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METHANE-PRODUCING HYDROGENOLYSIS OF (η^5 -CYCLOPENTADIENYL)-
(TRIPHENYLPHOSPHINE)DIMETHYLCOBALT(III). AN AUTOCATALYTIC
MECHANISM INVOLVING A BINUCLEAR METAL DIHYDRIDE/METAL
DIALKYL REACTION AS A CRITICAL STEP

Andrew H. Janowicz and Robert G. Bergman

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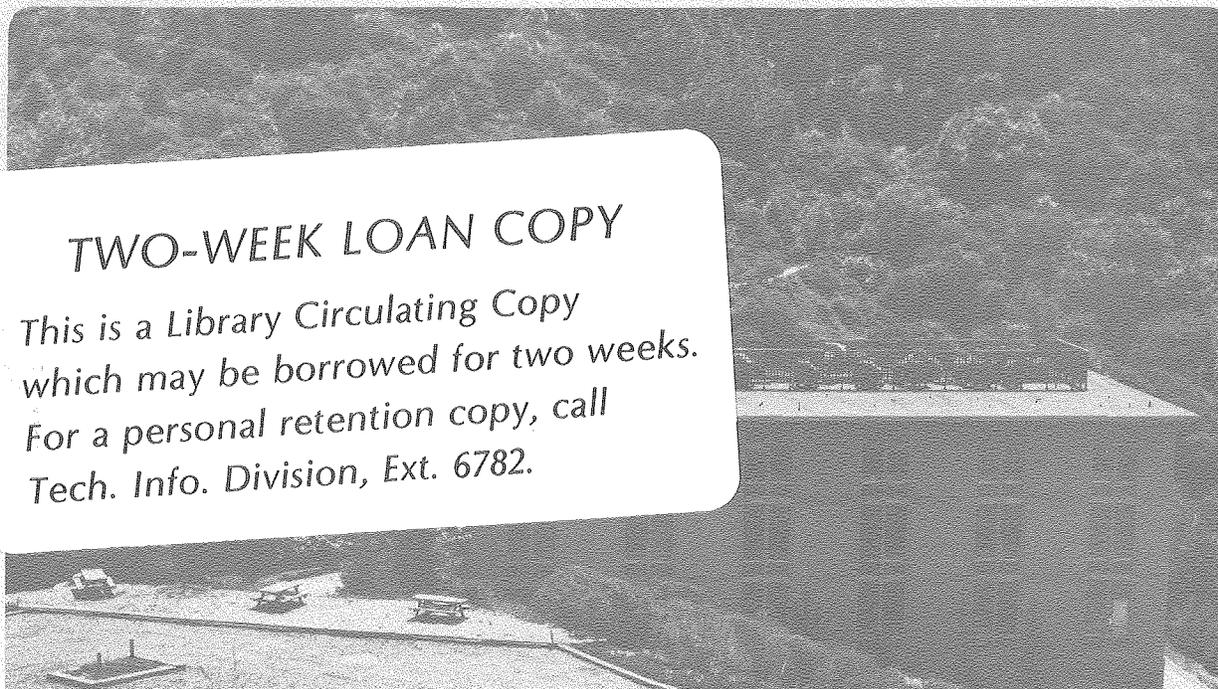
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Mechanism Involving a Binuclear Metal Dihydride/Metal Dialkyl
Reaction as a Critical Step.

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Abstract

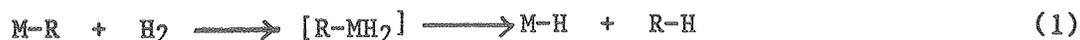
The cleavage of organotransition metal-carbon bonds by H_2 (hydrogenolysis) is a ubiquitous step in many catalytic processes, but its mechanism is not well understood. In an effort to study this process directly, the mechanism of hydrogenolysis of the title compound (1) has been investigated. Hydrogenolysis of 1 takes place under mild conditions, and leads to two moles of methane and (η^5 -cyclopentadienylbis-(triphenylphosphine)cobalt(I) (2). The reaction is autocatalytic; the rate is inhibited by added phosphine and accelerated by the addition of product 2 to the initial reaction mixture. A mechanism is proposed which postulates that 2 reacts with dihydrogen to give (η^5 -cyclopentadienyl)-(triphenylphosphine)dihydridocobalt(III) (5) as a transient species, and methane is formed by reaction of 5 with 1. Dihydride 5 is unknown and could not be prepared to test this hypothesis directly; however, it was found possible to generate solutions of the corresponding pentamethylcyclopentadienyl dihydride 7 by hydrogenolysis of 6, the pentamethylcyclopentadienyl analog of 1. As predicted, 7 and 6 react readily to give methane, and the kinetics of this reaction are consistent with the mechanism postulated for the hydrogenolysis of 1.

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Sir:

The cleavage of organotransition metal-carbon bonds by H_2 is an important part of many catalytic processes. For example, the terminating steps in hydroformylation¹ and homogeneous hydrogenation² require cleavage of a metal acyl or alkyl by H_2 , and the (heterogeneous) Fischer-Tropsch reaction requires several steps in which C-H bonds are formed, including the final release of hydrocarbon or oxygenate from the metal surface.³

It has commonly been assumed that M-R hydrogenolysis occurs by oxidative addition of H_2 to the metal center at which the carbon fragment is attached, followed by formation of a new C-H bond by reductive elimination (eq. (1)).⁴



However, evidence has recently been obtained⁵ that in hydroformylation, the final C-H bond forming step is a binuclear process, involving reaction between a transient cobalt acyl complex and the hydroformylation catalyst, $HCo(CO)_4$. Several other M-H/M-R reactions (eq. (2)) have also been discovered recently.⁶ Despite this, however, studies aimed at the direct investigation of the mechanism of metal-carbon bond hydrogenolysis reactions are rare. In this paper, we wish to report our results on the mechanism of

the facile methane-forming hydrogenolysis of cyclopentadienyldimethylcobalt derivatives. We chose these complexes for study because they give methane on hydrogenolysis, and yet it seemed unlikely that this process could be occurring by loss of phosphine followed by oxidative addition of H_2 to give a formally Co(V) intermediate. We find that even though no metal hydrides are added as reagents in this reaction, the new C-H bonds are still formed by a binuclear M-H/M-R reaction.

Reaction of $(\eta^5-C_5H_5)Co(PPh_3)(CH_3)_2$ (1) with dihydrogen in benzene- d_6 at $45^\circ C$ yields two equivalents of CH_4 and 0.5 equivalents of $(\eta^5-C_5H_5)Co(PPh_3)_2$ (2)(Scheme I). In the presence of an added equivalent of PPh_3 , the reaction rate is slower but the hydrogenolysis now gives two equivalents of CH_4 and nearly a full equivalent of 2 (eq. (3)). Treatment of complex 1 with D_2 under the same conditions gives CH_3D , establishing that the new hydrogen atom does in fact come from the hydrogen gas.

In agreement with the notion that a conventional mechanism might not be accessible for this process, monitoring the reaction of 1 with H_2 in the presence of added phosphine revealed the presence of an induction period, whose length was dependent upon the concentration of phosphine (Fig. 1). Following the induction period, the rate gradually accelerated until the system began to be depleted in complex 1. Such induction periods are often characteristic of free-radical chain processes; however, the operation of a radical chain in this system seemed somewhat unlikely, because it would presumably have to involve methyl radicals. These very reactive radicals would almost certainly produce some toluene by reaction with benzene solvent; in addition, because of the comparable bond energies of H_2 and methane, H_2 should not transfer hydrogen very rapidly to methyl radicals. Nevertheless, we carried out the hydrogenolysis using D_2 , $(\eta^5-C_5H_5)Co(PPh_3)(CD_3)$ and ten

equivalents (0.95M) of 1,4-cyclohexadiene, a very reactive reagent for transfer of hydrogen atoms to organic radicals.⁷ Under these conditions the methane produced was still exclusively CD₄. This suggested strongly that a radical chain process was not responsible for the observed induction period.

A second explanation for the induction period is that the hydrogenolysis is autocatalytic; we have been able to obtain much stronger experimental support for this hypothesis. As stated above, this rate behavior is observed when the reaction is performed in the presence of added phosphine. Adding both phosphine and the CpCo(PPh₃)₂ reaction product, however, makes the induction period disappear (although the overall rate still exhibits inhibition by PPh₃) and gradually increasing rates are observed immediately after mixing the reagents (Fig. 1). Clearly product 2 is a catalyst (or catalyst precursor) for the hydrogenolysis of 1.

An autocatalytic mechanism consistent with the observations reported above is outlined in Scheme II. We know that the thermal decomposition of 1 is slow at 45° and has a complicated mechanism, but some Co(I) species are produced in this reaction.⁸ We believe these initiate the hydrogenolysis, and once some 4 is produced, this takes over as the critical Co(I) species. Complex 1 is in equilibrium with small amounts of unsaturated complex 3 at 45°.⁸ Complex 2 dissociates phosphine even more rapidly ($k_{\text{dissoc}} = 1.15 \times 10^{-3} \text{ sec}^{-1}$ in toluene-d₈ even at -60° C),⁹ leading to 4. Oxidative addition of H₂ to 4 then gives dihydride 5. The critical step in this mechanism involves binuclear reaction of dihydride 5 with unsaturated dialkyl 3, leading to methane and CpCo(I) fragments; these either continue the autocatalysis, or are scavenged by PPh₃ to give 2.

We sought additional support for this mechanism by attempting to prepare dihydride 5, so that we might investigate its reactions with 1 directly.

Unfortunately, neither reaction of 1 with H₂, reaction of 2 with excess H₂, nor treatment of CpCo(PR₃)I₂ derivatives with hydride reagents gave any evidence for the formation of stable dihydrides. As an alternative, therefore, we prepared¹⁰ 6, the pentamethylcyclopentadienyl analog of 1. When 6 and excess H₂ were allowed to react in benzene-d₆ at 45°, methane was again produced, along with a new material whose proton NMR spectrum (δ 1.77 (15H, s), δ 6.90-7.10 (12H, m), δ 7.70-7.83 (6H, m), δ -16.54 (2H, d, J_{P-H} = 87 Hz) ppm) was consistent with its formulation as (η^5 -C₅Me₅)Co(PPh₃)H₂ (7). This material showed a strong absorption in the IR at 1908 cm⁻¹. This was assigned as ν_{M-H} on the basis of its shift to 1376 cm⁻¹ when metal-bound hydrogen was replaced with deuterium.¹¹

Evaporation of the benzene solvent left the dihydride as a green oil; however, this material decomposed rapidly in the absence of a hydrogen atmosphere. Supportive evidence that H₂ is lost rapidly from 7 came from the finding that it easily gave (η^5 -C₅Me₅)Co(PPh₃)D₂ upon exposure, in benzene solution, to an atmosphere of deuterium gas. Although rapid H₂ loss has prevented us from isolating 7 as a pure solid, benzene solutions of the dihydride are stable for relatively long periods of time. This stability encouraged us to carry out a study of the interaction of dimethyl complex 6 with dihydride 7.

Dialkyl 6 and dihydride 7 reacted readily at 45°, as predicted by Scheme II, to give two moles of methane. We have not yet been able to characterize the organometallic products of this reaction, but in the presence of excess 7 and PPh₃, the rate of disappearance of 6 (as determined by ¹H-NMR) showed good pseudo-first-order kinetics. Steady-state analysis of the mechanism shown in Scheme III predicts that the pseudo-first-order rate constant k_{obs} should depend upon the dihydride and PPh₃ concentrations as shown by the rate

law given in eq. (4). Rearranging gives eq. (5), which predicts that a plot of k_{obs}^{-1} vs. $[\text{PPh}_3]/[7]$ should be linear. The rate constant k_{obs} was

$$\frac{d[6]}{dt} = \frac{k_1 k_2 [7]}{k_2 [7] + k_{-1} [\text{PPh}_3]} [6] = k_{\text{obs}} [6] \quad (4)$$

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_1} + \frac{k_{-1} [\text{PPh}_3]}{k_1 k_2 [7]} \quad (5)$$

therefore determined at several different concentrations of PPh_3 and 7, and plotted according to eq. (5). As shown in Fig. 2, the predicted linear behavior is observed. From the slope and intercept of the plot, we calculate $k_1 = 1.83 \times 10^{-4} \text{ sec}^{-1}$, and $k_{-1}/k_2 = 1.44$.

Scheme III and the corresponding rate law posit a specific level of unsaturation of each reacting partner in the rate determining step associated with microscopic rate constant k_2 ; i.e., the dialkyl reactant is coordinatively unsaturated, whereas the hydride is saturated. The rate law itself rules out the possibility that both reactants are unsaturated; reversible dissociation of phosphine followed from both 7 and 6, followed by reaction of the two unsaturated species so produced, would give an inverse squared dependence upon the concentration of phosphine, which is not observed. That it is the dialkyl complex, rather than the dihydride, which is unsaturated is suggested by the ease with which PMe_3 replaces PPh_3 in 6. This result parallels that of 1 which undergoes PMe_3 substitution by a dissociative mechanism⁸ through intermediate 3.

In summary, even though the inaccessibility of the formal Co(V) oxidation state prevents oxidative addition of H_2 to

cyclopentadienylcobalt(III) derivatives, they still undergo facile hydrogenolysis, and this hydrogenolysis involves a metal alkyl/metal hydride reaction as a critical step. The lack of a stoichiometric amount of metal hydride reagent present at the beginning of the hydrogenolysis reaction leads to an autocatalytic mechanism; direct reaction between dialkyl and dihydride does not require autocatalysis. As in other reactions involving interaction of a metal hydride with a coordinatively unsaturated alkyl,⁶ we do not yet know the precise structure of the intermediate involved in the M-R/M-H step, but we assume interaction initially involves entry of the hydride end of the M-H bond into the metal coordination sphere of the dialkyl, forming a bridging hydride. The precise structure of this complex, and how reductive elimination occurs within it, is not yet clear. It is interesting, however, that on the basis of the relative rate constant ratio k_2/k_{-1} measured in our kinetic study, PPh_3 reacts with the unsaturated intermediate **8** only slightly more rapidly than does the dihydride **7**. In any case, it appears that M-H/-R reactions are relatively facile, and should be given serious consideration as alternatives to mononuclear steps in homogeneous catalytic processes involving C-H bond formation. It also seems possible that similar processes take place in surface-catalyzed reactions. That is, C-H bond forming steps in processes such as the Fischer-Tropsch reaction may involve sites (e.g, "steps" or "kinks",¹² as shown in Scheme IV) capable of coordinating both an alkyl group and bridging hydride ligand, and C-H bond formation may occur from these sites.

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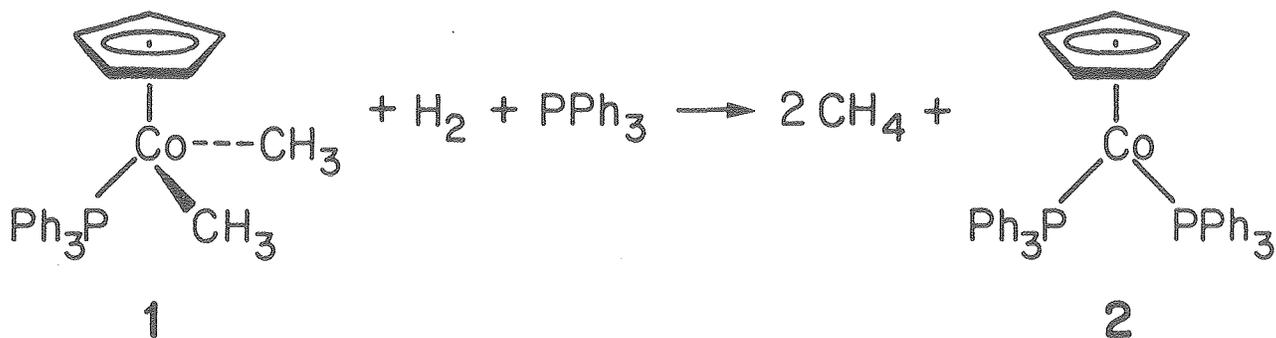
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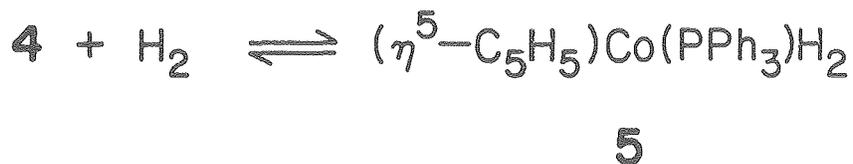
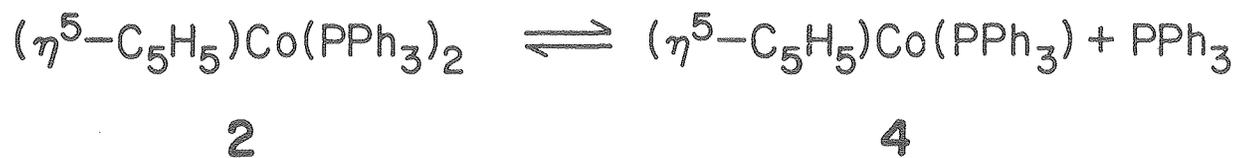
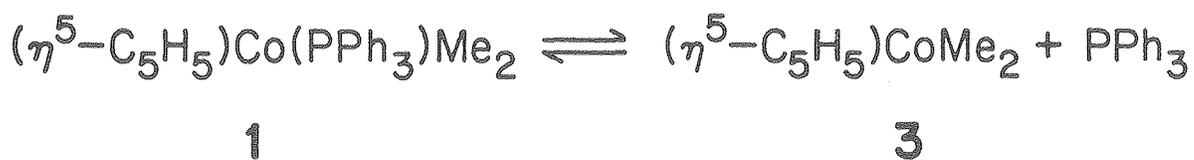
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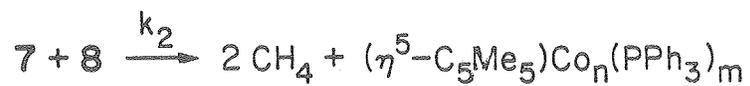
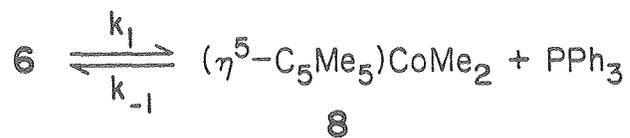
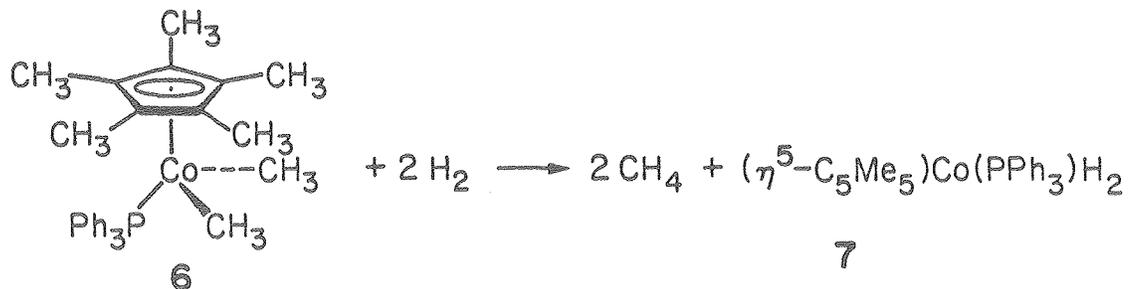
Scheme I



Scheme II



Scheme III



Scheme IV

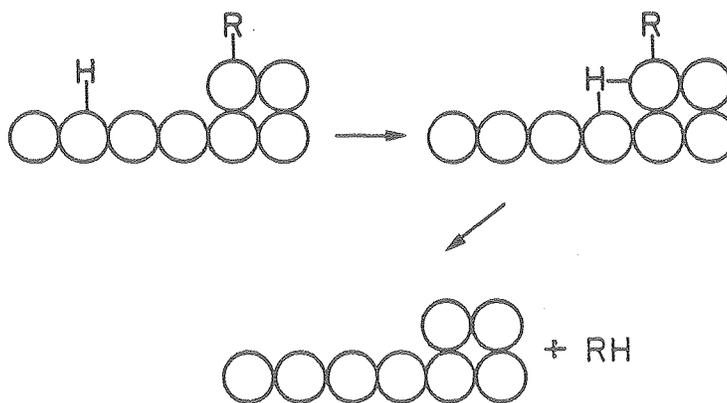


Figure Captions

Figure 1. Concentration vs. time plots for the disappearance of complex 1 (0.10 M initial concentration of 1; 3 atm H₂), in benzene-d₆ at 25° C., with the following additives: Δ : no additives; \diamond : 0.025 M PPh₃; \square : 0.05 M PPh₃; \times : 0.10 M PPh₃; \circ : 0.10 M PPh₃ and 0.017 M 2.

Figure 2. Dependence of the pseudo-first-order rate constant for reaction of complex 6 with dihydride 7 (measured in the presence of excess 7 and PPh₃) upon the ratio of PPh₃ to 7.

