Mechanistic Study of the Solvent-Induced Fragmentation of $Cp_3Co_3(CO)_2$

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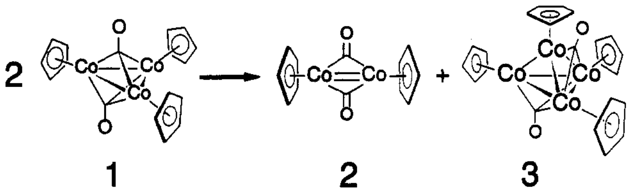
Summary: The cluster complex $Cp_3Co_3(CO)_2$ *(1) undergoes a unique, solvent-induced, two-step fragmentation reaction to give the di- and tetranuclear complexes* $Cp_2Co_2(CO)_2$ *(2) and* $Cp_4Co_4(CO)_2$ *(3). The mechanism of this reaction is shown to involve initial, reversible attack of solvent (benzene or THF) on 1, causing fragmentation to 2 and a solvated, mononuclear intermediate,* $CpCo(sol)_n$*. This intermediate subsequently reacts with a second molecule of 1 to form 3. The mononuclear species shows a surprising selectivity in its reactions with trapping agents depending upon the nature of the coordinated solvent.*

We recently reported[1] on the synthesis and properties of an unusual cluster complex, $Cp_3CO_3(CO)_2$ (1), which is the only all-Cp-containing example within a growing number of electronically unsaturated, 46-e$^-$ complexes.[2] Among these complexes, 1 is unique in undergoing a decomposition reaction in a variety of organic solvents, forming the di- and tetranuclear complexes $Cp_2Co_2(CO)_2$[3] (2) and $Cp_4Co_4(CO)_2$[4] (3), respectively. In this report evidence is presented for the initial fragmentation of 1 into 2 and a solvated, mononuclear intermediate of the form $CpCo(sol)_n$. This intermediate exhibits a surprising selectivity toward organometallic traps based on the properties of the coordinated solvent ligands. The properties of this intermediate are of interest with respect to a number of important organic reactions thought to be catalyzed by similar "CpCo" species.[5]

The decomposition reaction observed when 1 is dissolved in benzene or THF is shown in eq 1.



1 2 3

(1)

Preliminary investigations (NMR) of the course of this reaction yield two key observations. First, in all solvents investigated thus far, plots of ln[1] are linear with time over several half-lives, thus ruling out a simple bimolecular reaction. Second, the reaction is dramatically accelerated in THF as compared to aromatic solvents (benzene, k_{obs} = [7.5(3)] × 10^{-5} s^{-1}, T = 40 °C; THF, k_{obs} = [2.7(1)] × 10^{-3} s^{-1}, T = −50 °C).[6]

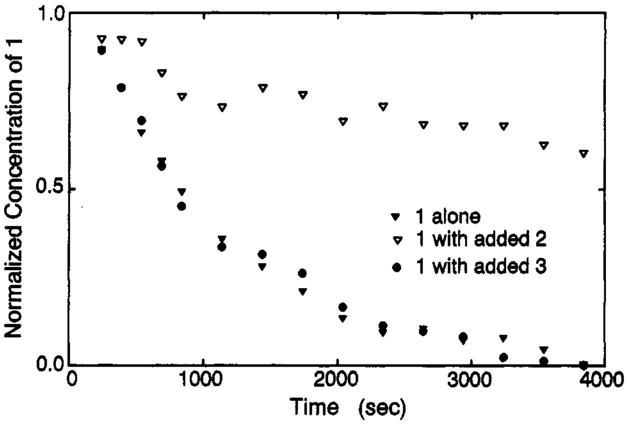


Figure 1. Effect of added 2 and 3 on the decomposition of $Cp_3Co_3(CO)_2$ (1).

Scheme I

$$1 + n\ \text{solvent} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2 + CpCo(sol)_n$$

$$CpCo(sol)_n + 1 \xrightarrow{k_2} 3$$

The effect of a large initial concentration of products 2 and 3 on the rate of decomposition of 1 in benzene is shown in Figure 1. When excess 3 is present, the rate is indistinguishable from that when only 1 is present at the outset. However, the presence of excess 2 at the outset of the reaction results in a dramatic inhibition of the rate. Identical results are observed when the solvent is THF (at −50 °C).

These observations are in accord with the mechanism shown in Scheme I. Initial attack of solvent on 1 causes reversible fragmentation to 2 and a mononuclear, solvated species which we formulate as $CpCo(sol)_n$. This intermediate subsequently encounters another molecule of 1, irreversibly forming the tetranuclear complex 3.

The influence of trapping agents on this reaction was also investigated. Selection of a suitable trapping agent which would only react with the intermediate and no other species present during the reaction was complicated by the high reactivity of both 1 and 2 with many potential traps.[3,7] The known dinuclear complex $Cp^*Ir(\mu\text{-}CO)_2$-

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(6) The importance of solvent in this reaction is further illustrated by the decomposition rate in diethyl ether compared to that in benzene or THF. The estimated half-life of 1 in ether is greater than 30 h at 298 K. The rates of decomposition of 1 in toluene-d_8 and p-xylene-d_{10} are approximately half and one-fourth, respectively, of the rate observed in benzene.

(7) The dinuclear complex 2 is quite reactive in this context. Mononuclear complexes of the form $CpM(CO)_2$ (M = Co, Rh, Ir), which would be ideal traps in this system, are observed to react with 2 to form new mixed-metal dicarbonyl complexes of the same form as 2 (unpublished results).

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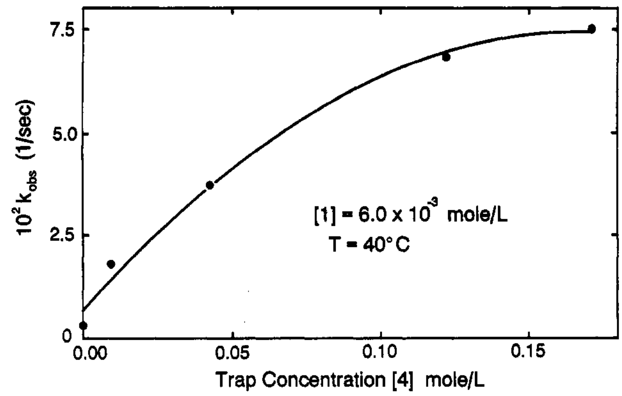


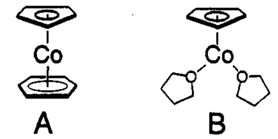
Figure 2. Effect of trap 4 on k_{obs} for the decomposition of $Cp_3Co_3(CO)_2$ (1) in benzene.

$CoCp^8$ (4), however, was found to function well in this system.[9] Trapping of the intermediate by 4 produces the known trinuclear complex $Cp^*Ir(CpCo)_2(\mu\text{-}CO)_2$[10] (5). The dependence of k_{obs} for the reaction in benzene vs trap concentration is illustrated in Figure 2.

k_{obs} increases as $[4]_{ini}$ is increased, until approximately a 20-fold excess is reached. Beyond this point increasing [4] causes little change in the rate of disappearance of 1 or the appearance of 2 or 5. The tetranuclear product 3 is not observed in reactions with a large excess of 4 present initially. These data are consistent with the trap 4 reacting only with the mononuclear intermediate and not directly with 1. Furthermore, under conditions of high trap concentration, k_{obs} is a pseudo-first-order rate constant comprised of k_1 (Scheme I) and the solvent term. Assuming a first-order dependence on benzene (vide infra), the limiting value for k_{obs} (7.5×10^{-2}) gives rise to a value of 6.8×10^{-3} L/(mol·s) for k_1.[11]

In surprising contrast to these results, identical trapping studies in THF-d_8 at −50 and 25 °C show no evidence of trapping of the THF solvate whatsoever. With a 10-fold excess of 4 in solution, the decomposition of 1 occurs at the same rate observed when 4 is not present. Products 2 and 3 are produced in equal amounts, just as is observed when 4 is absent. No trace of the trinuclear species 5 is observed in any of these experiments. The mononuclear intermediate in THF is not reactive toward 4 under conditions where quantitative trapping is observed in benzene.

Given the tendency of CpCo(arene) complexes to adopt 20-electron structures,[12] we propose that the solvated intermediate in benzene has the form of an η^6-arene sandwich complex (A). In THF we propose a structure containing two solvent molecules coordinated to the cobalt (B), yielding an 18-electron structure.



To our knowledge, no reports on the properties of the THF species have appeared. Our results indicate that the benzene complex readily reacts with both 2 and 4, while the THF complex reacts only with 2. The observations above indicate that while THF causes the fragmentation of 1 with much greater efficacy than aromatic ligands, once the solvated species (A and B) are formed, it is more difficult to displace coordinated THF ligands than a coordinated arene.[13] The ability of a coordinated arene ligand to slip to η^4- and η^2-coordination modes as an external ligand approaches allows this species to avoid unsaturated 16-e$^-$ species or slippage of the Cp ring to reduced coordination modes. In the case of B, displacement of a THF ligand by associative or dissociative mechanisms[14] appears to require such high-energy steps.

$Cp_3Co_3(CO)_2$ is the only 46-e$^-$ Cp_3M_3-type cluster complex for which this solvent-initiated fragmentation has been reported. Replacement of a single Cp ligand with pentamethylcyclopentadiene (Cp*) completely blocks this reaction. However, we have recently prepared[15] the analogue to 1 containing a single (trifluoromethyl)-tetramethylcyclopentadienyl ligand ($Cp^‡$), $Cp^‡Cp_2Co_3(CO)_2$, and found that it too exhibits this solvent-induced fragmentation reaction. The $Cp^‡$ ligand has been described as a Cp analogue with steric properties similar to those of Cp* and electronic properties similar to those of Cp.[16] With this in mind, these data indicate that attack of solvent and eventual fragmentation of a complex within this family of trinuclear clusters is a sensitive function of the electronic as well as steric nature of the attendant Cp ligands in each case.

Solvated CpCo fragments are likely intermediates in a number of reactions involving cobalt, including cyclotrimerization reactions[5,17] and the synthesis of trinuclear alkylidyne clusters.[18] The decomposition reaction of 1 has provided some insight into the reactivity of this important species as well as illuminated a fundamental cluster degradation reaction. Further studies into the properties of these species as well as the reactions of 1 with other weakly ligating solvents are in progress.

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[9] Other dinuclear complexes $[Cp^*M(\mu\text{-}CO)]_2$ react with 2 to form mixed-metal complexes of the form $[CpCo(\mu\text{-}CO)_2MCp^*]$.[3] In the case of 5, however, reaction with 2 is degenerate and does not produce any new species in the system.

[10] Herrmann, W. A.; Barnes, C. E.; Zahn, T.; Ziegler, M. L. *Organometallics* **1985**, *4*, 172.

[11] The concentration of C_6D_6 at 40 °C, 11.0 M, was obtained from the density for the protio analogue adjusted for the change in molecular weight and a 0.2% change in the molar volume.

[12] Jonas, K.; Deffense, E.; Habermann, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 716.

[13] Other studies in our laboratories show that independently synthesized arene complexes similar to A react with 5 to give 6 in benzene, similar to what is observed here. In THF no reaction between any arene complex and 5 is observed (manuscript in preparation).

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