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Author

Bryndza, H.E.

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Henry E. Bryndza and Robert G. Bergman

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Reaction of a Bridged Binuclear Dialkylcobalt Complex
with Carbon Monoxide and Phosphines: Observation of Competing
Inter- and Intramolecular Metal-to-Metal Methyl Transfer

Henry E. Bryndza and Robert G. Bergman

Abstract

The dinuclear cobalt complex $\text{CH}_2[\eta^5\text{-C}_5\text{H}_4\text{Co(CO)}_2]_2$ (**5**) has been prepared from dicyclopentadienylmethane and dicobalt octacarbonyl. Chemical reduction and methylation of this material gives the binuclear dimethyl complex $\text{CH}_2[\eta^5\text{-C}_5\text{H}_4\text{Co(CO)(CH}_3)]_2$ (**7**), which is considerably more stable than the corresponding complex which does not have CH_2 -linked cyclopentadienyl rings. Carbonylation of **7** occurs at 70° in benzene, and gives a quantitative yield of acetone and **5**. Crossover experiments demonstrate that this reaction occurs by competing inter- and intramolecular pathways, the extent of intramolecularity increasing as the concentration of **7** is lowered. Reaction of **7** with phosphines gives a highly specific reaction: no acetone is formed; rather, the sole product, formed quantitatively, is $(\text{PPh}_3)(\text{CH}_3)_2\text{Co}(\eta^5\text{-C}_5\text{H}_4)\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)\text{Co(CO)}_2$ (**8**). In this reaction, therefore, one metal retains its bonds to both carbonyls, and the methyl group initially attached to this metal migrates to the metal atom being attacked by phosphine. Surprisingly, this reaction is also substantially intermolecular at high concentrations of **7**; however, it becomes essentially completely intramolecular at low concentrations. The phosphine reaction exhibits clean pseudo-first order kinetics when an excess of phosphine is used; the dependence of k_{obs} on $[\text{PPh}_3]$ demonstrates that **7** is in equilibrium with an intermediate (suggested to be the singly-CO bridged, coordinately unsaturated species **E**) which subsequently reacts with PPh_3 .

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Sir:

bis- $[\eta^5\text{-cyclopentadienylcarbonylmethylcobalt}]$ (1) reacts rapidly with carbon monoxide at ambient temperature, leading to a quantitative yield of $\eta^5\text{-cyclopentadienyldicarbonylcobalt}$ (2) and acetone, a process in which a binuclear transition metal complex mediates the formation of two new carbon-carbon bonds. In a previous study¹, we established that $\eta^5\text{-cyclopentadienylcarbonyldimethylcobalt}$ (3) is an intermediate in this transformation. Labeling studies indicated that an intermolecular process was occurring, resulting in the formation of substantial amounts of acetone- d_3 upon carbonylation of equimolar mixtures of 1-d_6 and 1-d_0 .

In order to determine whether this intermolecular process is on the direct pathway leading from 1 to 3, we have now prepared 7 (Chart II), a complex analogous to 1, but having its two cyclopentadienyl rings joined by a methylene group. We find this structural modification allows us to control the intramolecularity of the carbonylation reaction by modifying reaction conditions. In addition, 7 undergoes a remarkable reaction with phosphines which sharply restricts mechanistic alternatives for these reactions.

Dicyclopentadienylmethane (4) was prepared² as a mixture of isomers and converted to the binuclear tetracarbonyl 5 by the route outlined in Chart II. As might be expected if decomposition of 1 involves initial dissociation into mononuclear fragments, complex 7 is less reactive than 1, and requires temperatures near 70° to achieve carbonylation at a reasonable rate. Under these conditions, the chemistry of 7 is quite comparable to that of 1, and acetone and tetracarbonyl complex 5 are produced in quantitative yield. Unlike 1,

however, the carbonylation can be made to follow a predominantly intra- or intermolecular pathway by varying the concentration of starting complex $\tilde{7}$. Thus, as shown in Table 1, approximately equimolar mixtures of $\tilde{7}$ -d₀ and $\tilde{7}$ -d₆ (labeled methyl groups) at 0.05 M total concentration of $\tilde{7}$ gives acetone in a reaction which is 90% intramolecular. At saturation (0.25M), however, 44% of the reaction takes place by an intermolecular path, presumably analogous to that¹ occurring in $\tilde{1}$.

Treatment of $\tilde{1}$ with triphenylphosphine gave a complicated reaction, leading to lowered (but still significant) yields of acetone, as well as several carbonylphosphine complexes. We believe this is partly due to the fact that the rate of reaction of $\tilde{1}$ with phosphine is comparable to that of its spontaneous thermal decomposition. In contrast, complex $\tilde{7}$, stable at room temperature in solution, reacted at a convenient rate with triphenylphosphine, giving a very clean reaction. This led to no acetone. Only one product was formed, an organometallic complex which had infrared absorptions in the metal carbonyl region (2015, 1958 cm⁻¹; THF) very similar³ to that of CpCo(CO)₂, and NMR absorption in the methyl region (δ 0.40, d, $J = 6\text{Hz}(\text{C}_6\text{D}_6)$) very similar⁴ to that of CpCo(CH₃)₂PPh₃ ($\tilde{9}$). Isolation and characterization by standard methods demonstrated this complex has structure $\tilde{8}$ (Chart III). In analogy to the carbonylation of $\tilde{9}$, heating $\tilde{8}$ with CO led to acetone and tetracarbonyl complex $\tilde{5}$.

Despite the cleanliness of the reaction of $\tilde{7}$ with PPh₃, its quantitative yield, and clear second-order kinetics, the intramolecularity of the reaction is still dependent upon the concentration of starting complex, just as in the carbonylation. Data once again obtained with mixtures of $\tilde{7}$ -d₆ and $\tilde{7}$ -d₀ are summarized in Table 1.

The two most reasonable mechanistic alternatives for these processes are

outlined in Chart IV. Our initial hypothesis (path (a)) involved unbridging both carbonyls followed by metal-metal bond cleavage (as observed with 1), to give intermediate A. However, reaction of A with an entering ligand, followed by methyl transfer from one metal to the other, simply cannot be the route to product (at least in the reaction of 7 with PPh_3), because this would lead to B, and B must necessarily give¹ complex 10 and acetone. In fact the appearance of two CO groups bound to one cobalt in the product of the PPh_3 reaction, in a system where the mixed phosphinecarbonyl is known to be more stable, requires that one cobalt atom retain its bonding to both carbonyls during the entire reaction. This restrictive requirement leaves little reasonable alternative other than path (b), at least in general outline. Here metal-metal cleavage must preserve one carbonyl bridge, giving bis-18-electron complex C. Cleavage of the remaining metal-carbonyl bond must occur now only at the "right-hand" metal atom, leading to D. In the intramolecular process, this intermediate transfers a methyl radical from the formally 19-electron cobalt to its 17-electron neighbor, leading to 8. At high concentrations, the methyl group may be transferred to a 17-electron cobalt in another molecule of D, generating intermolecular product.⁵

Kinetic studies provide further details concerning the intimate mechanism of the first step of this reaction scheme. Two distinct possibilities exist for the generation of species C: either 7 and phosphine react in a direct associative process or reaction proceeds through an unsaturated unstable intermediate, such as E, which is then trapped by phosphine to yield C. The dependence of the reaction rate upon phosphine concentration dramatically confirms the latter hypothesis. Reactions of 7 with excess phosphine show pseudo-first-order kinetics in the conversion of 7 to 8 (figure 2). As $[\text{PPh}_3]$ is raised from relatively low absolute concentrations the observed

reaction rate becomes independent of phosphine. This is exactly the behavior expected by the reaction scheme shown in Chart V. Analysis of the kinetic data yields $k_1 = 1.28 \times 10^{-4} \text{ sec}^{-1}$ and $k_{-1}/k_2 = 4.3 \times 10^{-2} \text{ M}^{-1}$.

This study emphasizes that even when organometallic reactions are kinetically well-behaved and give one product in quantitative yield, it is critically important to carry out crossover experiments to test their intramolecularity. In this case such experiments, combined with the specific nature of the transformation involved, have allowed us to delineate especially sharply the mechanism of a carbon-carbon bond forming reaction mediated by a binuclear organotransition metal complex.

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Henry E. Bryndza⁶, Robert G. Bergman
Department of Chemistry, University
of California, Berkeley, and Materials
and Molecular Research Division,
Lawrence Berkeley Laboratory, Berkeley,
California

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5. An alternative possibility involves methyl transfer from D to a second molecule of 7, initiating a chain process of the type suggested in ref. 1. We cannot rigorously rule out this process; however, no evidence for this type of autocatalysis was evident in our kinetics experiments.
6. Hertz Foundation Fellow, 1977-present.

Table 1. Isotope Labeling Data Obtained in Crossover Experiments on the Reaction of Mixtures γ -d₀ and γ -d₆ with CO and PPh₃.

Starting Complex (%)			Entering Ligand	T (°C)	Acetone Products ^c			Molecularity	
Total Conc. (m)	γ -d ₀	γ -d ₆			d ₀	d ₃	d 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 Isotope Analysis was by GC/MS. Acetone was obtained as the direct product of the carbonylation reaction. In the PPh₃ reaction, product 8 was carbonylated to generate acetone for GC/MS analysis.

Chart I

Chart II

Chart III

Chart IV

Chart V

$$k_{\text{obs}} = \frac{-d[Z]}{dt} = \frac{k_1 [L]}{(k_{-1}/k_2) + [L]}$$

Figure Captions

Fig. 1. 180 MHz FT NMR spectra (methyl region) of a mixture of $\tilde{7}$, PPh_3 and tetramethylsilane (TMS) internal standard as the complex is converted to $\tilde{8}$. (solvent: C_6D_6).

Fig. 2. Plot of the log of the ratio $[\tilde{7}]/[\tilde{7}]_0$ vs. time, as measured by integration of methyl absorptions in the NMR vs. TMS internal standard. (solvent: C_6D_6).

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