

Preliminary communication

REVERSIBLE INSERTION OF CO₂ INTO THE Re—H BOND OF PHOTOGENERATED [ReH(Ph₂PCH₂CH₂PPh₂)₂]

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Summary

Ultraviolet irradiation of solutions of [ReH₃(diphos)₂] results in elimination of H₂ and generation of [ReH(diphos)₂]. This highly reactive species is readily trapped by N₂, CO, and C₂H₄ to give known 1/1 adduct complexes. Irradiation in the presence of CO₂ yields the new formate complex, [Re(O₂CH)(diphos)₂] which derives by reversible insertion of CO₂ into the Re—H bond of [ReH(diphos)₂].

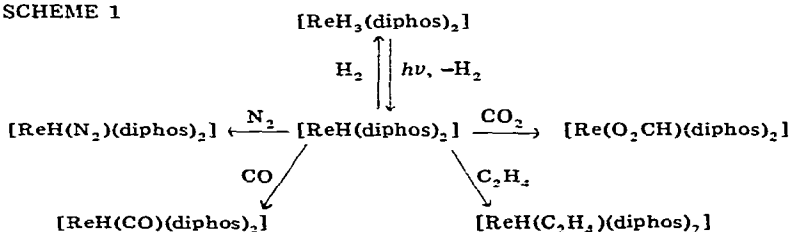
Photoinduced loss of H₂ is a common reaction pathway for transition metal di- and polyhydride complexes [1]. We have been exploring the utility of this photoelimination reaction for the generation of highly reactive coordinatively-unsaturated species which may be capable of activating molecules such as N₂ and CO₂ and hydrocarbon C—H bonds. Polyhydride complexes of the early transition metals are especially interesting in this regard, and herein we report our preliminary results of an investigation of [ReH₃(diphos)₂] (diphos = Ph₂PCH₂CH₂PPh₂).

Irradiation of a thoroughly degassed benzene solution of [ReH₃(diphos)₂] [2,3] with 366 nm light gives a slow color change from yellow to gold. Accompanying this color change is a smooth decrease in intensity of the characteristic ν (M—H) (1860 cm⁻¹) and δ (M—H) (850 cm⁻¹) IR bands of [ReH₃(diphos)₂] [2] and no new bands appear in the ν (M—H) region. The production of H₂ was confirmed by mass spectral and gas chromatographic analysis of the gases above irradiated solutions. Exhaustive irradiation (6–10 days) results in the release of 0.91 ± 0.18 mol of H₂ per mol of complex irradiated and suggests the overall stoichiometry shown in eq. 1.

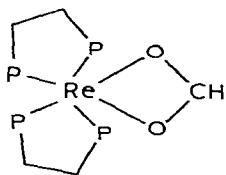


The primary photoproduct of this reaction, presumably $[\text{ReH}(\text{diphos})_2]$ or a solvated derivative, is highly reactive and is readily trapped by added substrate. Irradiation of benzene solutions of the trihydride under N_2 , CO and C_2H_4 atmospheres leads to the respective adduct complexes, $[\text{ReH}(\text{N}_2)(\text{diphos})_2]$, $[\text{ReH}(\text{CO})(\text{diphos})_2]$ and $[\text{ReH}(\text{C}_2\text{H}_4)(\text{diphos})_2]$, according to Scheme 1. The identity of these photoproducts was confirmed by comparison of their IR and ^1H NMR spectra to previously published data [4]. Although these photoreactions appear to proceed cleanly, they are difficult to drive to completion and only about 50% of the starting $[\text{ReH}_3(\text{diphos})_2]$ is converted to product during 20–24 h photolysis.

SCHEME 1



The photogenerated intermediate, $[\text{ReH}(\text{diphos})_2]$ is also readily scavenged by CO_2 . Irradiation of a benzene solution of $[\text{ReH}_3(\text{diphos})_2]$ under a CO_2 atmosphere gives a slow color change from yellow to orange, and a bright orange solid is obtained upon evaporation of solvent. Recrystallization of this material from benzene/2-propanol gives orange crystals which show two new CO_2 derived bands in the IR spectrum (KBr disc) at 1554 and 1356 cm^{-1} . Substitution of $^{13}\text{CO}_2$ in the photolysis experiment gives a similar orange solid in which these bands are shifted to 1515 and 1334 cm^{-1} , as expected for the $^{12}\text{C} \rightarrow ^{13}\text{C}$ substitution and evidencing the incorporation of CO_2 into the product. The IR spectrum shows no evidence for a $\text{Re}-\text{H}$ vibration, but a new weak band is apparent at 2825 cm^{-1} which may be assigned to the formate $\text{C}-\text{H}$ stretch. These data are in agreement with that reported for other metal complexes which have been given formate formations [5,6].



(I)

Conclusive evidence for the formate formulation of the photoproduct comes from an examination of the ^{13}C NMR spectrum of the complex (Fig. 1). The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows a single resonance at δ 171.9 ppm which splits into a doublet with $J(\text{C}-\text{H})$ 202 Hz in the proton coupled spectrum. Both the chemical shift and the coupling constant fall within the range found

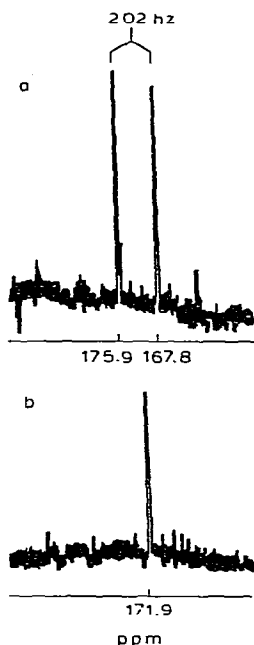
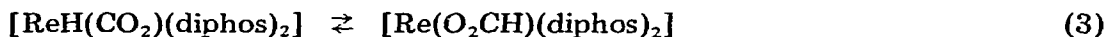
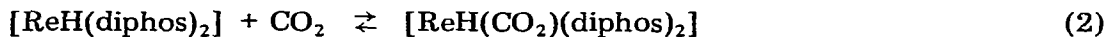


Fig. 1. ^{13}C (A) and ^{13}C ^1H (B) NMR spectra of $[\text{Re}(\text{O}_2\text{CH})(\text{diphos})_2]$ in C_6D_6 solution.

for organic formates [7]. The chemical shifts of ethyl formate and formic acid, for example, are 160.7 and 166.7 ppm, respectively [7]. The ^{13}C -H coupling constants for the formate carbon generally lie between 170–230 Hz with HCO_2^- showing a coupling constant of 194.8 Hz. The most reasonable structure for $[\text{Re}(\text{O}_2\text{CH})(\text{diphos})_2]$ is that sketched in I which is directly analogous to the structure of the dithioformate $[\text{Re}(\text{S}_2\text{CH})(\text{CO})_2(\text{PPh}_3)_2]$ complex recently reported by Freni et al. [8] and structured by Albano and coworkers [9].

Several experiments have indicated that addition of CO_2 to $[\text{ReH}(\text{diphos})_2]$ is reversible. Solid samples of the complex slowly decompose when heated to 80–100°C and mass spectral and gas chromatographic analysis of the gases above decomposed samples indicate the production of CO_2 . Toepler pump measurements gave a value of 0.97 ± 0.10 mol of gas produced per mol of complex decomposed. Storage of a benzene solution of $[\text{Re}(\text{O}_2\text{CH})(\text{diphos})_2]$ under N_2 gives quantitative conversion to $[\text{ReH}(\text{N}_2)(\text{diphos})_2]$ with release of carbon dioxide. Similarly, CO_2 can be displaced by H_2 to yield the starting trihydride, $[\text{ReH}_3(\text{diphos})_2]$.

These various experiment suggest that the $[\text{Re}(\text{O}_2\text{CH})(\text{diphos})_2]$ complex forms via the sequence of reactions shown in eqs. 2 and 3.



Presumably CO_2 initially adds to $[\text{ReH}(\text{diphos})_2]$ to generate a CO_2 complex similar to the adduct complexes which form with N_2 , CO , and C_2H_4 . Hydride migration to the coordinated CO_2 would then generate the observed formate

derivative. Both of these reactions must be reversible, however, since CO_2 is readily replaced by N_2 and H_2 under rather mild conditions.

Further experiments are currently in progress to more fully characterize the nature of the $[\text{ReH}(\text{diphos})_2]$ intermediate and to further examine its reactivity features. Preliminary experiments indicate that it is sufficiently active to insert into C—H bonds of aromatic hydrocarbons.

Acknowledgments

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