

the  $\text{Ru}(\text{bpy})_3^+$  is used to reduce  $\text{Co}^{\text{II}}\text{L}$  to a hydride which does not produce hydrogen efficiently under the *homogeneous* conditions used.

In the absence of well-defined schemes for homogeneously catalyzed reduction of water, the addition of heterogeneous catalysts such as platinum can clearly meet the need for efficient dark reactions. This study has shown that these reactions can be so efficient that the overall limiting factor in determining  $\Phi_{\text{H}_2}$  is the rapidity of back-reactions tending to destroy the primary photoproducts. Factors which determine these electron-transfer rate constants include the driving force for the back-reaction,<sup>1,39</sup> steric factors, the charges of the reacting species, and spatial

separation of the back-reactants, as well as other factors which are described in detail elsewhere.<sup>1,40</sup> Increased efficiency of both photochemical and dark reactions are the goals of ongoing research in this laboratory.

**Acknowledgment.** We thank Dr. D. Christman for performing the mass spectrometric analysis of bpy samples and Ms. E. Norton for her outstanding analytical efforts on our behalf. In addition, we gratefully acknowledge very helpful comments from Drs. G. M. Brown and H. A. Schwarz. This research was performed under the auspices of the U.S. Department of Energy and supported by its Division of Basic Energy Sciences.

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## Photogeneration of Reactive $[\text{ReH}(\text{diphos})_2]$ . Its Reversible Coordination of $\text{CO}_2$ and Activation of Aromatic C-H Bonds

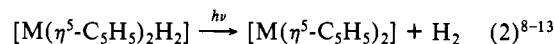
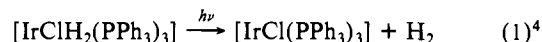
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**Abstract:** Irradiation of  $[\text{ReH}_3(\text{diphos})_2]$  (diphos =  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ) with UV light leads to elimination of  $\text{H}_2$  with a 366-nm quantum yield of  $0.07 \pm 0.02$ . The initial photoproduct is  $[\text{ReH}(\text{diphos})_2]$  or a solvated derivative, but this species is highly reactive and rapidly adds  $\text{N}_2$ ,  $\text{CO}$ , and  $\text{C}_2\text{H}_4$  to give the known  $[\text{ReH}(\text{N}_2)(\text{diphos})_2]$ ,  $[\text{ReH}(\text{CO})(\text{diphos})_2]$ , and  $[\text{ReH}(\text{C}_2\text{H}_4)(\text{diphos})_2]$  derivatives. Photolysis in the presence of  $\text{C}_2\text{H}_2$  gives a new species tentatively formulated as  $[\text{ReH}(\text{C}_2\text{H}_2)(\text{diphos})_2]$ . Irradiation in the presence of  $\text{CO}_2$  yields the new formate complex,  $[\text{Re}(\text{O}_2\text{CH})(\text{diphos})_2]$ , which derives by reversible insertion of  $\text{CO}_2$  into the  $\text{Re}-\text{H}$  bond of  $[\text{ReH}(\text{diphos})_2]$ . NMR evidence indicates that  $[\text{ReH}(\text{diphos})_2]$  undergoes rapid but reversible ortho metalation and insertion into the C-H bonds of benzene.  $[\text{ReH}(\text{diphos})_2]$  can also be generated via photoinduced loss of  $\text{N}_2$  from  $[\text{ReH}(\text{N}_2)(\text{diphos})_2]$ .

A number of studies have demonstrated that photolysis of transition metal di- and polyhydride complexes gives elimination of  $\text{H}_2$  as the dominant photoreaction.<sup>1-17</sup> Two such examples

are shown in eq 1 and 2. In order to further demonstrate the



M = Mo, W

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generality of this type of reaction and especially to attempt to employ it for the generation of thermally unattainable reactive intermediates, we have extended our previous studies<sup>3-8</sup> to include several polyhydride complexes of the early transition metals. We have focused especially on Re because of the variety of known polyhydride complexes of this metal<sup>18,19</sup> and herein describe the results of our study of  $[\text{ReH}_3(\text{diphos})_2]$  (diphos =  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ).

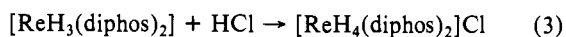
Although the chemistry of  $[\text{ReH}_3(\text{diphos})_2]$  has not been extensively examined, the complex is known to be thermally quite stable. It shows no tendency to lose  $\text{H}_2$  when heated to  $180^\circ\text{C}$  in an evacuated Carius tube,<sup>20</sup> and it will not react to give the known  $[\text{ReH}(\text{N}_2)(\text{diphos})_2]$  derivative when heated under 60 psi of  $\text{N}_2$ .<sup>21</sup> In contrast to most metal hydrides, treatment of

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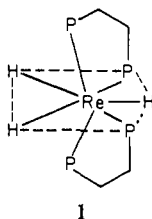
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[ReH<sub>3</sub>(diphos)<sub>2</sub>] with HCl gives simple protonation rather than loss of H<sub>2</sub>, eq 3.<sup>20</sup> The geometry of the ReH<sub>3</sub>P<sub>4</sub> core of



[ReH<sub>3</sub>(diphos)<sub>2</sub>] is that depicted in 1. The positioning of the



1

diphos ligands was determined by a single-crystal X-ray diffraction study, and the positions of the hydride ligands were inferred from potential energy calculations.<sup>22</sup> The <sup>1</sup>H NMR spectrum recorded at -50 °C is fully consistent with such a structure, although the complex is fluxional at room temperature.<sup>21</sup>

### Experimental Section

The [ReH<sub>3</sub>(diphos)<sub>2</sub>] and [ReH(N<sub>2</sub>)(diphos)<sub>2</sub>] complexes were generously supplied to us by A. P. Ginsberg and had been prepared by literature procedures.<sup>23,24</sup> Diphos was obtained from Strem Chemicals, Inc., and was used as received. All other chemicals were reagent grade and were used without further purification. Solvents employed were dried by standard methods and rigorously degassed prior to use. All manipulations of the compounds were carried out under purified Ar or N<sub>2</sub>. Acetylene (C.P.), carbon monoxide (C.P.), ethylene (C.P.), and carbon dioxide (Coleman Instrument Grade) were obtained from Matheson Gas Products. The carbon monoxide was deoxygenated and dried by passing it through BASF BTS Katalysator and Linde 5-Å molecule sieve columns prior to use. <sup>13</sup>CO<sub>2</sub> (90% enriched) was obtained from Merck, Sharp, and Dohme.

**General Irradiation Procedures.** Irradiations were conducted at 366 nm by using a 450-W Hanovia medium-pressure Hg lamp equipped with Corning Glass 0-52 and 7-37 filters (*I* ≈ 10<sup>-6</sup> einstein/min), with a 100-W Blak-Ray B100A lamp equipped with a 366-nm narrow band-pass filter, or in a 350-nm Rayonet photoreactor. The complex to be studied was placed in an evacuable quartz UV cell or a Schlenk tube, and after the cell or tube was degassed the appropriate solvent was distilled onto the sample. Solutions for IR studies were transferred in an N<sub>2</sub>-filled drybox or an Ar-filled glovebag to 0.5 mm NaCl solution IR cells. Samples for <sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C NMR spectra were similarly prepared and the NMR tubes sealed under vacuum. Solutions were irradiated with the appropriate lamp, and UV-vis, IR, and NMR spectra were periodically recorded. In some experiments the gases above the irradiated solutions were periodically removed and measured by Toepler pump techniques. Gases were analyzed by mass spectrometry and by gas chromatography on a Linde 5-Å molecular sieve column in series with a 60–80 mesh Fluorosilicone column. The quantum yield of elimination of H<sub>2</sub> from [ReH<sub>3</sub>(diphos)<sub>2</sub>] was determined by monitoring the decrease in intensity of the 320-nm absorption maximum of [ReH<sub>3</sub>(diphos)<sub>2</sub>] in CH<sub>2</sub>Cl<sub>2</sub> solution. Lamp intensities were measured by ferrioxalate actinometry.<sup>25</sup>

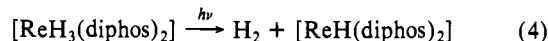
**Preparation of [Re(O<sub>2</sub>CH)(diphos)<sub>2</sub>].** A 366-nm irradiation of a 75-mL deoxygenated benzene solution of [ReH<sub>3</sub>(diphos)<sub>2</sub>] (100 mg, 0.1 mmol) under a slow, continuous CO<sub>2</sub> purge gave a color change from yellow to orange. Removal of solvent yielded a bright orange solid which was shown to contain [Re(O<sub>2</sub>CH)(diphos)<sub>2</sub>] by its spectral properties. In a typical experiment, approximately 50% of the [ReH<sub>3</sub>(diphos)<sub>2</sub>] was converted to [Re(O<sub>2</sub>CH)(diphos)<sub>2</sub>] after 15-h irradiation. The crude material can be purified somewhat by recrystallization from benzene/2-propanol, but it is difficult to remove all of the unreacted [ReH<sub>3</sub>(di-

phos)<sub>2</sub>] and an analytically pure sample was not obtained.

**Spectral Measurements.** The instruments employed in this study are as follows: a Cary 17 spectrophotometer for UV-visible spectra, a Perkin-Elmer Model 580 spectrophotometer for IR spectra, an AEI-MS-902 spectrometer for mass spectra, and JEOL PS-100-FT and Bruker WH 200 Fourier transform spectrometers for NMR spectra. <sup>13</sup>C NMR spectra were referenced internally to C<sub>6</sub>D<sub>6</sub>, <sup>1</sup>H NMR spectra to external Si(CH<sub>3</sub>)<sub>4</sub> or internal C<sub>6</sub>H<sub>6</sub>, and <sup>31</sup>P NMR spectra to external H<sub>3</sub>PO<sub>4</sub> with downfield chemical shifts reported as positive.

### Results

**Photolysis of [ReH<sub>3</sub>(diphos)<sub>2</sub>] in Degassed Solution.** Although H<sub>2</sub> loss from [ReH<sub>3</sub>(diphos)<sub>2</sub>] cannot be induced thermally,<sup>20,21</sup> it does occur upon photolysis. Irradiation of degassed benzene solutions of the complex with 366-nm light gives a color change from yellow to gold with a corresponding intensification and shift in the absorption maximum from 320 to 310 nm. In the IR, as the irradiation proceeds, the ν<sub>M-H</sub> (1860 cm<sup>-1</sup>) and δ<sub>M-H</sub> (850 cm<sup>-1</sup>) bands of [ReH<sub>3</sub>(diphos)<sub>2</sub>] decrease in intensity and no new bands appear in the metal hydride region. The production of H<sub>2</sub> during photolysis was verified by mass spectral and gas chromatographic analyses of the gases above irradiated solutions. In three separate experiments, the gases above exhaustively photolyzed (6–10 days) solutions were periodically removed and quantitated by Toepler pump techniques, giving an average value of 0.94 ± 0.18 mol of H<sub>2</sub> released/mol of complex irradiated. These results clearly demonstrate the elimination of H<sub>2</sub> and suggest the stoichiometry shown in eq 4.



The 366-nm quantum yield of H<sub>2</sub> loss from [ReH<sub>3</sub>(diphos)<sub>2</sub>] is 0.07 ± 0.02. Due to the air sensitivity of [ReH<sub>3</sub>(diphos)<sub>2</sub>], the quantum yield was determined by irradiating a CH<sub>2</sub>Cl<sub>2</sub> solution of the complex in a degassed and sealed UV cell. Since the reaction vessel was sealed and hence back-reaction with H<sub>2</sub> was not prevented, the measured quantum yield must be considered a lower limit value.

Although the stoichiometry of the reaction (eq 4) and the reactivity experiments detailed below indicate that the primary photoproduct from [ReH<sub>3</sub>(diphos)<sub>2</sub>] is almost certainly [ReH(diphos)<sub>2</sub>] or a solvated derivative, this species has proven difficult to directly detect and characterize because of its high reactivity. As shown by the following series of NMR and IR experiments, it undergoes reversible insertion into the C-H bonds of both benzene solvent and the phenyl groups of the diphos ligands. The <sup>1</sup>H NMR spectrum of a C<sub>6</sub>D<sub>6</sub> solution of [ReH<sub>3</sub>(diphos)<sub>2</sub>] shows a steady decrease in intensity of the δ -7.35 [ReH<sub>3</sub>(diphos)<sub>2</sub>] resonance as the sample is irradiated, but no new resonances appear anywhere in the metal hydride region (δ 0 → -30). Exposure of such solutions to N<sub>2</sub> does not yield the δ -9.5 resonance characteristic of the expected [ReH(N<sub>2</sub>)(diphos)<sub>2</sub>] product (see below); yet the IR spectrum of the solid material obtained after evaporation of solvent shows a strong ν<sub>N≡N</sub> at 2006 cm<sup>-1</sup> characteristic of this compound.<sup>24</sup> The lack of a <sup>1</sup>H NMR resonance for the product thus indicates that the dinitrogen complex actually formed is the deuterated analogue, [ReD(N<sub>2</sub>)(diphos)<sub>2</sub>], and thus its solution precursor must be [ReD(diphos)<sub>2</sub>]. Further support for the [ReD(N<sub>2</sub>)(diphos)<sub>2</sub>] formulation comes from the presence of a weak band in its IR spectrum at 1330 cm<sup>-1</sup> that is not present in the spectrum of [ReH<sub>3</sub>(diphos)<sub>2</sub>] and which may be attributed to a ν<sub>Re-D</sub> vibration.

The other significant features of the IR spectrum of this material are the weak three-band pattern at 1542, 1557, and 1575 cm<sup>-1</sup> characteristic of ortho-metalated arylphosphines<sup>4,27</sup> and a weak broad band centered at 2260 cm<sup>-1</sup>. The latter may be attributed to an aromatic C-D stretch (C<sub>6</sub>D<sub>6</sub>, ν<sub>C-D</sub> = 2277, 2267 cm<sup>-1</sup>; P(2,6-C<sub>6</sub>H<sub>3</sub>D<sub>3</sub>)<sub>3</sub>, ν<sub>C-D</sub> = 2254 cm<sup>-1</sup>) which is presumed to arise from ortho-deuterated diphos ligands. Further evidence for the incorporation of deuterium into the diphos ligands comes from

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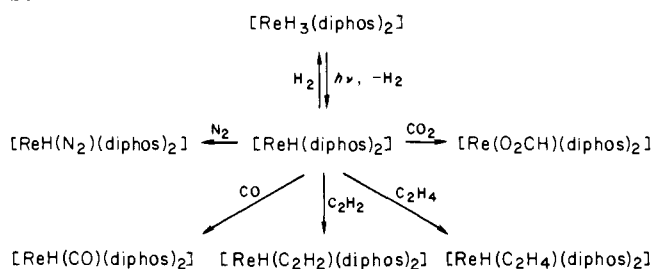
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(26) [ReH(N<sub>2</sub>)(diphos)<sub>2</sub>]: ν<sub>N≡N</sub> = 2006 cm<sup>-1</sup>, δ<sub>Re-H</sub> -9.7 (q) (lit.<sup>24</sup> ν<sub>N≡N</sub> = 2006 cm<sup>-1</sup>, δ<sub>Re-H</sub> -9.94 (q)). [ReH(CO)(diphos)<sub>2</sub>]: ν<sub>CO</sub> = 1845 cm<sup>-1</sup>, δ<sub>Re-H</sub> -6.0 (q) (lit.<sup>24</sup> ν<sub>CO</sub> = 1843 cm<sup>-1</sup>, δ<sub>Re-H</sub> 6.21 (q)). [ReH(C<sub>2</sub>H<sub>4</sub>)(diphos)<sub>2</sub>]: δ<sub>C<sub>2</sub>H<sub>4</sub></sub> 7.5, δ<sub>Re-H</sub> -6.7 (q) (lit.<sup>24</sup> δ<sub>C<sub>2</sub>H<sub>4</sub></sub> 7.64, δ<sub>Re-H</sub> -6.92 (q)). The slight difference between the observed vs. literature values presumably arises due to the different media employed. (CS<sub>2</sub> vs. C<sub>6</sub>D<sub>6</sub> for <sup>1</sup>H NMR spectra and CsI vs. KBr for IR spectra.)

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## Scheme I



the  $^1\text{H}$  NMR spectral changes in the  $\delta$  0–10 spectral region.  $[\text{ReH}_3(\text{diphos})_2]$  shows a broad singlet at  $\delta$  7.5, a multiplet at  $\delta$  7.0, and a broad singlet at  $\delta$  2.1. The relative intensities of these resonances are in the ratio of 2:3:1, and they are logically attributed to the diphos ortho, meta/para, and methylene protons, respectively. Upon photolysis of  $[\text{ReH}_3(\text{diphos})_2]$  in  $\text{C}_6\text{D}_6$  solution, the  $\delta$  7.5 resonance completely disappears while the other resonances remain relatively unchanged. At the same time the solvent  $\text{C}_6\text{D}_5\text{H}$  resonance increases in intensity, thus indicating  $\text{H}/\text{D}$  exchange between solvent and coordinated diphos.

An amorphous yellow-gold solid can be isolated from exhaustively photolyzed benzene solutions of  $[\text{ReH}_3(\text{diphos})_2]$  by solvent evaporation. This material shows a very broad, weak absorption centered at  $1845\text{ cm}^{-1}$  in its IR spectrum, a weak three-band pattern at  $1542$ ,  $1557$ , and  $1575\text{ cm}^{-1}$ , and a weak band at  $725\text{ cm}^{-1}$ . Although further characterization of this material has not proven possible because of its amorphous nature and its extreme air-sensitivity, the IR spectrum is not inconsistent with the presence of ortho-metalated diphos ligands.<sup>4,27</sup>

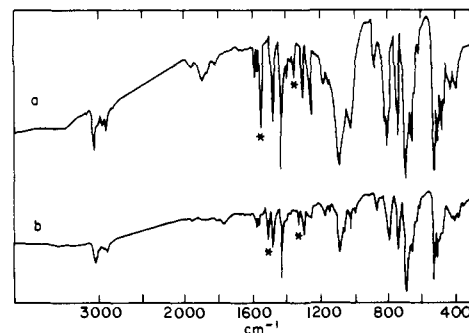
**Photolysis of  $[\text{ReH}_3(\text{diphos})_2]$  in the Presence of Reactant Gases.**

**(1)  $\text{N}_2$ ,  $\text{CO}$ , and  $\text{C}_2\text{H}_4$ .** Irradiation of benzene solutions of  $[\text{ReH}_3(\text{diphos})_2]$  under  $\text{N}_2$ ,  $\text{CO}$ , and  $\text{C}_2\text{H}_4$  atmospheres leads to the respective adduct complexes  $[\text{ReH}(\text{N}_2)(\text{diphos})_2]$ ,  $[\text{ReH}(\text{CO})(\text{diphos})_2]$ , and  $[\text{ReH}(\text{C}_2\text{H}_4)(\text{diphos})_2]$  (Scheme I). These previously described compounds were identified primarily by comparison of their IR and  $^1\text{H}$  NMR spectra to those reported.<sup>26</sup>

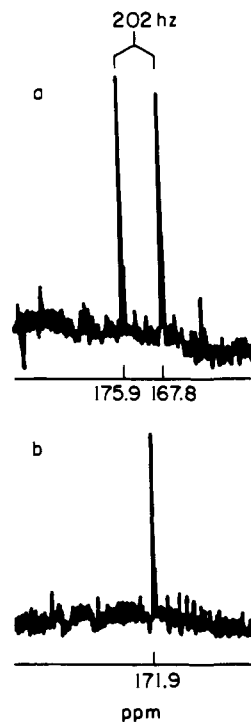
Although the infrared spectra of the  $[\text{ReH}(\text{L})(\text{diphos})_2]$  adduct complexes do not show the characteristic  $1860$ - and  $850\text{-cm}^{-1}$  bands of  $[\text{ReH}_3(\text{diphos})_2]$ , the  $^1\text{H}$  NMR spectra of the photoproducts show a quintet at  $\delta$   $-7.35$  ( $J_{\text{P-H}} = 17.8\text{ Hz}$ ) indicative of residual trihydride. A comparison of the relative intensities of the hydride resonances of  $[\text{ReH}_3(\text{diphos})_2]$  and  $[\text{ReH}(\text{L})(\text{diphos})_2]$  indicates that approximately 50% conversion to the corresponding  $[\text{ReH}(\text{L})(\text{diphos})_2]$  complexes occurs during 20–24-h irradiation. Increased conversion occurs with increased irradiation time, but it is difficult to drive these photoreactions entirely to completion. Adduct complexes prepared by this method are invariably contaminated with residual  $[\text{ReH}_3(\text{diphos})_2]$ .

**(2)  $\text{C}_2\text{H}_2$ .** The  $[\text{ReH}(\text{diphos})_2]$  intermediate can also be trapped by acetylene. Irradiation of benzene solutions of  $[\text{ReH}_3(\text{diphos})_2]$  under a  $\text{C}_2\text{H}_2$  atmosphere gives a slow color change from yellow to light brown, and a brown solid can be isolated by solvent evaporation from the irradiated solutions. This material shows a weak band in its IR spectrum at  $1690\text{ cm}^{-1}$  and a quintet at  $\delta$   $-4.35$  ( $J_{\text{P-H}} \approx 20\text{ hz}$ ) in its  $^1\text{H}$  NMR spectrum, in addition to a quintet at  $\delta$   $-7.35$  due to residual  $[\text{ReH}_3(\text{diphos})_2]$ . The product is thermally unstable and solutions darken considerably upon standing under  $\text{N}_2$ , eventually depositing an oily brown residue after several days.

The IR band at  $1690\text{ cm}^{-1}$  implies the presence of an alkyne ligand in the photoproduct, although  $\nu_{\text{C}\equiv\text{C}}$  in alkyne complexes varies considerably with the nature of the complex and with the alkyne substituents.<sup>29–32</sup> The  $1690\text{-cm}^{-1}$  band lies between the  $\nu_{\text{C}\equiv\text{C}}$  bands at  $1613\text{ cm}^{-1}$  and  $1774\text{ cm}^{-1}$  reported for  $[\text{Mo}(\eta^5\text{-}$



**Figure 1.** Infrared spectra of (a)  $[\text{Re}(\text{O}_2\text{CH})(\text{diphos})_2]$  and (b)  $[\text{Re}(\text{O}_2^{13}\text{CH})(\text{diphos})_2]$ . The bands which shift upon isotopic labeling are indicated with the asterisks.



**Figure 2.**  $^{13}\text{C}$  (a) and  $^{13}\text{C}\{^1\text{H}\}$  (b) NMR spectra of  $[\text{Re}(\text{O}_2^{13}\text{CH})(\text{diphos})_2]$ .

$\text{C}_5\text{H}_5)_2(\text{C}_2\text{H}_2)]^{30}$  and  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{PhC}\equiv\text{CPh})]^{31}$  respectively. The upfield hydride resonance at  $\delta$   $-4.3$  is in the range of the hydride resonances of the other adduct complexes,<sup>24,26</sup> and thus formulation of the product as  $[\text{ReH}(\text{C}_2\text{H}_2)(\text{diphos})_2]$  is indicated.

**(3)  $\text{CO}_2$ .** The photogenerated  $[\text{ReH}(\text{diphos})_2]$  intermediate is also readily scavenged by  $\text{CO}_2$ . Irradiation of benzene solutions of  $[\text{ReH}_3(\text{diphos})_2]$  in the presence of  $\text{CO}_2$  gives a slow color change from yellow to orange, and a bright orange solid can be isolated by evaporation of solvent from the irradiated solutions. The IR spectrum of this material is shown in Figure 1a. Two new bands are evident at  $1554$  and  $1356\text{ cm}^{-1}$  which are not present in the spectrum of  $[\text{ReH}_3(\text{diphos})_2]$ . Substitution of  $^{13}\text{CO}_2$  in the photolysis experiment gives an orange product with the infrared spectrum shown in Figure 1b. The  $1554$ - and  $1356\text{-cm}^{-1}$  bands shift to  $1515$  and  $1334\text{ cm}^{-1}$  as expected for the  $^{12}\text{C} \rightarrow ^{13}\text{C}$  substitution, and thus  $\text{CO}_2$  has clearly been incorporated into the molecule. No  $\nu_{\text{Re-H}}$  vibration is apparent in the metal hydride region of the IR spectrum. A group of bands is centered at  $1960\text{ cm}^{-1}$ , but these appear to be due to the coordinated diphos ligands. The  $^1\text{H}$  NMR spectrum of a benzene solution of the orange solid shows no new upfield resonances, although the ever present quintet at  $\delta$   $-7.35$  due to residual  $[\text{ReH}_3(\text{diphos})_2]$  is evident. The  $^{13}\text{C}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of the  $^{13}\text{CO}_2$ -enriched product are shown in Figure 2. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum shows a single resonance at  $\delta$   $171.9$  which splits into a doublet with  $J_{\text{C-H}} = 202$

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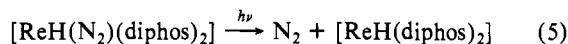
(32) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley: New York, 1978; p 387.

Hz in the proton coupled spectrum.

The product of the reaction with CO<sub>2</sub> is sensitive to thermal substitution of carbon dioxide. Storage of a benzene solution of the complex under an N<sub>2</sub> atmosphere results in a slow color change from orange to yellow. Removal of solvent from the yellow solution gives yellow crystals of [ReH(N<sub>2</sub>)(diphos)<sub>2</sub>], characterized by its strong ν<sub>N=N</sub> at 2066 cm<sup>-1</sup>. This reaction appears to be quantitative as evidenced by the complete disappearance of the 1554- and 1356-cm<sup>-1</sup> IR bands. Similar treatment of the orange product with H<sub>2</sub> gives [ReH<sub>3</sub>(diphos)<sub>2</sub>]. The orange product slowly decomposes when heated to 80–100 °C, and mass spectral and gas chromatographic analyses of the gases above decomposed samples show the presence of CO<sub>2</sub>. Quantitative Toepler pump analysis of the evolved gases upon decomposition of the highest purity material that we have obtained gave a value of 0.97 mol of CO<sub>2</sub> given off/mol of complex.

In an effort to drive the photoreaction to completion, [ReH<sub>3</sub>(diphos)<sub>2</sub>] was irradiated in benzene solution in a sealed Carius tube under 5 atm of CO<sub>2</sub>. A similar color change from yellow to orange resulted and removal of solvent gave an orange solid which showed the familiar IR bands at 1554 and 1356 cm<sup>-1</sup> and a new weak band in the ν<sub>C=O</sub> region at 1825 cm<sup>-1</sup>. Substitution of <sup>13</sup>CO<sub>2</sub> in a similar experiment gave a product with infrared bands at 1515, 1334, and 1775 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum of this material showed the presence of unreacted [ReH<sub>3</sub>(diphos)<sub>2</sub>]. Thus, photolysis under CO<sub>2</sub> pressure did not lead to an improved yield of product but rather to an even more complex mixture containing a new, apparent carbonyl complex.<sup>33</sup>

**Photolysis of [ReH(N<sub>2</sub>)(diphos)<sub>2</sub>].** Elimination of H<sub>2</sub> from [ReH<sub>3</sub>(diphos)<sub>2</sub>] occurs with a relatively low quantum yield (φ = 0.07), and stoichiometric elimination of H<sub>2</sub> requires greater than 1 week of continuous photolysis. The latter presumably arises because of the high affinity of the [ReH(diphos)<sub>2</sub>] photoproduct for H<sub>2</sub>, and thus once the concentration of the former builds up, it efficiently scavenges H<sub>2</sub> released from the remaining molecules of [ReH<sub>3</sub>(diphos)<sub>2</sub>]. It occurred to us that a more convenient means of generating reactive [ReH(diphos)<sub>2</sub>] would be to photoinduce loss of N<sub>2</sub> from [ReH(N<sub>2</sub>)(diphos)<sub>2</sub>] (eq 5). Photoe-



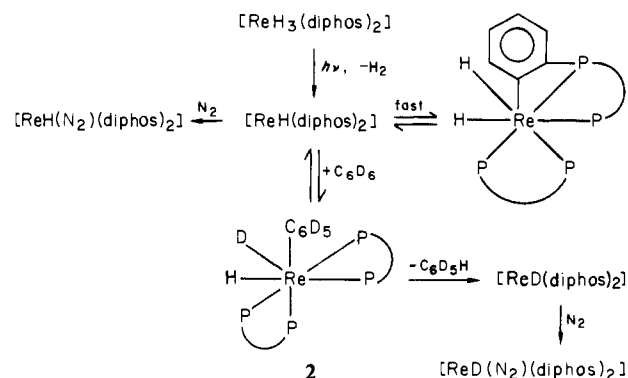
limination of N<sub>2</sub> is a common photoreaction, generally occurring with high quantum yield.<sup>34–37</sup> Furthermore, [ReH(diphos)<sub>2</sub>] was not expected to scavenge the photoreleased N<sub>2</sub> as efficiently as it picks up H<sub>2</sub>.

These expectations were indeed realized. Irradiation of benzene solutions of [ReH(N<sub>2</sub>)(diphos)<sub>2</sub>] with 366 nm light leads to a rapid color change from yellow to gold. Although a quantum yield for the reaction has not been measured, a stoichiometric amount of released N<sub>2</sub>, determined by quantitative Toepler pump techniques, results after only 45 min of 366-nm irradiation, in contrast to the 7–10 days required for a comparable quantity of [ReH<sub>3</sub>(diphos)<sub>2</sub>]. Continued irradiation of these [ReH(N<sub>2</sub>)(diphos)<sub>2</sub>] solutions for 12 h yielded no additional gas products. In all respects, the behavior of the photoproduct is identical with that obtained from [ReH<sub>3</sub>(diphos)<sub>2</sub>].

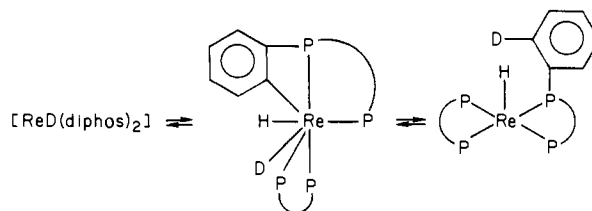
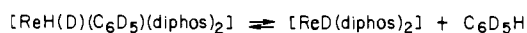
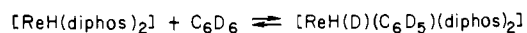
## Discussion

**Photogeneration of [ReH(diphos)<sub>2</sub>].** The results reported herein clearly demonstrate that [ReH(diphos)<sub>2</sub>] or a solvated derivative can be generated via photoinduced loss of H<sub>2</sub> from [ReH<sub>3</sub>(diphos)<sub>2</sub>] or more conveniently by photoinduced elimination of N<sub>2</sub> from [ReH(N<sub>2</sub>)(diphos)<sub>2</sub>]. This species is extremely reactive and

## Scheme II



## Scheme III



rapidly adds N<sub>2</sub>, H<sub>2</sub>, CO, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, and CO<sub>2</sub> to give adduct complexes (Scheme I). Furthermore, the photolysis experiments conducted in degassed solutions indicate that [ReH(diphos)<sub>2</sub>] readily inserts into the C–H bonds of both benzene solvent and the phenyl groups of the diphos ligands as outlined in Scheme II. Insertion into the C–D bonds of C<sub>6</sub>D<sub>6</sub> presumably yields the seven-coordinate complex **2**. This reaction must be readily reversible since the NMR and IR experiments detailed above indicate that it leads to H/D exchange to produce [ReD(diphos)<sub>2</sub>] and C<sub>6</sub>D<sub>5</sub>H. The ready reversibility of this reaction presumably obtains because of severe steric crowding in **2** in which there are nine phenyl groups located around the central Re atom.

[ReH(diphos)<sub>2</sub>] also undergoes reversible intramolecular insertion into the C–H bonds of the phenyl groups of the diphos ligands, i.e., ortho metalation. If H/D exchange with solvent has previously occurred to yield [ReD(diphos)<sub>2</sub>], this reaction leads to incorporation of deuterium into the diphos ligands via the sequence of reactions shown in Scheme III.

It is noteworthy that exposure of exhaustively photolyzed benzene solutions of [ReH<sub>3</sub>(diphos)<sub>2</sub>] to N<sub>2</sub> and CO<sub>2</sub> atmospheres immediately leads to the formation of [ReH(N<sub>2</sub>)(diphos)<sub>2</sub>] and [Re(O<sub>2</sub>CH)(diphos)<sub>2</sub>], respectively, demonstrating the persistence of the [ReH(diphos)<sub>2</sub>] intermediate. In one experiment, a solution of [ReH(N<sub>2</sub>)(diphos)<sub>2</sub>] was photolyzed until 1 equiv of N<sub>2</sub> evolved, and the sample was placed under an N<sub>2</sub> atmosphere to reform [ReH(N<sub>2</sub>)(diphos)<sub>2</sub>]. The sample was then thoroughly degassed and continued photolysis for 1 h released 0.87 mol of N<sub>2</sub>/mol of complex initially irradiated.

Repeated attempts to characterize the [ReH(diphos)<sub>2</sub>] intermediate by <sup>31</sup>P NMR spectroscopy have been singularly unsuccessful. Photolysis of C<sub>6</sub>D<sub>6</sub> solutions of [ReH(N<sub>2</sub>)(diphos)<sub>2</sub>] results in ~95% decrease in intensity of the δ 46.62 resonance of this compound, but no new resonances appear anywhere in the +300 to –300-ppm spectral region. Yet, exposure of these solutions to N<sub>2</sub> results in partial restoration of the original intensity of the [ReH(N<sub>2</sub>)(diphos)<sub>2</sub>] resonance. We are at a loss to explain these results although it may well be that the signal due to [ReH(diphos)<sub>2</sub>] lies outside of this spectral range or more likely that the <sup>31</sup>P nuclei in this intermediate have unusually long relaxation times. Several new, weak bands were observed when the pulse repetition rate was increased to 15 s, but difficulties in obtaining a suitable signal-to-noise ratio in these experiments because of the lengthy spectrometer time required have precluded unambiguous char-

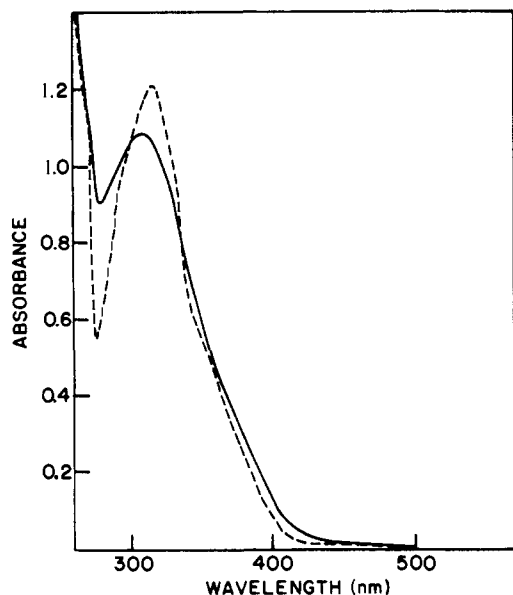
(33) The carbonyl species presumably arises via disproportionation with another molecule of CO<sub>2</sub> to yield CO and CO<sub>3</sub><sup>2-</sup> complexes. See: Herskovitz, T.; Guggenberger, L. *J. Am. Chem. Soc.* **1976**, *98*, 1615.

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**Figure 3.** Electronic absorption spectra of [ReH<sub>3</sub>(diphos)<sub>2</sub>] in 5:5:2 diethyl ether-isopentane-ethanol solution at 298 K (—) and 77 K (---). The 77 K spectrum has been corrected for solvent contraction upon cooling.

**Table I.** Electronic Absorption Spectral Data

complex	T, K	$\lambda_{\max}$ , nm	$\epsilon_{\max}^{\text{M}^{-1} \text{cm}^{-1}}$
[ReH <sub>3</sub> (diphos) <sub>2</sub> ]	298 <sup>a</sup>	295 (sh)	2230
		320	8900
	77 <sup>b</sup>	360 (sh)	3300
		320	9890
[ReH(N <sub>2</sub> )(diphos) <sub>2</sub> ]	298	392 (sh)	4340
[ReClH <sub>2</sub> (diphos) <sub>2</sub> ]	298	323	11800
		386 (sh)	7940
		297 (sh)	3350
[ReClN <sub>2</sub> (diphos) <sub>2</sub> ]	298	397 (sh)	3060
		325 (sh)	9010
		302	9740

<sup>a</sup> C<sub>6</sub>H<sub>6</sub> solution. <sup>b</sup> 5:5:2 diethyl ether-isopentane-ethanol glassy solution.

acterization of the species responsible for these resonances.

An important question concerns the role of excitation in inducing H<sub>2</sub> elimination from [ReH<sub>3</sub>(diphos)<sub>2</sub>]. The lack of sufficient detail in the electronic absorption spectrum of [ReH<sub>3</sub>(diphos)<sub>2</sub>] (Figure 3 and Table I) does not permit a detailed assignment, although the intense band centered at 320 nm ( $\epsilon$  8900 M<sup>-1</sup> cm<sup>-1</sup>) is most likely a Re → P charge-transfer transition. The weak shoulders on the low-energy side of this band may be less intense charge-transfer transitions or ligand field transitions. Although it has been proposed that a M → P charge-transfer state can promote H<sub>2</sub> loss,<sup>1,6</sup> our limited data do not permit us to argue the case here.

In a related study, we have shown that [ReH<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>4</sub>] is much more photoactive than is [ReH<sub>3</sub>(diphos)<sub>2</sub>] and that the primary photoreaction is not H<sub>2</sub> loss but rather PR<sub>3</sub> elimination.<sup>38</sup> Loss of PMe<sub>2</sub>Ph from [ReH<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>4</sub>] occurs with a 366-nm quantum yield of 0.4. Thus, loss of H<sub>2</sub> from [ReH<sub>3</sub>(diphos)<sub>2</sub>] may occur solely because phosphine loss is suppressed by the chelating diphosphines.

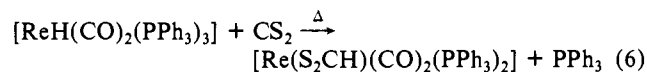
The resolution in the UV-vis spectrum of [ReH(N<sub>2</sub>)(diphos)<sub>2</sub>] is no better than that of [ReH<sub>3</sub>(diphos)<sub>2</sub>], and definitive spectral assignments cannot be made. It should be noted, however, that the spectra of these two compounds are remarkably similar. Since the energetics of Re → P charge-transfer excitations are a sensitive

function of the metal ion oxidation state, the spectral data imply that the degree of oxidation of the central Re atom in the two complexes is similar, i.e., ~Re(I).

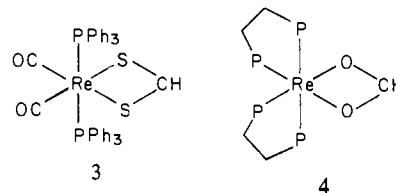
**Spectroscopic Characterization of [Re(O<sub>2</sub>CH)(diphos)<sub>2</sub>].** The most interesting product isolated from the photolyses experiments described herein is the complex obtained upon irradiation of [ReH<sub>3</sub>(diphos)<sub>2</sub>] in the presence of CO<sub>2</sub>. That CO<sub>2</sub> is incorporated into the molecule is clearly evidenced by the shift in the 1554- and 1356-cm<sup>-1</sup> IR bands to 1515 and 1334 cm<sup>-1</sup> when <sup>13</sup>CO<sub>2</sub> is substituted for <sup>12</sup>CO<sub>2</sub> (Figure 1). The spectral properties of this compound are most consistent with its formulation as a formate derivative. Specifically, the IR bands at 1554 and 1356 cm<sup>-1</sup> may be respectively attributed to the  $\nu(\text{CO}_2)_{\text{asym}}$  and  $\nu(\text{CO}_2)_{\text{sym}}$  vibrations of a bidentate formate ligand. For comparison, [RuH(O<sub>2</sub>CH)(PPh<sub>3</sub>)<sub>3</sub>], whose bidentate structure has been established by X-ray diffraction,<sup>39</sup> shows bands at 1565 and 1340 cm<sup>-1</sup>. Similarly, [IrClH(O<sub>2</sub>CH)(PPh<sub>3</sub>)<sub>2</sub>] with a presumed bidentate structure has IR bands at 1550 and 1345 cm<sup>-1</sup>.<sup>40</sup> In contrast, complexes with unidentate formate ligands generally show the  $\nu(\text{CO}_2)_{\text{asym}}$  above 1600 cm<sup>-1</sup>.<sup>40-42</sup> For example, addition of CO to the above-mentioned [IrClH(O<sub>2</sub>CH)(PPh<sub>3</sub>)<sub>2</sub>] gives [IrClH(O<sub>2</sub>CH)(CO)(PPh<sub>3</sub>)<sub>2</sub>] with a unidentate formate ligand, and the corresponding IR bands are at 1687 and 1362 cm<sup>-1</sup>.<sup>40</sup> The IR spectrum of [Re(O<sub>2</sub>CH)(diphos)<sub>2</sub>] shows no evidence for a  $\nu_{\text{M-H}}$  vibration but does show a weak  $\nu_{\text{C-H}}$  band at 2825 cm<sup>-1</sup> that is not present in [ReH<sub>3</sub>(diphos)<sub>2</sub>] and which may be attributed to the formate C-H vibration.

The most definitive evidence for the formate formulation for [Re(O<sub>2</sub>CH)(diphos)<sub>2</sub>] is the doublet at  $\delta$  171.9 ( $J_{\text{C-H}} = 202$  Hz) in its <sup>13</sup>C NMR spectrum (Figure 2). Both the chemical shift and the coupling constant fall within the ranges established for organic formates.<sup>43</sup> The chemical shifts of ethyl formate and formic acid, for example, are  $\delta$  160.7 and 166.7, respectively.<sup>43</sup> The <sup>13</sup>C-H coupling constants for the formate carbon generally lie between 170 and 230 Hz with HCO<sub>2</sub><sup>-</sup> showing a coupling constant of 194.8 Hz.<sup>43</sup>

The rhenium dithioformate complex [Re(S<sub>2</sub>CH)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], prepared by Freni et al.<sup>44</sup> via the reaction shown in eq 6, has been



characterized by X-ray diffraction and shown to have the structure 3.<sup>45</sup> This complex is isoelectronic with [Re(O<sub>2</sub>CH)(diphos)<sub>2</sub>], and thus, by analogy to [Re(S<sub>2</sub>CH)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], the most reasonable structure for [Re(O<sub>2</sub>CH)(diphos)<sub>2</sub>] is that shown in 4.



The formation of [Re(O<sub>2</sub>CH)(diphos)<sub>2</sub>] presumably proceeds via initial addition of CO<sub>2</sub> to photogenerated [ReH(diphos)<sub>2</sub>] to give an adduct complex similar to those obtained with N<sub>2</sub>, CO, and C<sub>2</sub>H<sub>4</sub> (eq 7). Hydride migration to CO<sub>2</sub> would then generate

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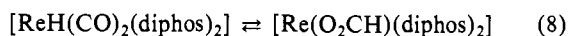
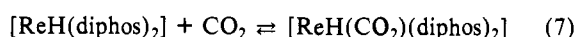
(42) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley: New York, 1978; pp 232-233.

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the observed formate derivative (eq 8). Both of these reactions



must be reversible, however, since  $\text{CO}_2$  is readily displaced by  $\text{N}_2$  and  $\text{H}_2$  to yield  $[\text{ReH}(\text{N}_2)(\text{diphos})_2]$  and  $[\text{ReH}_3(\text{diphos})_2]$ , respectively, and  $\text{CO}_2$  is liberated upon thermal decomposition of  $[\text{Re}(\text{O}_2\text{CH})(\text{diphos})_2]$ . Reactivity studies of this complex directed toward further reduction or release of the coordinated  $\text{HCO}_2^-$  ligand and attempts to prepare other adduct complexes are currently underway in these laboratories.

**Acknowledgment.** We are indebted to Dr. A. P. Ginsberg of Bell Laboratories for the generous gifts of  $[\text{ReH}_3(\text{diphos})_2]$  and  $[\text{ReH}(\text{N}_2)(\text{diphos})_2]$ . We thank Alan Freyer and Dr. Robert Minard for assistance in obtaining NMR and mass spectra, respectively, and the National Science Foundation for support of this research. The JEOL PS-100-FT NMR spectrometer and the AEI-MS-902 mass spectrometer used in this research were purchased with the aid of grants from the National Science Foundation's major equipment grant program. G.L.G. gratefully acknowledges the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Award and the Alfred P. Sloan Foundation for a research fellowship.

## Magnetic Exchange Interactions in Binuclear Copper(II) Complexes with Only a Single Hydroxo Bridge: The X-ray Structure of $\mu$ -Hydroxo-tetrakis(2,2'-bipyridine)dicopper(II) Perchlorate

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**Abstract:** The X-ray structure of  $[(\text{bpy})_2\text{Cu}-\text{OH}-\text{Cu}(\text{bpy})_2](\text{ClO}_4)_3$ , where bpy is 2,2'-bipyridine, has been determined on an automatic Picker four-circle diffractometer, by use of 4528 ( $F_o > 3\sigma$ ) unique reflections, to give final discrepancy indices of  $R_1 = 0.069$  and  $R_2 = 0.087$ . The complex crystallizes in the monoclinic space group  $P2_1/n$  in a cell having the dimensions of  $a = 14.839$  (8) Å,  $b = 18.197$  (9) Å,  $c = 16.491$  (8) Å, and  $\beta = 92.87$  (3)°. The observed and calculated densities are 1.61 (2) and 1.594 g cm<sup>-3</sup>, respectively. The complex is comprised of perchlorate counterions and binuclear  $[(\text{bpy})_2\text{Cu}-\text{OH}-\text{Cu}(\text{bpy})_2]^{3+}$  cations. The two copper(II) ions in the binuclear unit are bridged by only a single hydroxide ion with an Cu-O-Cu bridging angle of 141.6 (3)°. No crystallographic symmetry is imposed on the binuclear units. The coordination geometry about each copper ion is approximately trigonal bipyramidal with the bridging hydroxide ion occupying an equatorial site. The distortion from trigonal-bipyramidal coordination geometry is greater for one of the copper ions in the binuclear cation by virtue of one perchlorate oxygen atom approaching the copper ion in a sixth site to give an Cu-O distance of 3.047 (9) Å. Magnetic susceptibility data were collected from 286 to 4.2 K for  $[(\text{bpy})_2\text{Cu}-\text{OH}-\text{Cu}(\text{bpy})_2](\text{ClO}_4)_3$  and the analogous compound  $[(\text{phen})_2\text{Cu}-\text{OH}-\text{Cu}(\text{phen})_2](\text{ClO}_4)_3$ , where phen is 1,10-phenanthroline. Relatively strong antiferromagnetic exchange interactions are present in both complexes, as evidenced by the 286 K effective magnetic moments of 1.56 and 1.35  $\mu_B$ , respectively. The data were least-squares fit to the theoretical susceptibility equation resultant from the spin Hamiltonian  $\hat{H} = -2J\hat{S}_1\hat{S}_2$  to give  $J = -161$  cm<sup>-1</sup> for the bpy complex and  $J = -177$  cm<sup>-1</sup> for the phen complex.

### Introduction

A linear relationship has been noted<sup>3-6</sup> between the bridge angle, Cu-O-Cu, and the magnetic exchange parameter  $J$  (i.e., parameter in the spin Hamiltonian  $\hat{H} = -2J\hat{S}_1\hat{S}_2$ ) for a series of some 11 binuclear dihydroxo-bridged copper(II) complexes. Kahn, Jeannin, and co-workers<sup>7</sup> reported that the compound di- $\mu$ -hydroxo-tetrakis(cyclohexylamine)dicopper(II) perchlorate does not fit into the linear relationship. This compound is different from all other dihydroxo-bridged systems in that the coordination planes about the two copper(II) ions are not coplanar but are bent at a dihedral angle of 147.5°. Hydroxo-bridged binuclear copper(II) complexes have very recently been found<sup>8</sup> to be catalytically active for oxidative coupling reactions, a fact that adds to the

practical importance of studying the electronic structure of such complexes.

Until recently, no examples of binuclear copper(II) complexes bridged by *only* a single hydroxide ion were known. The preparation and physical properties of  $[(\text{tren})\text{Cu}-\text{OH}-\text{Cu}(\text{tren})]\text{X}_3$ , where tren is tris(2-aminoethyl)amine and X is  $\text{PF}_6^-$  or  $\text{ClO}_4^-$ , have been reported.<sup>9</sup> As far as we know, these are the only reported examples of binuclear copper(II) complexes bridged by only one hydroxide ion. Strong antiferromagnetic exchange interactions characterized by  $J$  values of  $-350$  ( $\text{PF}_6^-$ ) and  $-360$  cm<sup>-1</sup> ( $\text{ClO}_4^-$ ) were noted.

In this paper are reported the preparation and characterization of two new binuclear copper(II) complexes bridged by only a single hydroxide ion,  $[(\text{bpy})_2\text{Cu}-\text{OH}-\text{Cu}(\text{bpy})_2](\text{ClO}_4)_3$  and  $[(\text{phen})_2\text{Cu}-\text{OH}-\text{Cu}(\text{phen})_2](\text{ClO}_4)_3$ . Magnetic susceptibility data are presented and, consequently, it was important to determine the structure of at least one of these two complexes. The results of an X-ray structure of the bpy complex are given.

In addition to examining further the relationship between Cu-O-Cu angle and exchange parameter, binuclear copper(II) complexes with one hydroxide bridge could prove useful in es-

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