

Evidence for Reversible α -Hydrogen Abstraction from Methyl-cobalt and -rhodium Complexes Involving the Possible Formation of Hydrido-carbene Intermediates

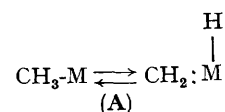
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Summary Evidence for a reversible α -hydrogen abstraction from methyl groups of $\text{CoCH}_3(\text{PPh}_3)_3$ and $\text{RhCH}_3(\text{PPh}_3)_3$ involving intermediate carbene-hydride formation is presented on the basis of the mass spectrometric analysis of polydeuteriated methanes formed in the reaction of D_2 with $\text{CoCH}_3(\text{PPh}_3)_3$ and $\text{RhCH}_3(\text{PPh}_3)_3$ in toluene.

In discussing the stability of a transition-metal alkyl complex, β -hydrogen abstraction from the metal alkyl has often been assumed as the main pathway leading to the decomposition of the alkyl complex¹ and an α -hydrogen abstraction process² has been regarded less likely, despite

evidence for the occurrence of the reversible α -hydrogen abstraction process involving the possible formation of an intermediate hydride-carbene complex (A).



Methyltris(triphenylphosphine)cobalt(I),⁵ (1) and methyltris(triphenylphosphine)rhodium(I),⁶ (2), are thermally stable in the solid state, but they release methane slowly in solution at room temperature *via* internal oxidative addition of the triphenylphosphine ligand and reductive elimination of the methyl-hydrido-complexes. Methane is also formed by contact of H_2 gas at room temperature with solutions containing (1) and (2) by oxidative addition of H_2 and reductive elimination of the methyl-dihydrido-complexes.⁶

Mass spectroscopic examination of methane formed in the reaction of D_2 with (1) and (2) showed polydeuteriated methanes. The Figure shows the distribution of isotopically labelled methanes formed in the reactions of (1) and (2) with excess of D_2 (isotopic purity 99%) at *ca.* 1 atm (D_2 : complex = 20:1) at room temperature and 0° for 12–20 h.

The most striking feature is the formation of CD_4 , CD_3H , and CD_2H_2 in addition to CH_3D and CH_4 which are expected on the basis of the above mentioned properties of (1) and (2). The formation of highly deuteriated methanes can only be explained by assuming that rapid reversible processes take place comprising α -hydrogen abstraction from the methyl group, exchange of the abstracted hydrogen with deuterium derived from the gas phase, and back migration of the deuterium to the hydrogen-abstracted methyl group, followed by reductive elimination of the methyl-hydride intermediate. The reaction is complicated by the presence of several reversible and irreversible processes occurring simultaneously, as in the Scheme.

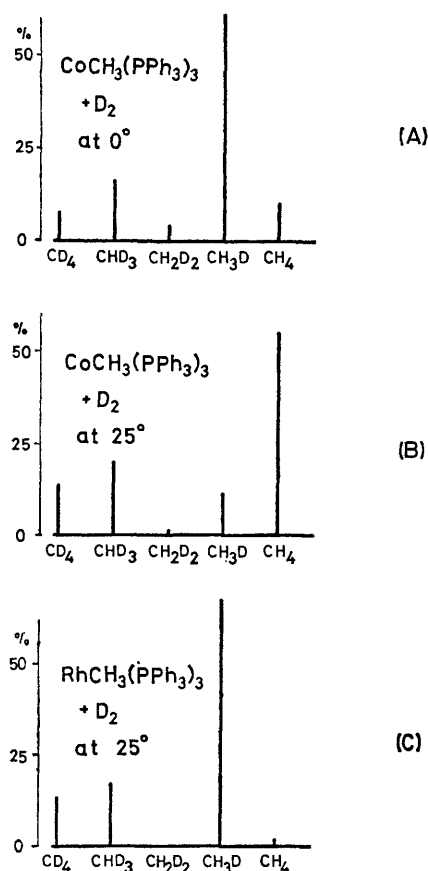
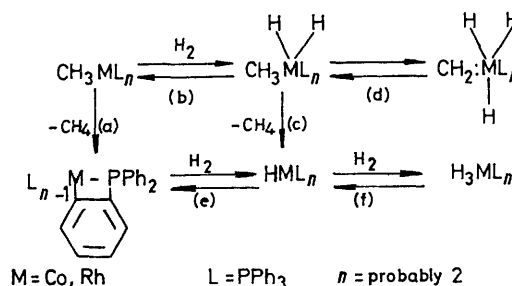


FIGURE. The distribution of deuteriated and non-deuteriated methanes formed by the reaction of $\text{CoCH}_3(\text{PPh}_3)_3$ with D_2 at 0° (A) and at 25° (B) and of $\text{RhCH}_3(\text{PPh}_3)_3$ with D_2 at 25° (C). The distribution was deduced from the mass spectra.

a few reports presenting indirect evidence supporting the α -elimination process.³ We have shown that an ethyl complex susceptible to reversible β -hydrogen abstraction can exist as a thermally stable complex,⁴ and we now report



M = Co, Rh L = PPh₃ n = probably 2

SCHEME

The three triphenylphosphine ligands are probably partly dissociated in solution and n is probably 2 in accordance with the 18-electron rule. The results shown in the Figure suggest that the exchange processes involving the steps (b) and (d) are taking place at comparable rates with the step (c). Lowering the reaction temperature of the

methylcobalt complex decreased the amount of CH_4 formed by process (a). Extensive scrambling of deuterium with *ortho*-hydrogens of the phenyl groups in triphenylphosphine⁷⁻⁹ was demonstrated by the i.r. spectrum of the reaction product of (1) with D_2 at 0 and 25 °C and also by analysis of D_2 , HD, and H_2 after the reaction. The appearance of the characteristic $\nu(\text{N}\equiv\text{N})$ band at 2085 cm^{-1} after the reaction of (1) with D_2 followed by treatment with N_2 suggests the formation of a cobalt hydride complex which can be converted into a dinitrogen complex. The methylrhodium complex (2) is less reactive in step (a) than

(1) and the amount of undeuteriated CH_4 formed in the reaction at room temperature was very small and the incorporation of deuterium into phenyl rings was also negligible.

The other possibility of the formation of polydeuteriated methanes by an H-D exchange reaction¹⁰ of CH_4 with D_2 catalysed by (1) or (2) seems less likely on the basis of the distribution of the polydeuteriated methanes.

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