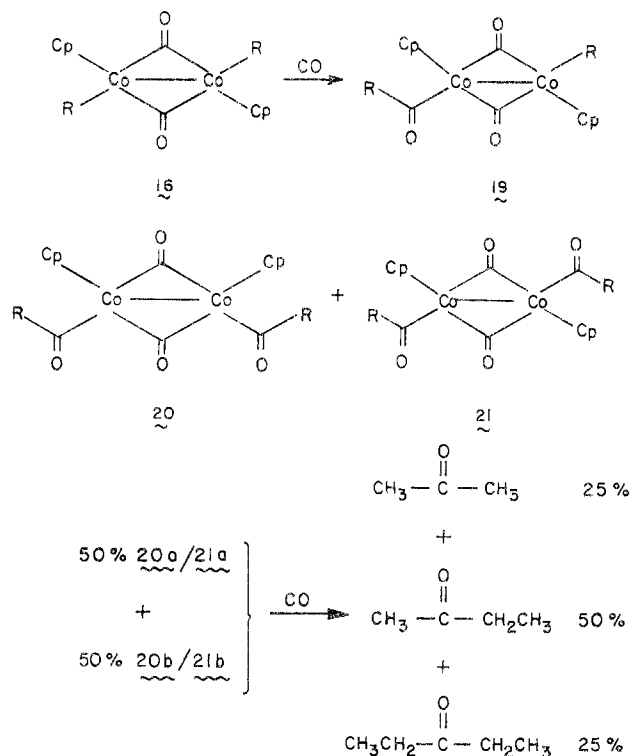
Carbonylation of Binuclear Cobalt Dialkyls

Carbonylation of complexes **16** is both cleaner and more rapid than thermal decomposition, and in the case of the dimethyl and diethyl complexes leads to improved yields of ketone. In the case of **16b**, β -elimination is suppressed and ketone formation becomes the exclusive process observed. The simplest reaction is exhibited by **16c**. Carbonylation gives a quantitative yield of $\text{CoCo}(\text{CO})_2$ and **4c**, and the reaction is complete in 15 min at room temperature. This result is clearly consistent with the thermal decomposition of **16c**, assuming the unsaturated cyclopentadienylcobalt fragments which formed clusters in the absence of CO are

(15) A word is appropriate here about two other approaches we have taken to this problem. In principle, one should be able to obtain the type of information obtained in the **16a** + **16c** reaction by carrying the isotope crossover reaction to partial completion, reisolating **16**, and analyzing it mass spectroscopically. However, **16** exhibits no parent ion, even at low voltages; the ion of highest m/e corresponds to exactly half the molecular weight of **16**. That the complex is dimeric in solution was indicated by the presence of a normal NMR spectrum, showing the complex is diamagnetic, and confirmed by cryoscopic molecular weight experiments.

In a second approach, we have carried out variable-temperature ESR studies on **16a** and **16c**. Both exhibit ESR signals in the region expected for Co(II) species (the g value observed for the radical species formed from **16a** is 2.012; in the case of **16c** it is 2.214). Unfortunately, however, we were unable to resolve the cobalt hyperfine splitting in liquid solution, even at low temperature. In frozen solution, some hyperfine splitting is seen, but the resolution is still not clear enough to provide truly definitive evidence that these signals are due to $\text{CpCo}(\text{R})(\text{CO})$ species.

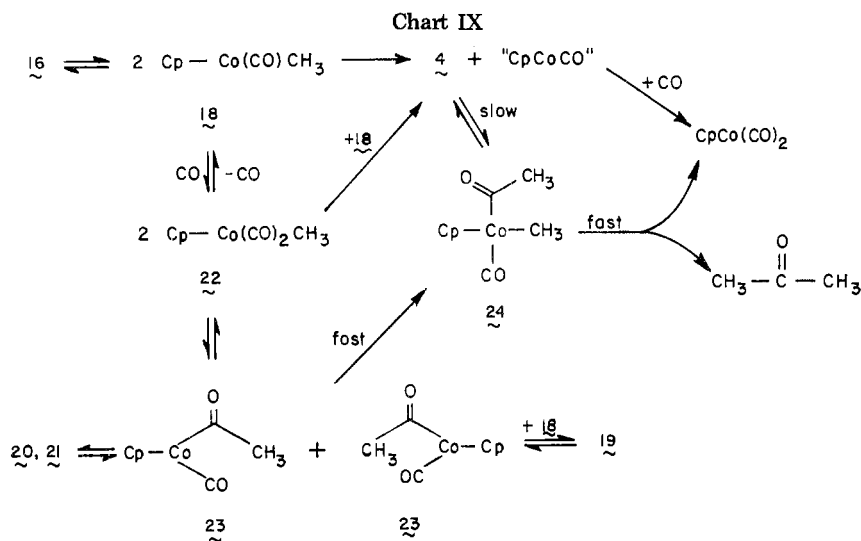
Chart VIII



diverted completely to $\text{CpCo}(\text{CO})_2$ in its presence.

Some surprising observations were made on carbonylation of **16a** and **16b**. These reactions were more rapid than the thermal decompositions, and monitoring them by NMR spectrometry allowed us to detect intermediates which did not appear in the thermal decomposition.¹⁶ In the case of the dimethyl complex **16a**, for example, $\text{CpCp}(\text{CO})_2$ and $\text{CpCo}(\text{CO})(\text{CH}_3)_2$ were observed, but at least three new species also appeared. We believe two of these are the cis and trans diacetyl complexes **20a** and **21a** shown in Chart VIII. These materials could be isolated by low-temperature chromatography and were pure by NMR criteria, but their thermal instability prevented our obtaining good elemental analyses. During the course of the carbonylation a new metal-bound methyl signal grew into the NMR spectrum and then disappeared. A new acyl signal was also associated with this resonance, and we believe this material to be the partially carbonylated complex **19a**. Carbonylation of diethyl complex **16b** behaved similarly. Although the monopropionyl complex could not be detected in this experiment, once again a mixture of two isomeric propionyl dimers (**20b** and **21b**) was observed and isolated by low-temperature chromatography. Allowing the carbonylations to pro-

(16) M. A. White and R. G. Bergman, *J. Chem. Soc., Chem. Commun.*, in press.



ced at room temperature eventually converted all these materials quantitatively to ketones and CpCo(CO)_2 .

Studies of the rates and products of decomposition of isolated diacyl complexes **20** and **21** are interesting with regard to the mechanism of ketone formation in these reactions. We have found (a) decomposition of **20a/21a** gives acetone and **20b/21b** gives 3-pentanone, both quantitatively in the presence of carbon monoxide; (b) decomposition of a 50:50 mixture of the diacyl and dipropionyl complexes gives a 1:2:1 ratio of acetone, 2-butanone, and 3-pentanone, indicating that the reaction is intermolecular, as was determined using isotope crossover experiments for the decomposition of **16a**; (c) the conversion to ketone is surprisingly rapid, proceeding at reasonable rates at 0 °C in $\text{THF-}d_8$. Decomposition in the absence of CO gave similar results, except that some cobalt clusters were observed as final organometallic products in addition to CpCo(CO)_2 . The rates of decomposition are once again first order in acyl complex and show essentially no sensitivity to changes in CO pressure;¹⁶ the rate constants are given in Table I. Most intriguing is the fact that conversion of the diacyl complexes to acetone occurs substantially more rapidly than the mononuclear complex **4a** reacts under the same conditions. This requires that **16a**, and presumably **16b**, are converted to ketone by two distinct routes—one slower path which proceeds through **4** and another more rapid process, involving diacyls **20** and **21**, which completely bypasses **4**.

The mechanism outlined earlier in Chart VI can be modified in a relatively straightforward way to explain these observations, and this is done in Chart IX. The critical assumption of the expanded mechanism is that in the presence of CO, Co(II) intermediate **18** can be trapped with CO, leading to **22**, in competition with its bimolecular conversion to the mononuclear dimethyl complex **4**. As a 19-electron, or perhaps a 17-electron, η^3 -cyclopentadienyl, intermediate there should be a strong driving force for CO insertion leading to **23**.

Complex **23** accounts for the formation of both **20/21** and **19**. It also explains the rapid production of acetone if it can operate as a methyl rather than acetyl transfer reagent, in analogy to the hydride transfer propensity shown by the anionic formyl complexes of Casey¹⁷ and

Gladysz.¹⁸ This leads directly to **24**, which is undoubtedly the same intermediate formed more slowly by CO insertion in **4**, and this material gives acetone by direct reductive elimination. That **23** should be able to do this seems reasonable, because methyl transfer leaves behind coordinatively saturated CpCo(CO)_2 , whereas acyl transfer between two molecules of **23**, and methyl transfer between two molecules of **18**, must both generate 16-electron species, and are therefore slower processes.

Reactions of Bridged Binuclear Dialkyls

The observations summarized above served to identify a number of the intermediates involved in the thermal decomposition and carbonylation reactions of binuclear cobalt dialkyls. They also convinced us that the scrambling of alkyl groups, initially revealed by isotope crossover experiments in the decomposition of **16**, was ubiquitous in these decompositions and occurred at a rate much more rapid than that of product formation. As indicated earlier, this raised an important question: is alkyl group scrambling a process actually located on the path to ketone product, or is it a side reaction which simply produces completely scrambled starting material, which then proceeds on to ketone by an intramolecular mechanism? Our further experiments, described below, provide strong evidence that scrambling and ketone formation result from the same process.

In order to answer this question, we decided to prepare and examine the chemistry of bridged complex **28**. We reasoned that the $28 \rightleftharpoons 29$ equilibrium shown in Chart X would favor **28** more than **16** was favored in the unbridged case, because of the smaller amount of translational entropy associated with **29**, compared with the two independent fragments presumably released in the dissociation of **16**. This predicts that conversion to acetone should be slower for **28** than for **16** if dissociation is in fact the first step on the route to ketone. Additionally, we thought the forced proximity of the metal centers in **28** might cause the reaction to be completely intramolecular in this system.

Bridged complex **28** was prepared from dicyclopentadienylmethane by the route shown in Chart X. The reactions of **26** and **28** are quite parallel to those

(17) C. P. Casey and S. M. Neumann, *J. Am. Chem. Soc.*, **100**, 2545 (1978).

(18) J. Gladysz and W. Tam, *J. Am. Chem. Soc.*, **101**, 4766 (1979).

Chart X

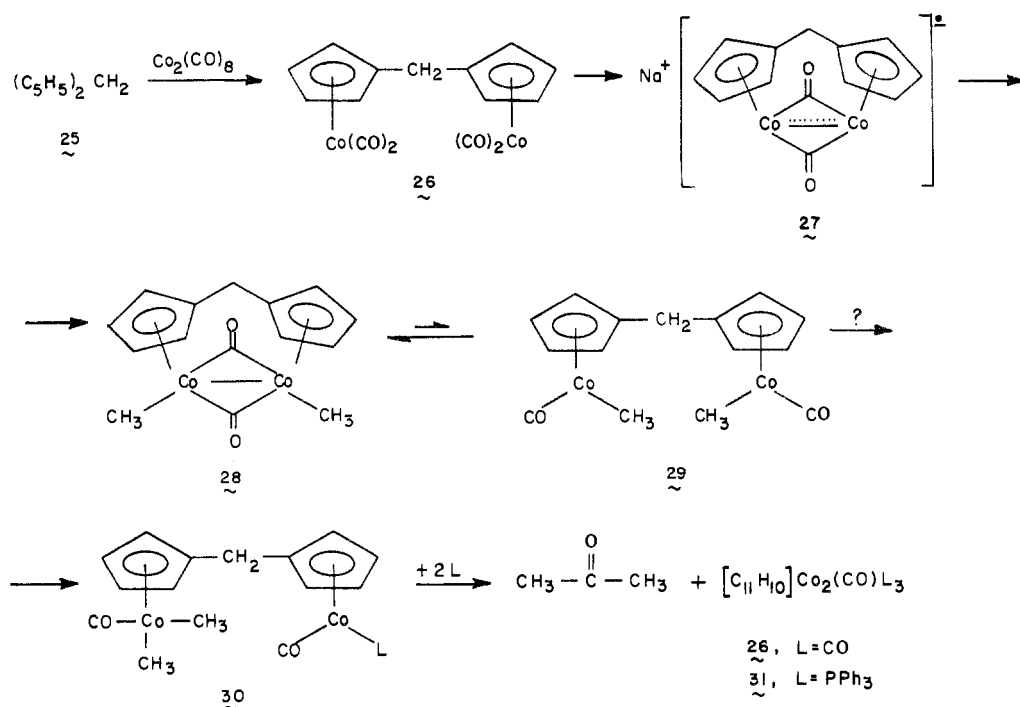


Table II
Isotope Labeling Data Obtained in Crossover Experiments on the Reaction of Mixtures 28-*d*₀ and 28-*d*₆ with CO and PPh₃

starting complex			entering ligand	temp, °C	acetone products, ^c %			molecularity, %	
total concn, M	% 28- <i>d</i> ₀	% 28- <i>d</i> ₆			<i>d</i> ₀	<i>d</i> ₃	<i>d</i> ₆	intra-	inter-
0.25	53	47	CO ^a	70	40	28	32	44	56
0.05	55	45	CO ^a	70	52	5	43	90	10
0.25	46	54	PPh ₃ ^b	25	38	16	46	67	33
0.05	49	51	PPh ₃ ^b	25	49	1	50	98	2
0.25	69	31	PPh ₃ ^b	70	69	3	28	93	7

^a Toluene solvent. ^b Benzene solvent. ^c Acetone was obtained as the direct product of the carbonylation reaction and analyzed by mass spectroscopy. In the PPh₃ reaction, product 32a was first diluted to a concentration ≤ 0.05 M and then carbonylated to generate acetone for analysis (the run at 0.05 M 28 precludes the possibility of significant label scrambling during the carbonylation of 32a at these concentrations; see footnote 5b).

of the parent compounds.¹⁹ Complex 26 is reduced with sodium amalgam to radical anion 27, which can be alkylated to give 28. This, in turn, gives acetone and insoluble cluster complexes on thermal decomposition, and acetone and 26 quantitatively on carbonylation. Consistent with our mechanistic hypothesis, these reactions are considerably slower than those observed with 16. Temperatures near 80 °C are required to induce thermal decomposition of 28, and even carbonylation requires a temperature of 70 °C to achieve a reasonable rate. Because metal-metal bond cleavage is now slower, neither complex 30 nor binuclear diacyl complexes build up during the course of these reactions.

Having determined that the chemistry of 28 is analogous to that of 16, we again carried out crossover experiments to examine the intramolecularity of the carbonylation. Our first studies, carried out at relatively high concentration of starting complex, showed a significant amount of crossover (Table II). Interestingly, we did not observe a completely statistical ratio of labeled acetones. Furthermore, runs at varying concentrations of 28 demonstrated that the intramolecularity

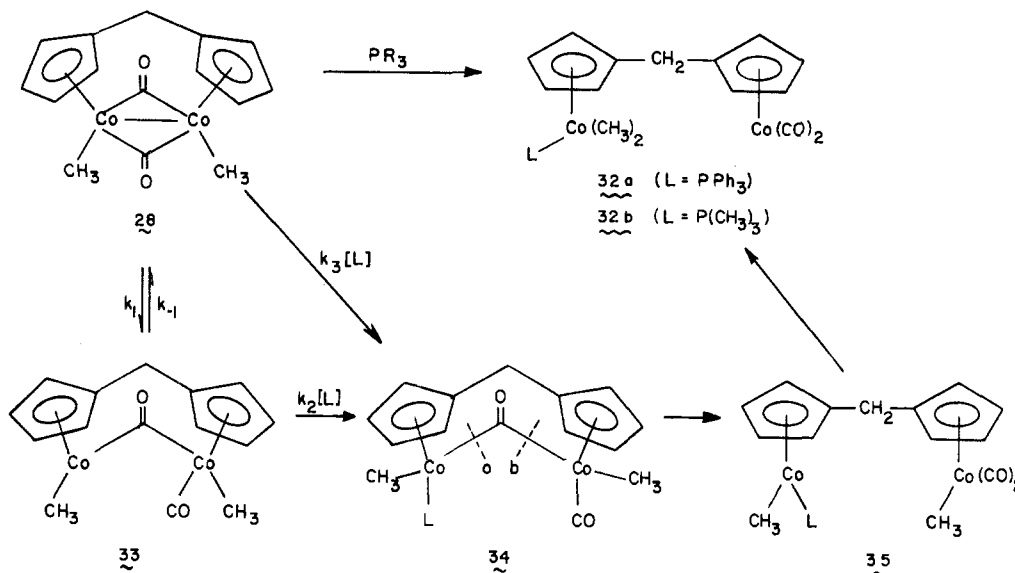
of the process increased at lower concentrations. Because of the linked cyclopentadienyl rings, dissociation-recombination of the metal-metal bond in 28 cannot produce label scrambling. Just to be sure some other scrambling mechanism was not operative, this was confirmed by isolation and isotope analysis of 28 after partial reaction. Therefore, for complex 28 at least, label scrambling in the ketone product is *not* a result of some completely independent randomization process in the starting material.

The mechanistic hypothesis suggested earlier accounts nicely for this result. One need only assume that, as predicted, metal-metal bond cleavage in 28 gives 29; CO then attacks one of the metal centers in 29, forcing a methyl group to migrate to the other, leading to 30. When the concentration of 29 is high enough, transfer of methyl to a Co(II) center in a different molecule becomes competitive, and this is the concentration-dependent intermolecular component of the reaction. Complex 30 (L = CO) then undergoes insertion/reductive elimination as discussed earlier for related mononuclear complexes, leading to acetone and 26.

However, nature was not about to provide us with such a tidy conclusion. Given the relative stability of

(19) H. E. Bryndza and R. G. Bergman, *J. Am. Chem. Soc.*, **101**, 4766 (1979).

Chart XI



28 and the cleanliness of its carbonylation, we next decided to examine its reaction with phosphines. We had made an attempt to examine the corresponding reaction of **16a**; this reaction gave a lowered yield (58%) of acetone, as well as a mixture of mononuclear and cluster complexes;²⁰ the complexity of this reaction discouraged our attempts to investigate it in detail. In the case of **28**, we expected that phosphine would simply replace CO as the methyl-migration-inducing ligand. Thus phosphine, written as "L" in Chart X, would attack one of the metal centers in **29** and force methyl migration as in the CO case, leading to **30** ($L = PR_3$). This should rapidly give acetone and **31**. In the event,¹⁹ reaction of **28** with phosphine was quite clean, proceeding at a reasonable rate even at 25 °C (see Figure 1). However, no acetone was formed in this reaction. As shown in Chart XI, the sole product was the single organometallic complex **32**.

The most surprising thing about this result is that complex **32** has both CO groups bound to the same metal atom. In view of this result, we had to question the hypothesis that **29** is the initially formed intermediate, because it is difficult to devise a convincing mechanism to explain why one of the metal-CO bonds broken in the generation of **29** should find a way to re-form. A more reasonable explanation is that both metal-carbonyl bonds at one of the metal centers in **28** remain intact during the entire reaction. Our mechanistic hypothesis must therefore be modified. As shown in Chart XI, we suggest that only two, rather than three, bonds in **28** are cleaved upon reaction with an entering ligand, leading to **34**. This intermediate, although undoubtedly reactive, has two 18-electron cobalt atoms.²¹ When $L = CO$, the two metal centers are chemically identical, and cleavage of either bond a or bond b may occur. When $L =$ phosphine, however, cleavage of bond a is favored because this process places the relatively electron-donating phosphine ligand on the less electron-rich metal center. This leads to **35**; transfer of the

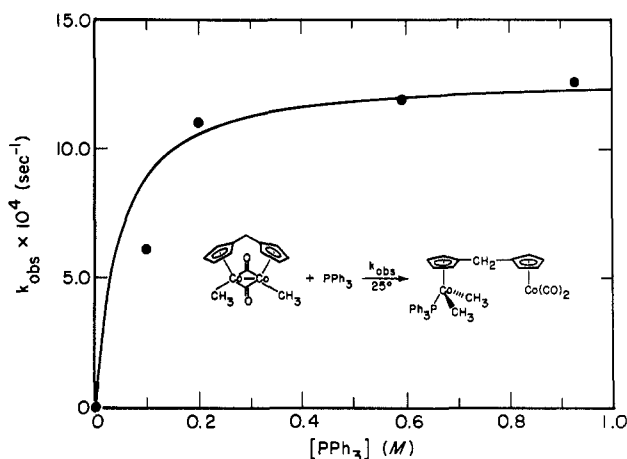


Figure 1. Dependence of the pseudo-first-order rate constant for reaction of **28** with excess PPh_3 (benzene- d_6 , 25 °C) upon the concentration of PPh_3 .

methyl group then gives the product **32**.²² That this transfer may become intermolecular at high enough concentrations is once again demonstrated by the appropriate crossover experiments (Table II).

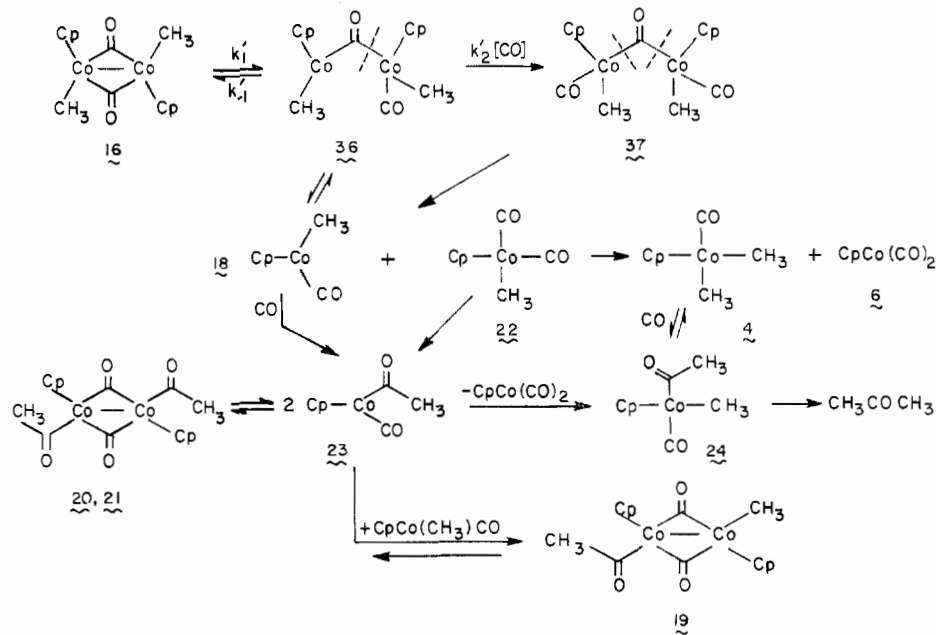
Kinetic studies yielded one further piece of information about the first part of the mechanism of this reaction.¹⁹ Reaction of phosphine with **28** might occur in one step (k_3 in Chart XI). Alternatively, **28** might suffer bond cleavage to give **33**, followed by reaction of PR_3 with the 16-electron metal center so generated. These mechanisms are kinetically distinguishable if the latter mechanism obtains, and the quantity $k_2[L]$ can be made larger than the recombination rate constant k_{-1} . This is exactly the case for the reaction of **28** with PPh_3 . At moderate phosphine concentrations the rate is approximately first order in phosphine. However, as the concentration of PPh_3 is raised, the reaction approaches a limiting rate which is independent of $[PPh_3]$. This is strong evidence for the dissociative mechanism,

(20) N. E. Schore and R. G. Bergman, unpublished results.

(21) A very similar binuclear intermediate, also containing a single carbonyl bridge and no metal-metal bond, was observed recently; cf. D. R. Tyler, M. A. Schmidt, and H. B. Gray, *J. Am. Chem. Soc.*, 101, 2753 (1979).

(22) This hypothesis suggests that phosphine ligands comparable in π acidity to CO might result in the formation of some acetone, since in this case cleavage of bonds a and b should be more competitive. In agreement with this prediction, reaction of **28** with PF_3 gives acetone (~10% yield) in addition to a predominant amount of the PF_3 analogue of complex **32**.

Chart XII



and from these data one can extract the dissociation rate constant $k_1 = 1.28 \times 10^{-4} \text{ s}^{-1}$ and the ratio $k_{-1}/k_2 = 4.3 \times 10^{-2} \text{ M}^{-1}$ (25 °C).

Conclusions

It is possible that each of the reactions of 16 and 28 discussed here takes place by independent mechanisms. However, this assumption seems neither reasonable nor economical. We suggest instead that the chemistry of these differently substituted systems is related, and provide insight into a general pattern of behavior for the ligand-induced decompositions of complexes related to 16.

In Chart XII we have combined the information obtained on these related systems into a generalized mechanistic hypothesis, illustrated for simplicity for only the parent dimethyl complex 16 and the single ligand CO. As with 28, we assume that metal-metal bond cleavage in 16 also begins by conversion to 36. In the absence of added ligand, dissociation to 18 may occur, and this overall process is rapid and reversible at room temperature and below. In the presence of an external ligand such as CO, 37 is formed. This may dissociate to one molecule of 18 and one molecule of dicarbonyl 22. Reaction of these two species with one another gives 4 and 6, and 4 is converted to acetone, presumably via 24, at a moderate rate at room temperature.

Besides transferring a methyl group to 18, 22 may also undergo CO insertion to give 23. Reversible dimerization of 23 leads to isolable binuclear diacetyls 20 and 21, and reaction of 23 with 18 gives 19. Alternatively, one molecule of 23 may transfer a methyl group to another, releasing a molecule of 6 and 24. This

provides a rapid route to acetone which bypasses dimethyl complex 4.

In summary, it is perhaps reasonable to derive the following generalizations from our studies of these binuclear systems. First, the decomposition of 16 and its derivatives is now one of the few carbon-carbon bond-forming reactions initiated in a binuclear complex which is understood at a reasonable level of detail. Second, crossover experiments have played a crucial role in delineating credible mechanistic hypotheses in this work; these experiments have taught us that there is often a real possibility that intermolecular mechanisms intervene in processes which we at first naively guess to be intramolecular.

Third, our results reemphasize the concern that the reactive species in so-called "cluster-catalyzed" reactions might in fact be reactive fragments of lower nuclearity. Finally, in a somewhat more general sense, we have tried to point out in this account how knowledge of the chemistry of mononuclear complexes has been crucial to our understanding of their binuclear relatives. We hope, in turn, that current and future investigations of binuclear systems will provide a base for understanding the chemistry of larger clusters.

I am grateful to my collaborators, whose names are mentioned in the references; the work described in the Account benefited immeasurably from their hard work, intellectual insight, and good humor. I also am grateful to the California Institute of Technology, where a significant part of the research described here was carried out. Finally, I acknowledge financial support from the National Science Foundation (Grant No. CHE 78-08706) and the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. W-7405-48.