

Decarbonylation of Methanol by Highly Reactive Rhenium Complexes

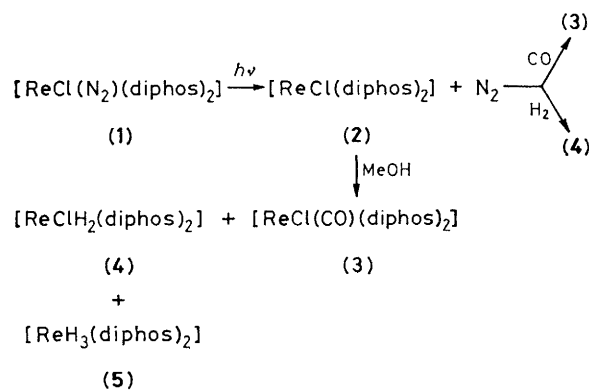
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The reaction of photogenerated $[\text{ReCl}(\text{diphos})_2]$ (diphos = $\text{Ph}_2\text{P}[\text{CH}_2]_2\text{PPh}_2$) with methanol gives decarbonylation under mild conditions and yields $[\text{ReCl}(\text{CO})(\text{diphos})_2]$ and $[\text{ReClH}_2(\text{diphos})_2]$.

The metal promoted decarbonylation of aldehydes and acid halides is well known.¹ These reactions are common for Group 8 metals, particularly rhodium, and examples of stoichiometric and catalytic abstraction of carbon monoxide from these substrates under mild conditions have been reported. The decarbonylation of alcohols has been less studied, although alcoholic solvents have frequently been used as a source of CO in many synthetic reactions. Basic alcohols such as allyl alcohol and 2-methoxyethanol are readily decarbonylated by a variety of metal salts resulting in the formation of carbonyl and hydridocarbonyl complexes.² Saturated alcohols normally require the presence of strong base such as hydride or hydroxide for the reaction to proceed.² The direct, metal induced decarbonylation of methanol to CO and H_2 is an interesting reaction in view of the possible mechanistic relationship to Fischer-Tropsch synthesis. Although the decomposition of methanol on metal surfaces is well documented,³ there are few examples of unassisted decarbonylation by discrete metal complexes. In fact, $[\text{RhCl}(\text{PPh}_3)_3]$, one of the most versatile complexes for abstraction of CO from organic substrates, shows no tendency to decarbonylate MeOH even at 80 °C in an autoclave.⁴ We report here the decarbonylation of methanol under mild conditions by highly reactive rhenium species generated from $[\text{ReCl}(\text{N}_2)(\text{phosphine})_4]$ complexes.

$[\text{ReCl}(\text{N}_2)(\text{diphos})_2]$ ⁵ (1) (diphos = $\text{Ph}_2\text{P}[\text{CH}_2]_2\text{PPh}_2$) reacts in refluxing methanol to yield the known carbonyl adduct, $[\text{ReCl}(\text{CO})(\text{diphos})_2]$ ⁶ (3),† in low yield. Presumably, the first step of the reaction involves the loss of N_2 from the starting material yielding $[\text{ReCl}(\text{diphos})_2]$ (2) which then reacts with methanol. The overall conversion into product is low even after 24 h, evidently as a result of the relatively high thermal stability of (1) to nitrogen loss.⁵ The reaction is greatly accelerated by u.v. light, and irradiation of (1) with 366 nm light for several hours in MeOH gives high yield



Scheme 1

(44–67%) conversion into (3).‡ Independent experiments in benzene solution establish that the photoreaction involves loss of N_2 and generation of the reactive five-coordinate complex, (2),§ and that reaction of MeOH with (2) occurs readily at room temperature even in the dark (Scheme 1). The complex (3) can also be prepared in quantitative yield by addition of CO to benzene solutions of (2).

The rhenium dihydride, $[\text{ReClH}_2(\text{diphos})_2]$ ⁷ (4),† is also formed in moderate yield (26–56%) during the decarbonylation reaction. The product ratio is dependent on light intensity, irradiation time, and reaction conditions. In some experiments, $[\text{ReH}_3(\text{diphos})_2]$ ⁷ (5) is also formed in low yield (<10%). Since the decarbonylation of MeOH also involves the production of H_2 , (4) is likely to be formed by trapping

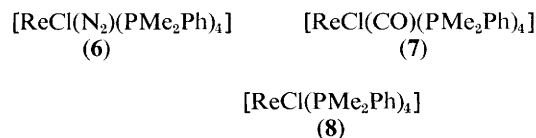
† In a typical experiment 25–50 mg of (1) was suspended in 5–10 ml of thoroughly dried and deoxygenated MeOH and irradiated with a Blak-Ray Longwavelength Lamp (Ultra-violet Products B-100A) equipped with a 366 nm filter.

§ Complex (2) can be isolated as a dark green solid by evaporation of benzene from irradiated solutions of (1), and gives the expected spectroscopic data (i.r. and ^1H and ^{31}P n.m.r. analyses).

‡ All products have been characterized by comparison of i.r. and n.m.r. (^1H and ^{31}P) spectral data with samples prepared independently according to literature methods.

(2) with hydrogen. In fact, (4) can be obtained in quantitative yield from (2) by reaction with hydrogen. Complex (5) may be formed during the hydrogen abstraction process which accompanies decarbonylation by elimination of HCl rather than H₂. The decarbonylation of MeOH by (2) is stoichiometric, but photolysis of (3) or (4) could provide a pathway for regeneration of (2).

The precise mechanism of the decarbonylation has not yet been determined, but it could well involve either O–H or C–H oxidative addition to rhenium followed by formation of a formyl or hydroxycarbene intermediate by hydrogen transfer. Both of these possibilities are intimately related to the hydrogenation of CO in the Fischer–Tropsch reaction.⁸ The reaction could also occur *via* dehydrogenation of MeOH followed by the decarbonylation of HCHO in a subsequent reaction. Complex (2) does react with paraformaldehyde to give moderate conversion to (3). However, the predominance of (3) in the product mixture favours direct decarbonylation of methanol by (2), since (4) would be expected to be the major product if the reaction proceeded by initial dehydrogenation to form formaldehyde.



Carbonyl and hydride complexes are also formed upon photolysis of [ReCl(N₂)(PMe₂Ph)₄]⁵ (6)[†] in methanol, although the reaction is not as clean as with chelating phosphine ligands. At least four distinctly different metal hydride species are apparent in the ¹H n.m.r. spectrum of the product mixture in addition to [ReCl(CO)(PMe₂Ph)₄]⁶ (7).[†] The photogenerated intermediate, [ReCl(PMe₂Ph)₄] (8), appears

to be even more reactive than the diphos analogue. The intermediate (8) readily decarbonylates paraformaldehyde with production of (7) in high yield, and reacts with acetone to give low yield conversion into (7) and a mixture of rhenium hydrides similar to those obtained from the reaction of (8) with MeOH. A number of interesting hydride complexes are also formed on reaction of (8) with water. Details of these reactions will be reported separately.

We thank the National Science Foundation for support of this work through the NSF–MRL program, and acknowledgement is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society for partial support of this work.

Received, 28th June 1982; Com. 746

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