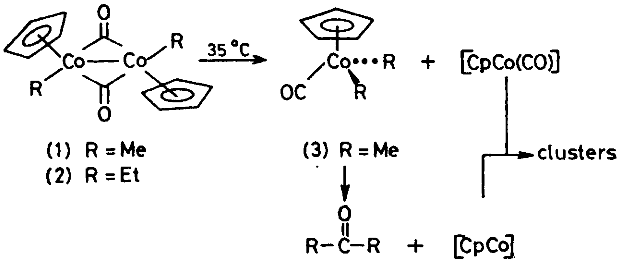
Identification of Binuclear Acyl Complexes as Intermediates in the CO-induced Conversion of $[(\eta^5\text{-}C_5H_5)Co(CO)(Me)]_2$ into Acetone, and $[(\eta^5\text{-}C_5H_5)Co(CO)(Et)]_2$ into Pentan-3-one

By MARY ANN WHITE and ROBERT G. BERGMAN*
(*Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California* 91125; *Department of Chemistry, University of California, and Lawrence Berkeley Laboratory, Berkeley, California* 94720)

Summary Studies of the carbonylation of $[(\eta^5\text{-}C_5H_5)Co(CO)(R)]_2$ (R = Me, Et) at temperatures below ambient have revealed that these complexes may be converted into ketones *via* binuclear diacyl complexes $[(\eta^5\text{-}C_5H_5)Co(CO)(COR)]_2$; the postulated mechanistic pathway circumvents the earlier-identified intermediate $(\eta^5\text{-}C_5H_5)Co(CO)R_2$, and involves alkyl transfer from a Co^{II} acyl complex as a critical step.



SCHEME 1. Cp = $\eta^5\text{-}C_5H_5$.

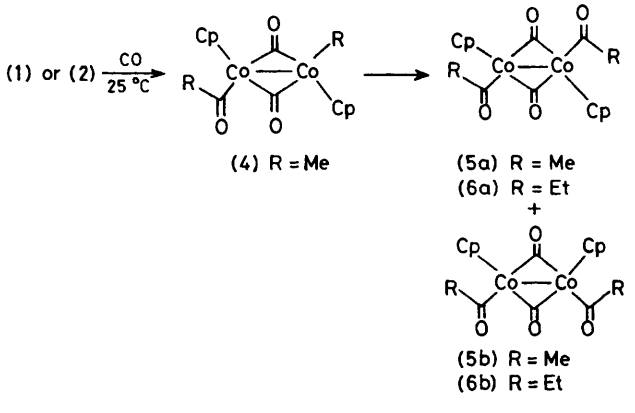
THERMAL decomposition of bis[$(\eta^5$-cyclopentadienyl)-(carbonyl)methylcobalt] $[(\eta^5\text{-}C_5H_5)Co(CO)(Me)]_2$ (**1**) in a number of organic solvents leads to good yields of acetone (a process involving the formation of two new carbon–carbon bonds) and cobalt cluster complexes.[1,2] Examination of this reaction by n.m.r. spectroscopy demonstrated that the transformation involves initial conversion into the intermediate mononuclear complex $(\eta^5\text{-}C_5H_5)Co(CO)(Me)_2$ (**3**, Scheme 1) and crossover experiments showed[2] that this 'rearrangement' reaction is an inter-, rather than an intra-molecular process.

Carbonylation of (**1**) leads to acetone and $(\eta^5\text{-}C_5H_5)Co(CO)_2$ (**7**) in quantitative yield. Complex (**3**) can again be detected by n.m.r. spectroscopy during the reaction at 35 °C suggesting that the thermal decomposition and carbonylation reactions proceed through the same intermediate.[2] We report here, however, that this apparent similarity is deceptive. Lower temperature kinetic and n.m.r. studies show that (**1**) may be converted into acetone in a rapid process involving binuclear, acyl-containing intermediates, which completely circumvents the mononuclear dimethyl complex (**3**).

Upon treatment of a 0·1 M solution of (**1**) in [$^2H_8$]tetrahydrofuran (THF) with an excess of CO, the n.m.r. and i.r. bands due to (**1**) disappeared within a few minutes at room temperature and were replaced by several new signals. These were due (Scheme 2) to the presence of (**3**), (**7**), and acetone (all of which had been identified earlier[2]), as well as two new sets of signals due to the *E*- and *Z*-isomers (**5a**) and (**5b**), formed in a *ca.* 3 : 1 ratio.† Complex (**5**) could be

---

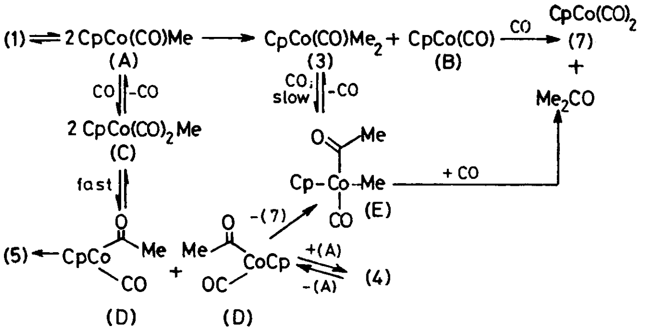
† Although we believe (**5a**) and (**5b**) are *E*- and *Z*-isomers owing to the similarity of their spectral properties, we do not yet know which is *E* and which *Z*; the assignments in Scheme 2 are arbitrary.



Scheme 2. Cp = η^5-C_5H_5.

isolated as a brown solid by low-temperature column chromatography under an inert atmosphere. Although n.m.r. and i.r. analysis indicated that the material was pure, its extreme thermal instability frustrated attempts at elemental analysis. During the carbonylation an even more transient material, exhibiting both metal-bound methyl and acetyl signals, appeared and then disappeared as (**5**) was formed. Although this material was not isolable, its spectral characteristics were consistent with its assignment as the partially carbonylated binuclear complex (**4**). Similar results were obtained when $[(\eta^5\text{-}C_5H_5)Co(CO)(Et)]_2$ (**2**)‡ was treated with CO. Again, a 3 : 1 ratio of binuclear diacyl complexes (**6a**) and (**6b**) could be detected spectroscopically and these could be isolated by low-temperature chromatography. In contrast to the behaviour of (**1**), however, neither a monoacyl intermediate nor $(\eta^5\text{-}C_5H_5)Co(CO)(Et)_2$ were observed in the mixture during carbonylation.

When either (**5**) or (**6**) was allowed to decompose in the presence of CO, quantitative formation of (**7**), and acetone and pentan-3-one, respectively, was observed. Decomposition of a 50 : 50 mixture of (**5**) and (**6**) gave a 1 : 2 : 1 ratio of acetone, butan-2-one, and pentan-3-one, indicating [as was observed[2] in the decomposition of (**1**)] that the ketone-forming reaction is intermolecular. These reactions were surprisingly rapid, proceeding at reasonable rates even at 0 °C in $[^2H_8]$THF. Decomposition in the absence of CO gave similar results, except that some cobalt clusters were observed as final organometallic products in place of (**7**). Kinetic studies demonstrated that the rate of carbonylation of (**5**) is first order in complex concentration; addition of excess of CO has essentially no effect on the rate [at 0·5 atm CO, $k_{\text{obs}} = 5{\cdot}5 \times 10^{-5}\ \text{s}^{-1}$; at 9·5 atm CO, $k_{\text{obs}} = 3{\cdot}23 \times 10^{-5}\ \text{s}^{-1}$ (0 °C)]. The most critical feature of these observations is that none of the mononuclear dimethyl complex (**3**) is formed during the decomposition of (**5**), and the rate of conversion of (**5**) into acetone is much faster than the rate at which (**3**) is converted into acetone. From these data we conclude that carbonylation of (**1**) can take place by two distinct routes: one (slower) process involves the intermediacy of the mononuclear complex (**3**), and another, more rapid reaction involves the binuclear diacyl complexes (**5a**) and (**5b**).



Scheme 3. Cp = η^5-C_5H_5.

These seemingly disparate results are accommodated by the mechanism outlined in Scheme 3. As suggested earlier,[2] we believe that the binuclear complex (**1**) is in rapid equilibrium with small amounts of the mononuclear Co^{II} species (A). In the absence of large amounts of CO, methyl transfer from one molecule of (A) to another occurs,§ leading to (**3**) and (B), which either forms clusters or reacts rapidly with CO to give (**7**). As the amount of CO available increases, (A) is diverted to the dicarbonyl (C). At partial conversion, reaction between (C) and (A) may occur, leading directly to (**3**) and (**7**), which is undoubtedly why (**3**) is often produced along with (**5**) during the carbonylation of (**1**). At higher CO pressures, (A) is scavenged more efficiently, and larger amounts of (C) are produced. 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 the 17-electron acyl species (D) which dimerizes to give (**5**).

We believe that (D) is the critical species which accounts both for the formation of (**5**) from (**1**) and for the rapid production of acetone from (**5**). As with the dialkyl complexes (**1**) and (**2**), small concentrations of the mononuclear Co^{II} species (D) are in equilibrium with (**5**). It is possible that acyl transfer occurs leading to the diacyl analogue of (**3**); however, the complete absence of biacetyl in the product mixtures makes this seem unlikely. Apparently (D) operates as a *methyl* transfer reagent (in analogy to the hydride transfer propensity shown by the anionic formyl complexes of Casey[3] and Gladysz[4]). Disproportionation of (D) by this route leads to (**7**) and the acylmethyl complex (E), the direct precursor of acetone. In this way, the route from (**5**) to acetone avoids the apparently slower CO insertion step in (**3**).

In summary, our results show that complexes such as (**1**) may be converted into the same products [acetone and (**7**)] by two different mechanisms which, though related to one another, involve distinctly different intermediates. They

---

‡ Prepared analogously to (**1**) by treatment[1] of $Na[(\eta^5\text{-}C_5H_5)Co(CO)]_2$ with EtI. Satisfactory spectral and analytical data were obtained for this material; on thermal decomposition it is converted rapidly (room temperature) into ethylene, ethane, and pentan-3-one, but carbonylation leads quantitatively to pentan-3-one.

§ This is a somewhat simpler version of the chain mechanism suggested earlier;[2] transfer of a methyl group between two molecules of the intermediate (A) now seems more likely in view of the first-order kinetics observable here.

also emphasize that reactions of multinuclear complexes [even those that produce products of the same nuclearity, such as the conversion of (**1**) into (**5**) and (**2**) into (**6**)] may proceed *via* reactive mononuclear fragments.

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

(*Received, 17th July* 1979; *Com.* 769.)

[1] N. E. Schore, C. S. Ilenda, and R. G. Bergman, *J. Amer. Chem. Soc.*, 1977, **99**, 1781.
[2] N. E. Schore, C. S. Ilenda, and R. G. Bergman, *J. Amer. Chem. Soc.*, 1976, **98**, 7436.
[3] C. P. Casey and S. M. Neumann, *J. Amer. Chem. Soc.*, 1978, **100**, 2544.
[4] J. Gladysz and W. Tam, *J. Amer. Chem. Soc.*, 1978, **100**, 2545.