Catalytic Activation of H_2 and C−H Bonds by Electron-Deficient Ruthenium(II) Porphyrins

James P. Collman,*,[†] H. T. Fish,[†] Paul S. Wagenknecht,[†] David A. Tyvoll,[†] Leng-Leng Chng,[†] Todd A. Eberspacher,[†] John I. Brauman,[†] Jeffrey W. Bacon,[‡] and Louis H. Pignolet*,[‡]

Department of Chemistry, Stanford University, Stanford, California 94305,
and Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received November 22, 1995[⊗]

The Ru_2 and RuNi derivatives of 1,8-bis(10,15,20-trimesityl-5-porphyrinato)anthracene—a recently reported cofacial diporphyrin ligand comprising two hindered porphyrins spanned by an anthracene bridge—have been synthesized. Both Ru_2(DPAHM) and RuNi(DPAHM) are *extremely* reactive species that apparently contain 14-electron Ru(II) centers and, as is the case for their monoporphyrin analog, (5,10,15,20-tetramesitylporphyrinato)ruthenium [Ru(TMP)], must be rigorously protected from oxygen, nitrogen, and other ligating agents. In addition, these electron-deficient Ru(II) porphyrins all appear to bind aromatic solvents such as benzene and toluene, the weakest ligating solvents in which these Ru(II) porphyrins have been found soluble. Ru(TMP) and its metallodiporphyrin analogs, Ru_2(DPAHM) and RuNi(DPAHM), catalyze H_2/D_2 exchange in benzene solution and as solids. When adsorbed on a particularly nonpolar carbon support, these Ru(II) porphyrins all manifest significant activity with respect to catalytic H_2/D_2 exchange [approximately 40 turnovers s^{-1}, when normalized for Ru(II) content]. In addition, these molecules *slowly* catalyze the exchange of H_2 into deuterated aromatic hydrocarbons and, in the absence of solvent, the exchange of D_2 into CH_4. Kinetic studies of H_2/D_2 exchange catalyzed by these Ru(II) porphyrins on carbon supports indicate that exchange is likely to be effected by one face of a single Ru(TMP) moiety. The activity of each supported catalyst was suppressed by the presence of ligands, either exogenous (CO irreversibly and N_2 reversibly) or from polar functionalities on the surface of the supporting matrix.

Activation of a strong C−H or H−H bond by transition metal complexes can often be detected even if the equilibrium product concentration of a reversible oxidative addition reaction is too low for direct observation.[1] Detection of H/D exchange provides convincing, though indirect, evidence of H−H or C−H activation. Two types of H/D exchange experiments can be used as indicators of reversible oxidative addition of dihydrogen or a hydrocarbon to a metal center. First, hydrides and alkyl hydrides may undergo solvolysis in protic media; thus, one observes isotopic scrambling in solvent containing exchangeable deuterium. Second, if the reacting metal complex contains hydride or dihydrogen ligands, one may expect *direct* H/D exchange into D_2 or a deuterated hydrocarbon.[2]

Metal surfaces, metal clusters, metal oxides, and hydrogenase enzymes are among the many species known to effect catalytic H_2/D_2 exchange.[3] Several transition metal dihydrogen and dihydride complexes have also been observed to catalyze the *direct* exchange of H_2 and D_2 to yield HD gas.[4] H_2 activation is a model for the more complex and intriguing activation of C−H bonds by transition metal complexes; thus, mechanistic insight into this fundamental reaction could aid in the rational design of catalysts for activation and functionalization of saturated hydrocarbons.

Because H_2/D_2 exchange should require a site for the coordination of dihydrogen, a variety of neutral iron and ruthenium metalloporphyrins with vacant coordination sites have been surveyed for exchange activity. In benzene, Fe(OEP) and a cofacial analog, Fe_2(DPB), each exhibited extremely low catalytic activity. $[Ru(OEP)]_2$, a dimer containing a Ru−Ru bond, exhibited slightly faster catalytic behavior, but its efficacy appeared to increase over time, suggesting mechanistic complexities such as cleavage of the Ru=Ru bond.[4e]

Ru(TMP), first described by Dolphin,[5] is a 14-electron species devoid of axial ligands. We report here the discovery that Ru(TMP) catalyzes H_2/D_2 exchange both in aromatic solvents and in the solid state. We also report the results of kinetic studies that indicate that H_2/D_2 exchange can be catalyzed by one open face of a single Ru porphyrin.

We originally expected that two ruthenium centers would be involved in the direct, catalytic exchange of H_2/D_2. Wayland reported the oxidative addition of H_2 and selected C−H bonds by Rh derivatives of both TMP and a tethered diporphyrin analog.[6] These reactions appear to involve 4-centered transition states in which two Rh(II) porphyrin moieties participate in the

---

[†] Stanford University.

[‡] University of Minnesota.

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1996.

(1) Acronyms used frequently in this manuscript to describe a variety of porphyrin monomers and dimers include the following: TMP, tetramesitylporphyrin; OEP, octaethylporphyrin; DPA, diporphyrinylanthracene; DPB, diporphyrinylbiphenylene.

(2) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Reidel Publishing Company: Dordrecht, The Netherlands, 1984; and references cited therein.

(3) (a) Bond, G. C. *Catalysis by Metals;* Academic Press: New York, 1962. (b) Somorjai, G. A. *Chemistry in Two Dimensions: Surfaces;* Cornell University Press: Ithaca, NY, 1981. (c) Kung, H. H. *Transition Metal Oxides: Surface Chemistry and Catalysis;* Elsevier Scientific Publishing Company: New York, 1989. (d) Krasna, A. I.; Rittenberg, D. *J. Am. Chem Soc.* **1954,** *76,* 3015. (e) Aubart, M. A.; Pignolet, L. H. *J. Am . Chem Soc.* **1992,** *114,* 7901. (f) Tadros, M. E.; Vaska, L. *J. Colloid Interface Sci.* **1982,** *85,* 389.

(4) (a) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem Soc.* **1986,** *108,* 7000. (b) Kubas, G. J.; Ryan, R. R.; Wroblewski, D. *J. Am. Chem. Soc.* **1986,** *108,* 1339. (c) Upmacis, R. K.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986,** *108,* 3645. (d) Aubart, M. A.; Chandler, B. D.; Gould, R. A. T.; Krogstad, D. A.; Schoondergang, M. F. J.; Pignolet, L. H. *Inorg. Chem.* **1994,** *33,* 3724. (e) Wagenknecht, P. S. Ph.D. Dissertation, Stanford University, Stanford, CA, 1991.

(5) Camenzind, M. J.; James, B. R.; Dolphin, D. *J. Chem Soc., Chem. Commun.* **1986,** 1137.

(6) (a) Wayland, B. B.; Sherry, A. E. *J. Am. Chem. Soc.* **1990,** *112,* 1259. (b) Wayland, B. B.; Ba, S.; Sherry, A. E. *J. Am. Chem. Soc.* **1991,** *113,* 5305. (c) Wayland, B. B.; Ba, S.; Sherry, A. E. *Inorg. Chem.* **1992,** *31,* 148. (d) Zhang, X.-X.; Wayland, B. B. *J. Am. Chem. Soc.* **1994,** *116,* 7897.

S0020-1669(95)01495-9 CCC: $12.00

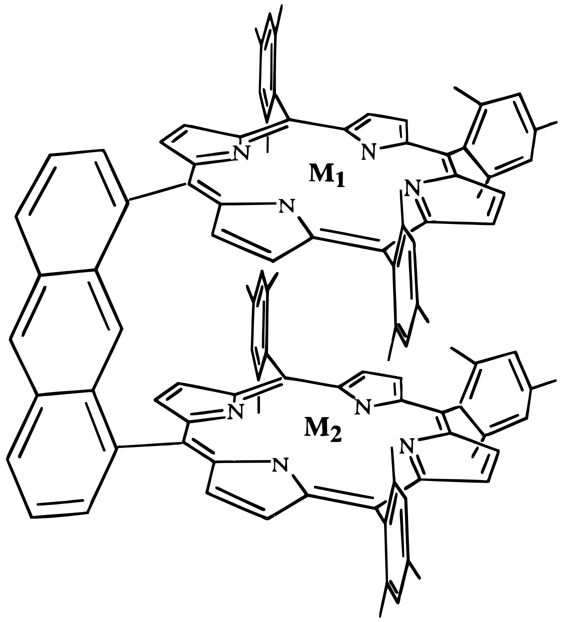

Figure 1. Metalated derivatives of DPAHM, a hindered diporphyrin ligand, catalyze H_2/D_2 exchange: $M_1 = Ru(II)$, $M_2 = Ru(II)$ or Ni(II).

oxidative addition. In addition, we have previously demonstrated that a Ru(II) anionic hydride bimolecularly eliminates dihydrogen immediately upon 1-electron oxidation.[7]

The primary goal of the present work was to determine the reaction order with respect to ruthenium of H_2/D_2 exchange catalyzed by Ru(TMP); i.e., does the reaction proceed through a bimolecular coupling of two Ru(TMP) complexes, or can the exchange occur on a single face of one metalloporphyrin? Toward this end, we have employed Ru_2 and RuNi derivatives of a recently reported bridged diporphyrin ligand, DPAHM [bis(trimesitylporphyrinato)anthracene], in which two TMP analogs are spanned by an anthracene bridge (Figure 1).[8] The ligand is designed to allow the generation of two 14-electron Ru centers in close proximity. The presence of sterically bulky mesityl substituents precludes *intermolecular* metal−metal bonding, while the anthracene bridge is too long to allow the formation of *intramolecular* metal−metal bonds.

Direct H_2/D_2 exchange mediated by Ru porphyrins was initially observed in solution; however, early attempts to obtain mechanistic information employing solution studies of these three catalysts were thwarted by our inability to obtain reproducible kinetic data. Ru(TMP) is *extremely* oxygen sensitive; it also binds 2 equiv of N_2, a very weak ligand. In addition, we have found no solvent in which this complex is soluble that does not also act as a ligand. For example, the asymmetry of its diamagnetic ^{1}H NMR in C_6D_6 has been explained by invoking a very weak η^2-benzene complex[5] in slow exchange with solvent, although such a complex has defied isolation. In solution, the diporphyrin catalysts employed in this study also suffer from the same problems as those described for Ru(TMP).

The presence of trace impurities in the solvent and the fact that solvent itself inhibits the catalysis of H_2/D_2 exchange caused us to abandon mechanistic studies in solution. Instead, these catalysts have been put on carbon supports, and a flow reactor has been employed to examine their efficacy as H_2/D_2 exchange catalysts. In this article, the synthesis of Ru_2 and RuNi derivatives of DPAHM and their activities on carbon supports with respect to catalysis of H_2/D_2 exchange are reported. Also, the activities of these bimetallic molecules are compared with that of Ru(TMP), and mechanistic conclusions regarding the reaction order of catalytic H_2/D_2 exchange with respect to ruthenium are drawn. In addition, this article reports that these molecules slowly catalyze both the direct exchange of H_2 into deuterated aromatic hydrocarbons and the exchange of D_2 into CH_4.

Results

Synthesis Structure and Reactivity of Diporphyrin Catalysts. H_4DPAHM was synthesized according to the method recently reported by Collman.[8] The method involves consecutive porphyrin condensations under modified Lindsey conditions.[9] Metal insertions can be achieved before and/or after the second condensation; thus, both hetero- and homo-bimetallic systems are readily accessible. Syntheses of Ru_2 and RuNi derivatives of DPAHM were accomplished by using modified literature procedures.[10] The synthetic precursors of Ru_2(DPAHM) and RuNi(DPAHM) were well characterized by a variety of techniques, including mass spectrometry and IR, UV−vis, and ^{1}H NMR spectroscopies. All precursors of Ru_2(DPAHM) and RuNi(DPAHM) exhibit sharp, diamagnetic ^{1}H NMR spectra, which are consistent with octahedral Ru(II) and/or square planar Ni(II) porphyrin complexes.

Both Ru_2(DPAHM) and RuNi(DPAHM) are highly reactive species as solids and in solution. Their reactivity parallels that of Ru(TMP), as originally described by Dolphin.[5] These molecules must be rigorously protected from oxygen, nitrogen, and presumably most other ligating agents. In addition, a preliminary crystal structure of Ni_2(DPAHM) indicates that the Ni centers are approximately 6.7 Å apart, demonstrating that the molecule is exceedingly distorted by the presence of the bulky mesityl substituents. For comparison, a crystal structure of Ni_2(DPA) (an anthracene-bridged, cofacial diporphyrin in which the constituent etioporphyrins are flat) exhibits a metal−metal distance of approximately 4.6 Å.[11]

Neither Ru_2(DPAHM) nor its RuNi analog can be definitively characterized spectroscopically. The ^{1}H NMR (C_6D_6) spectra of these molecules exhibit broad resonances in both the aromatic and aliphatic regions, which appear to be the result of a mixture of species in solution. This is not particularly surprising for two reasons. First, the ^{1}H NMR in C_6D_6 of the monoporphyrin analog, Ru(TMP), exhibits axial asymmetry, an indication of a weak benzene complex in slow exchange with solvent.[5] The cofacial derivatives undoubtedly also bind benzene weakly; however, these molecules present two porphyrins, each with distinct faces—one face inside and one outside the cavity created by the cofacial diporphyrin moieties—which can bind the aromatic solvent. One envisions that Ru_2(DPAHM) exists in benzene as a mixture of species with two benzene molecules bound in slow exchange as out/out, in/out, and possibly in/in isomers; thus, we expect these metallodiporphyrins to exhibit

---

[7] Collman, J. P.; Hutchison, J. E.; Wagenknecht, P. S.; Lewis, N. S.; Lopez, M. A.; Guilard, R. *J. Am. Chem. Soc.* **1990,** *112,* 8206.

[8] Collman, J. P.; Tyvoll, D. A.; Chng, L. L.; Fish, H. T. *J. Org. Chem.* **1995,** *60,* 1926.

[9] (a) Rothemund, P. *J. Am. Chem. Soc.* **1936,** *58,* 625. (b) Rothemund, P. *J. Am. Chem. Soc.* **1939,** *61,* 2912. (c) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. *J. Org. Chem.* **1987,** *52,* 827. (d) Lindsey, J. S.; Wagner, R. W. *J. Org. Chem.* **1989,** *54,* 828.

[10] (a) Hopf, F. R.; O'Brien, T.; Scheidt, W. R.; Whitten, D. G. *J. Am. Chem. Soc.* **1975,** *97,* 277. (b) Antipas, A.; Buchler, J. W.; Gouterman, M.; Smith, P. D. *J. Am. Chem. Soc.* **1978,** *100,* 3015. (c) Collman, J. P.; Barnes, C. E.; Collins, T. J.; Brothers, P. J.; Gallucci, J.; Ibers, J. A. *J. Am. Chem. Soc.* **1981,** *103,* 7030. (d) Collman, J. P.; Barnes, C. E.; Swepston, P. N.; Ibers, J. A. *J. Am. Chem. Soc.* **1984,** *106,* 3500.

[11] Fillers, J. P.; Ravichandran, K. G.; Abdalmuhdi, I.; Tulinsky, A.; Chang, C. K. *J. Am. Chem. Soc.* **1986,** *108,* 417.

^{1}H NMR spectra that are very complex. Second, this mix of species is also consistent with the preliminary crystal structure of Ni_2(DPAHM), which suggests possible agostic interactions between the interior mesityl methyl groups—proximal to the anthracene bridge—on one porphyrin and the Ni atom in the other porphyrin moiety. If agostic interactions exist in Ni_2(DPAHM), they are probably accentuated in the RuNi and Ru_2 derivatives, which contain nominally 14-electron Ru(II) centers. These interactions may contribute to the complex ^{1}H NMR spectra that these molecules manifest.

The reactivity of Ru_2(DPAHM) and RuNi(DPAHM) with a variety of substrates provides significant evidence supporting the contention that they contain 14-electron Ru(II) centers analogous to that found in Ru(TMP). Both Ru_2(DPAHM) and RuNi(DPAHM) mimic the extreme reactivity of Ru(TMP). Exposure to oxygen results in a mixture of unidentified oxidation products. The Ru_2 and RuNi derivatives of DPAHM each bind dinitrogen reversibly both in benzene solutions and as lyophilized solids. Upon exposure to 1 atm of N_2 (an extremely weak ligand), both Ru_2(DPAHM) and RuNi(DPAHM) exhibit two absorptions in their IR spectra. These absorptions, between 2170 and 2200 cm^{-1}, are close to those exhibited by the mono- and bis-N_2 adducts of Ru(TMP).[5] These dinitrogen adducts of Ru_2(DPAHM) and RuNi(DPAHM) have not yet been isolated and fully characterized. Exposure of Ru_2(DPAHM) or RuNi(DPAHM) to acetonitrile, a relatively weak ligand, cleanly regenerates the well-characterized, acetonitrile-substituted precursors reported in this work. This behavior indicates that coordination to solvent and/or intramolecular agostic interactions are relatively weak.

Exposure of these molecules to CO in benzene followed by treatment with methanol regenerates the Ru(CO)(CH_3OH) centers found in the products of Ru insertion into the free-base ligands. Direct, clean removal of carbon monoxide ligands from these Ru(II) diporphyrins cannot be accomplished except by solution photolysis under a continuous sparge of an inert gas. This behavior is quite consistent with that previously described for CO adducts of other Ru(II) porphyrins.[12]

H_2/D_2 and H/D Exchange Catalysis. Ru(TMP), Ru_2(DPAHM), and RuNi(DPAHM) catalyze H_2/D_2 exchange, both in benzene solutions and as molecular solids. Benzene solutions of catalysts in millimolar concentrations were stirred under a 50/50 mixture of H_2/D_2 at 1 atm of total pressure, and the formation of HD was monitored by gas chromatography. Kinetic data were not reproducible (*vide infra*), but significant formation of HD in the headspace of the reaction vessel was observed. Ni(TMP) does not catalyze H_2/D_2 exchange either in solution or as a solid, and exchange does not occur above benzene in the absence of catalyst.

Addition of excess acetonitrile, pyridine, or THF to catalyst solutions completely quenches any catalytic activity. Presumably, these molecules, which can all act as ligands, competitively inhibit H_2 coordination to catalyst molecules. These results indicate that H_2/D_2 exchange occurs at the Ru(II) porphyrin sites of these soluble catalysts, rather than on some elemental Ru impurity. Each time a catalyst was prepared it was tested for impurities by employing this technique.

Attempts to characterize the intermediates of exchange in solution were unsuccessful. The ^{1}H NMR spectrum of Ru(TMP) in toluene-d_8 under 1 atm of dihydrogen was recorded; it is different from the spectrum of Ru(TMP) taken in the absence of H_2. Porphyrin resonances have not been assigned, because several species were evident. The spectrum exhibits two upfield signals at approximately −29 and −36 ppm, which may possibly correspond to dihydrogen, dihydride, or monohydride complexes. Free dihydrogen is not observed by ^{1}H NMR even at −70 °C, although GC analysis indicates its presence in the headspace. These results are intriguing, and they indicate that H_2 is involved in one or more rapid equilibria. Spectra of either Ru_2(DPAHM) or RuNi(DPAHM) in toluene-d_8 under H_2 provide even less illumination due to the added complexity of these diporphyrin molecules.

Ru(TMP), Ru_2(DPAHM), and RuNi(DPAHM) each catalyzes H_2 exchange into C_6D_6. Solutions of each catalyst in C_6D_6 were stirred under 1 atm of H_2. After 1 week, approximately 3 equiv (relative to catalyst) of HD gas was observed in the headspace by gas chromatography; the quantity of protio solvent also increased as measured by ^{1}H NMR. The diporphyrin catalysts are not appreciably faster than Ru(TMP). The rate of this exchange is extremely slow—many orders of magnitude slower than the rate of catalyzed H_2/D_2 exchange in benzene solutions.

As molecular solids, Ru(TMP), Ru_2(DPAHM) and RuNi(DPAHM), each actively catalyzes H_2/D_2 exchange. Under 1 atm of H_2/D_2 (50/50), stirred, lyophilized powders of these molecular solids exhibit turnover frequencies (TOFs) of roughly 0.5/s.[13] Catalytic activity is highly dependent on stir rates, and it appears to increase the longer a catalyst sample is stirred. We assume that particle size decreases with longer and more vigorous stirring; thus, the increase in catalytic activity is due to higher surface area and the concomitant increase in accessibility to hydrogen.

Remarkably, by GC analysis, 10 equiv (relative to catalyst) of HD was observed in the headspace of D_2/CH_4 (10/90) mixtures stirred for 3 days over Ru_2(DPAHM) (both as a lyophilized powder and on carbon supports). ^{1}H NMR analysis (C_6D_6) of the headspace gas clearly indicates the presence of CH_3D. D_2 appears to be a competitive inhibitor of methane activation; D_2/CH_4 mixtures that contain a higher percentage of D_2 exhibit even slower production of HD. When a lyophilized powder of Ru_2(DPAHM) was stirred under D_2 for 1 week, no HD was detected; thus, the catalyst itself is not the source of hydrogen atoms in the production of HD. These data indicate that methane is being activated; however, the reaction is extremely slow, and the possibility that methane activation is caused by some trace impurity has not been eliminated absolutely.

Kinetic Study of Catalytic H_2/D_2 Exchange. The inability to collect reproducible kinetic data by employing these porphyrin catalysts—either in solution or as molecular solids—led us to examine their abilities to effect catalytic H_2/D_2 exchange when adsorbed on solid supports. Ru(TMP), Ru_2(DPAHM), and RuNi(DPAHM) exhibit no catalytic activity when adsorbed on silica or neutral alumina, supports that each contain significant polar functionalities; however, the Ru(II) porphyrins, when adsorbed on relatively apolar carbon supports, are very active and surprisingly robust catalysts. The two carbon supports employed in this investigation exhibit significantly different surface polarities. Carbon powder 93-0602 supplied by Strem Chemical Company has approximately 100 times the carboxylate and 200 times the quinoidal functionalities per square meter as does the Armak BHC carbon supplied by Dow Chemical Company (determined from a comparison of desorbed CO_2 and CO, respectively, in TPD experiments as described in the Experimental Section). In addition, the average pore diameter of the Armak carbon support is approximately 7.5 Å, which is

---

[12] Collman, J. P.; Brothers, P. J.; McElwee-White, L.; Rose, E., Wright, L. J. *J. Am. Chem. Soc.* **1985,** *107,* 4570.

[13] Though this appears to be a surface phenomenon, TOFs are calculated under the assumption that all catalyst molecules are active and accessible to H_2/D_2.

Table 1. Catalytic Activity with Respect to H_2/D_2 Exchange[a]

		TOF[b] (HD production molecule^{-1} s^{-1})	
support	catalyst	high vacuum at 130 °C[e]	N_2 followed by high vacuum at 130 °C[f]
Strem carbon, 5N 93-0602	Ru(TMP)	0.13	2.0
	RuNi(DPAHM)	0.84	2.2
	Ru_2(DPAHM)	1.2	4.2
Armak BHC carbon[d]	Ru(TMP)	29	45
	RuNi(DPAHM)	16	36
	Ru_2(DPAHM)	25	82

[a] Flow conditions reported for Ru mono- and diporphyrin catalysts (footnote *b*), each supported on two different types of carbon (footnotes *c* and *d*) and subjected to two different pretreatment regimens (footnotes *e* and *f*). [b] Data were acquired and analyzed as described in the Experimental Section. Catalytic activity is expressed as turnover rate/molecule (HD production/molecule/second), and is not normalized for ruthenium content. The experimental error in turnover rate is estimated to be ±10%. Values reported are corrected for catalyst dispersion and are averages of at least two determinations. Catalyst loadings for tabulated experiments are between 1 and 2%; however, turnover rate was independent of loading over the investigated range of 1−5%. [c] Carbon powder, 99.999% pure, was supplied by Strem Chemicals, Inc., catalog no. 93-0602. See characterization data in Experimental Section.[14] [d] Armak BHC carbon spheres, supplied by Dow Chemical Company, contain approximately one-hundredth the carboxylate and quinoidal functionality per square meter found on 93−0602 carbon.[14] [e] Supported catalysts were subjected to high vacuum at 135 °C until a base pressure of 30 nTorr was reached (pretreatment steps 1 and 2, *vida infra*). Pretreatment step 2, a repeat of step 1, was run to monitor precision for a given set of flow experiments done on the same reactor load of catalyst. Turnover rates reported are the average of catalytic activity determined after pretreatment steps 1 and 2 (which exhibited no significant differences). [f] Supported catalysts were exposed to 800 Torr of N_2 for 15 min followed by high vacuum at 135 °C until a base pressure of 30 nTorr was reached (pretreatment step 4).

too small to accommodate the bulky porphyrin catalysts employed in this study. If we assume that the potentially ligating polar groups are evenly distributed over the entire surface of the support, the catalyst molecules probably are not accessible to a high percentage of the polar functionalities. The Strem carbon has a very low surface area—approximately 5 m^2/g—and is not highly porous; thus, the porphyrin catalysts should be accessible to virtually all of the surface functionalities of this support. TOFs on the order of 40−80/s and total TOs of over 50 000/molecule without the loss of activity were observed by employing catalysts supported on the nonpolar Armak BHC carbon. By themselves, the carbon supports employed in this study do not catalyze H_2/D_2 exchange.

Under argon, benzene solutions of Ru(TMP), Ru_2(DPAHM), and RuNi(DPAHM) were evaporated on the two different carbon supports at loadings of 1−5% by mass. The supported metalloporphyrins were then examined at room temperature for catalytic activity with respect to H_2/D_2 exchange (Table 1) by employing a gas flow reactor directly attached to a high-performance gas/vac manifold.

Flow rates of H_2 and D_2 were adjusted to minimize the effects of back-reactions involving HD while assuring at least 5% H_2/D_2 conversion. The compositions of reactant and product mixtures were followed by a mass spectrometer directly in line with the flow reactor. TOFs were corrected for variations in the percentage of accessible Ru porphyrin centers—as determined by CO chemisorption—and also for slight variations in temperature from run to run. In addition, the poisoning effects of CO and N_2 were examined.

CO chemisorption experiments were run to determine the extent of catalyst accessibility. We assumed irreversible chemisorption of one CO molecule per Ru(II) center and that Ni(II) centers would not irreversibly bind CO over the pressure range employed (0−100 Torr).[14] Generally, between 40 and 60% of the Ru(II) sites were accessible to CO for all supported catalysts. The departure from 100% accessibility is possibly a vestige of the less than ideal method used to apply these catalysts to their supports. Catalysts were applied to the solid supports by slow evaporation of benzene solutions, and this may result in this clumping of catalyst molecules. This method was employed because the affinity of the catalysts for their supports is relatively low—true adsorption did not allow catalyst loadings that gave measurable HD production within the limitations imposed by our reactor volume and flow rates.

The catalytic activity (as represented by the TOF) of each sample with respect to H_2/D_2 exchange was examined at room temperature after each of five different conditioning processes, run consecutively on each sample: (1) The supported catalyst was heated at 135 °C under high vacuum until a base pressure of approximately 30 nTorr was reached. (2) Step 1 was repeated until base pressure was attained. (3) The supported catalyst was exposed to 800 Torr of N_2 for 15 min; catalytic activity was checked without the evacuation of the reactor prior to H_2/D_2 flow. (4) The supported catalyst was exposed to 800 Torr of N_2 for 15 min; step 1 was repeated until base pressure was reached. (5) The supported catalyst was exposed to 100 Torr of CO during chemisorption experiments, followed by a repeat of step 1 until base pressure was attained. The construction of the gas-vac manifold to which the flow reactor was attached allowed this entire battery of tests to be run consecutively, on each individual sample, without exposure to air. Reactants were passed through the reactor until catalytic activity stabilized.

Though TOFs are quite dependent on the polarity of the carbon support, Ru(TMP) and its Ru_2 and RuNi diporphyrin analogs, when adsorbed on the same type of support and exposed to the same pretreatment, exhibit qualitatively similar behavior. Each catalyst is more active by approximately a factor of 20 when it is supported on the apolar Armak carbon. TOFs appear independent of catalyst loadings between 1 and 5%. All supported catalysts examined are poisoned reversibly by N_2 and irreversibly by CO, paralleling their behavior both in solution and as molecular solids.

None of the supported catalysts exhibit any observable induction period. Ru(TMP) displays relatively constant catalytic activity from beginning to end of each flow experiment; however, both diporphyrin catalysts exhibit an unusual, gradual loss of activity during each catalytic run. Regardless of preconditioning treatment, catalytic activity is at its highest immediately upon introduction of the reagents. Over the subsequent 10−15 min, their activities gradually decrease before stabilizing at approximately half the initial rate observed during that particular run (Figure 2). This behavior is reproducible (including consecutive reactions done on an individual catalyst sample using identical pretreatment), and it is observed regardless of which solid support is employed.

In addition, the maximum activity of each catalyst on a particular support is observed after the supported catalyst has been exposed to N_2 followed by high vacuum at elevated temperature (pretreatment 4 described earlier). This pretreatment enhances the activity anywhere from 2 to 20 times (depending on the catalyst and the support) compared to pretreatments 1 and 2, which involve just high vacuum at elevated temperature. Conclusions regarding the mechanism

---

(14) We are unaware of any instance in which CO binds to a Ni(II) porphyrin.

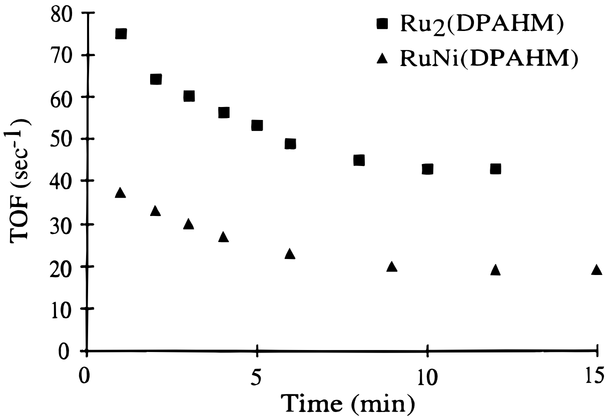

Figure 2. Exposed only to $H_2/D_2/HD$, the catalytic activity of both Ru_2 and RuNi derivatives of DPAHM decreases and then stabilizes over time. Shown here are representative data that were collected for the diporphyrin catalysts, each supported on apolar Armak BHC carbon and pretreated by exposure to 800 Torr of N_2 for 15 min followed by highvacuum at 135 °C for 30 min (pretreatment 4).

will be drawn by comparison of maximum observed catalyst TOFs determined after this activation step (*vida supra*).

These catalysts do not appear to be irreversibly transformed by interaction with their carbon supports. When catalyst molecules are removed from their supports (with benzene, under argon) and exposed to acetonitrile, the well-characterized, acetonitrile-substituted catalyst precursors are regenerated. When these catalysts are rinsed from their supports after exposure to CO, subsequent treatment with methanol results in the regeneration of Ru(II)(CO)(CH_3OH) centers (which are characteristic of the products of Ru insertion into the free-base ligands). This behavior exactly mimics that expressed by catalyst molecules that had never been exposed to solid supports.

Discussion

H_2/D_2 Exchange Catalyzed by Supported Ru(II) Porphyrins. The catalytic activities of Ru(TMP) and two diporphyrin analogs, Ru_2(DPAHM) and RuNi(DPAHM), when adsorbed on two carbon supports of differing surface polarities have been determined. Each of these supported catalysts are more active when adsorbed on Armak BHC carbon supports, which have relatively little surface polarity. The catalytic activity of all systems examined is reversibly poisoned by N_2 and irreversibly poisoned by CO, mimicking behavior exhibited by these molecules both in solution and as molecular solids. Although N_2 is a reversible inhibitor of this catalytic H_2/D_2 exchange, exposure of these supported catalysts to N_2 followed by high vacuum at 135 °C (pretreatment 4 described earlier) actually enhanced catalytic activity, resulting in the maximum TOFs observed for each of the supported catalysts examined.

Order with Respect to Ruthenium. To draw mechanistic conclusions regarding the molecularity in ruthenium of this catalytic H_2/D_2 exchange, it is best to compare maximum catalytic rates to one another (*vide supra*); thus, the discussion of molecularity will be restricted to a comparison of maximum TOFs of these catalysts supported on the Armak carbon and determined after pretreatment step 4 (far right column of Table 1).

Ru(TMP) and RuNi(DPAHM) each exhibit maximum TOFs of approximately 40/s, Ru_2(DPAHM) turns over approximately 80/s, and Ni(TMP) is unable to catalyze H_2/D_2 exchange by itself. When normalized for the number of ruthenium porphyrin moieties, TOFs exhibited by Ru(TMP), RuNi(DPAHM), and Ru_2(DPAHM) are nearly identical to one another.

Results reported independently by Wayland[6] and Collman[7] led us to believe that Ru(TMP) might catalyze H_2/D_2 exchange bimetallically. Although a bimetallic mechanism cannot be eliminated, there is little evidence to support it as the dominant pathway. If a bimetallic mechanism were possible, Ru_2(DPAHM) might catalyze H_2/D_2 exchange either intramolecularly or intermolecularly. In the first case, the two metals would come from within the same molecule, and bimetallic catalysis would occur inside the diporphyrin cavity, while in the second case, two metals from adjacent molecules would be involved.

The *intramolecular* mechanism is unlikely for two reasons. First, the metal centers in Ru_2(DPAHM) and its RuNi analog appear to be too far apart. A preliminary crystal structure of Ni_2(DPAHM) indicates that 6.7 Å separates the two metals. By assuming a similar metal−metal distance in the Ru_2 and RuNi derivatives, and by assuming that the active species involves dihydrogen or hydride ligands (M−H distances ≤ 2 Å)[15] , it is unlikely that this molecule, in the solid state, is capable of mediating catalytic H_2/D_2 exchange bimetallically inside the diporphyrin cavity. Second, if the proposed intramolecular bimetallic mechanism requires two Ru centers, RuNi(DPAHM) should be completely inactive toward catalytic H_2/D_2 exchange. In fact, RuNi(DPAHM) turns over approximately half as fast as its Ru_2 analog. The Ni(TMP) monomer does not catalyze H_2/D_2 exchange by itself, and RuNi(DPAHM) can be considered a 50/50 mixture of Ru(TMP)/Ni(TMP) bridged by an anthracene spacer. For an intramolecular bimetallic mechanism to be consistent with the observed TOFs, one must assume that some unexpected synergy between the Ni and Ru centers of RuNi(DPAHM) allows the Ni(TMP) moiety to actively participate in the catalysis [approximately half as effectively as the second Ru center in Ru_2(DPAHM)]. This assumption is contrary to behavior exhibited by the Ni(TMP) monomer, but the possibility cannot be eliminated entirely.

For the data to be consistent with an *intermolecular*, bimetallic mechanism, a great deal of order is required of these supported catalysts. The activity of RuNi(DPAHM), when normalized for Ru content, is approximately equal to that of Ru_2(DPAHM). If we assume that there is no synergy between the Ni and Ru centers of RuNi(DPAHM), and that Ni does not participate in the catalytic exchange of H_2/D_2, then the argument in support of an intermolecular bimetallic mechanism requires that, in the case of all three catalysts, Ru(TMP), RuNi(DPAHM), and Ru_2(DPAHM), each Ru porphyrin moiety has another Ru porphyrin center as its nearest intermolecular neighbor.

In the case of Ru_2(DPAHM), each Ru porphyrin moiety has by definition another Ru porphyrin as its nearest neighbor; however, for each ruthenium center of RuNi(DPAHM) to have as its nearest neighbor another Ru center, all RuNi(DPAHM) molecules must be aligned in a head-to-head and tail-to-tail fashion. The steric bulk of Ru(TMP) moieties likely precludes *intermolecular* interactions, which could result in significant deviation from a statistical distribution of RuNi(DPAHM) on the solid carbon supports. Solely on the basis of statistics, one expects that 50% of the Ru centers in RuNi(DPAHM) would have a nickel center for its nearest neighbor. By assuming that nickel is unable to participate in catalysis, only 50% of the Ru centers in RuNi(DPAHM) would reside in sites capable of effecting intermolecular, bimetallic catalysis; thus, if a statistical

---

(15) (a) Heinekey, D. M.; Oldham, W. J. *Chem. Rev.* **1993,** *93,* 913. (b) *Transition Metal Hydrides;* Dedieu, A., Ed., VCH: New York, 1992.

(16) (a) Groves, J. T.; Quinn, R. *Inorg. Chem.* **1984,** *23,* 3844; *J. Am. Chem. Soc.* **1985,** *107,* 5790. (b) Masuda, H.; Taga, T.; Osaki, K.; Sugimoto, H.; Mori, M.; Ogoshi, H. *J. Am. Chem. Soc.* **1981,** *103,* 2199. (c) Collman, J. P.; Barnes, C. E.; Brothers, P. J.; Collins, T. J.; Ozawa, T.; Gallucci, J. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1984,** *106,* 5151.

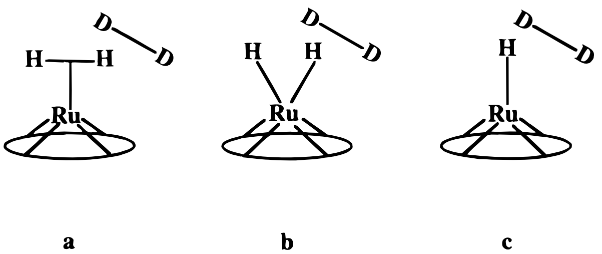

Figure 3. D_2 approaching possible intermediates involved in catalytic H_2/D_2 exchange on one face of Ru(TMP): (a) dihydrogen complex; (b) dihydride complex; and (c) monohydride complex. Axial asymmetry results in out-of-plane metal binding, which may allow *cis* coordination of the approaching D_2.

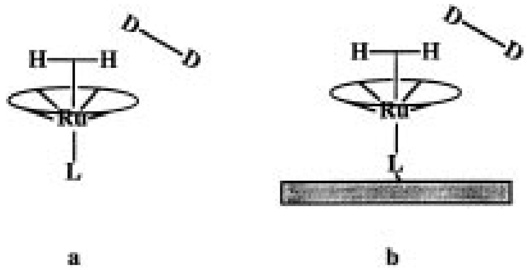

Figure 4. Trans-axial ligand (L), either exogenous (a) or from the catalyst support (b), should force the Ru center back into or possibly through the porphyrin plane, likely precluding *cis* coordination to Ru on the distal face of the porphyrin. This effect is demonstrated here using the dihydrogen complex of Ru(TMP), one of the possible intermediates shown in Figure 3.

distribution of RuNi(DPAHM) is assumed, we would expect RuNi(DPAHM) to manifest only half the catalytic activity (when normalized for ruthenium content) of Ru_2(DPAHM). The data indicate that RuNi(DPAHM) is as catalytically active per Ru center as its Ru_2 analog.

Although the possibility has not been completely eliminated, it is doubtful that Ru(TMP) catalyzes H_2/D_2 exchange bimetallically. The simplest mechanism consistent with the data involves catalysis on one face of a single ruthenium porphyrin. This is surprising, because metalloporphyrins with the metal complexed in the porphyrin plane rarely exhibit *cis* coordination sites on one face. Figure 3 presents three possible intermediates through which H_2/D_2 exchange might occur on one face of a single Ru porphyrin.

Structures a, b, and c, dihydrogen, dihydride, and monohydride complexes, respectively, exhibit a metal bound out of the porphyrin plane. Asymmetry with regard to *trans* ligation of a metalloporphyrin always results in such out-of-plane metal binding, and this type of coordination might allow *cis* binding of additional ligands on that side of the porphyrin plane. The presence of an axial ligand (including H_2, D_2, or HD) *trans* to dihydrogen, dihydride, or hydride ligands should force the metal back into or even through the porphyrin plane (Figure 4), precluding *cis* coordination on the distal side and diminishing catalytic activity. The presence of a *trans* axial ligand may even inhibit initial formation of the proposed intermediates. This description is consistent with data that will be discussed in the sections involving catalyst/support interactions, the loss of activity by diporphyrin catalysts, and the inhibitory effects of exogenous ligands.

Loss of Activity by Diporphyrin Catalysts. As previously mentioned, both diporphyrin catalysts exhibit an unusual loss of activity during each catalytic run (Figure 2). Regardless of preconditioning and the nature of the carbon support, the catalytic activities of Ru_2(DPAHM) and RuNi(DPAHM) are at a maximum immediately upon the introduction of H_2 and D_2. Within 10−15 min, TOFs gradually decrease to approximately 60% of the initial rate, where they remain for the duration of the catalytic run. This partial loss of activity seems to be a function only of exposure to H_2/D_2/HD and it is not manifested by the Ru(TMP) monomer, which displays relatively constant catalytic activity throughout each run.

By assuming a monometallic mechanism, H_2/D_2 exchange can be catalyzed at either face of a single Ru(II) porphyrin moiety. In the case of Ru_2(DPAHM), there are four porphyrin faces—two facing outside and two facing inside the diporphyrin cavity—each able to catalyze H_2/D_2 exchange. For steric reasons, the outer faces of the diporphyrin are more accessible, and the predominance of H_2/D_2 exchange should occur at these monometallic sites. Despite the surrounding steric bulk, reactants may slowly diffuse into the diporphyrin cavity. Once there, catalysis should be effected by each inner face, but steric bulk should also slow the rate of product diffusion out of the cavity. There is a possibility that, once inside the cavity, H_2/D_2/HD form some species—possibly even a catalytically active one—that exhibits a *trans* labilizing effect and inhibits formation of the catalytically active species on the outer face of the porphyrin (*vide supra*). This explanation is consistent with the behavior exhibited by the cofacial catalysts examined.

Inhibition by Ligands. Regardless of the nature of the carbon support, all of the catalysts were poisoned reversibly by N_2 and irreversibly by CO (pretreatment steps 3 and 5, respectively), paralleling their behavior both in solution and as molecular solids. In the case of each catalyst poisoned by N_2, catalytic activity with respect to H_2/D_2 exchange was restored by exposing the poisoned catalyst to high vacuum and elevated temperature.

The poisoning effects of N_2 and CO can be correlated with their abilities to ligate unsupported Ru(II) porphyrins. CO binds tightly to Ru(II) porphyrins, and it cannot be removed cleanly by pyrolysis. In contrast, dinitrogen binds rather weakly to such Ru(II) centers. Lyophilized powders of Ru(TMP), Ru_2(DPAHM), and RuNi(DPAHM) each bind N_2, but the "axially naked", catalytically active species can be easily regenerated by exposure of the dinitrogen adducts to moderate heat and vacuum. The inhibitory effects of N_2 and CO are a result of their abilities to bind, competitively, Ru(II) porphyrin sites that could otherwise catalyze H_2/D_2 exchange. In addition, the ligands may exert a *trans* labilizing effect that precludes formation of a catalytically active species (Figure 4).

Catalyst Support Interactions. Polarity of the carbon support dramatically affected the catalytic activity of Ru(TMP), Ru_2(DPAHM), and RuNi(DPAHM). Each catalyst was less active by about a factor of 20 when adsorbed on the carbon support known to have a higher surface polarity. When adsorbed on alumina or silica (supports that contain more polar functionalities than do the carbon supports employed in the present study), Ru(TMP) exhibits no ability to catalyze H_2/D_2 exchange. We suspect that this inhibitory effect results from the ligation of ruthenium by polar functionalities on the surface of the support. Ligating functionalities on the support surface not only appear to compete directly with H_2/D_2 for a face of each active Ru porphyrin site but it appears that their ligation to the Ru center also inhibits catalytic activity via the exertion of some *trans* labilizing effect (*vide infra*). As demonstrated by the poisoning effects of N_2, even very weak ligands can markedly inhibit the activity of these supported catalysts.

In addition, catalytic activity was affected by the pretreatment regimen employed. Supported catalysts were dried in the reactor at 135 °C until a base pressure of 30 nTorr was reached. Catalytic activity was greater for all catalyst/support combinations when this pretreatment was preceded by the exposure of the catalyst to 800 Torr of N_2 for 15 min. One possible explanation of this surprising behavior is that the weakly ligating polar moieties on the support are displaced by N_2, resulting in a change of the catalyst/support morphology. Exposure of the supported catalyst to high vacuum and elevated temperature subsequently removes ligated N_2, but at least some of the catalyst is not religated by the support; thus, more Ru(II) centers are left available to effect catalysis.

The observed rate enhancement following this N_2 pretreatment was greatest in the case of Ru(TMP) adsorbed on the polar carbon. Ru(TMP) is a monomer, and as such, axial ligation by polar surface moieties may completely suppress its activity (a free face remains, but axial ligation may even suppress catalysis on the *trans* face).[16] In contrast, both cofacial catalysts have two metals that can be in contact with the solid support. There is likely inhibitory surface ligation to only one of the metal centers; thus, the second metal center remains free for catalysis. By assuming that N_2 irreversibly disrupts some catalyst/support interactions, this pretreatment regimen is expected to enhance the activity of the Ru(TMP)/polar support system disproportionately.

C−H Bond Activation. Catalytic C−H bond activation by these electron-deficient ruthenium(II) porphyrins is extremely interesting, although orders of magnitude slower than the rates of H_2/D_2 exchange. Wayland[6] has demonstrated that Rh derivatives of TMP and a tethered diporphyrin analog bimetallically effect the oxidative addition of methane and the benzylic C−H bond of toluene. Those reactions appear to proceed through highly ordered, 4-centered activated complexes. Benzene solutions of rhodium porphyrins are stable for months, apparently because the aryl C−H bonds cannot participate in such a transition state. Ru(TMP) and Ru_2(DPAHM) both appear able to *catalyze* H/D exchange into methane, benzene, and *both* the benzyl and *aryl* positions of toluene. The ability of Ru(TMP) to activate aryl C−H bonds indicates that a mechanism different from that proposed by Wayland is operating in this system. We have not yet undertaken serious mechanistic studies of this C−H activation; however, given the evidence that catalytic H_2/D_2 exchange can occur on one face of a single porphyrin, we are disposed to believe that H/D exchange into hydrocarbons can be effected similarly. We are continuing to study this remarkable, catalytic activation of C−H bonds.

Conclusion

Ru(TMP), Ru_2(DPAHM) and RuNi(DPAHM), catalyze H_2/D_2 exchange in benzene solution, as molecular solids, and when adsorbed on carbon supports. Surprisingly, data indicate that exchange is effected by one face of a single Ru(TMP) moiety via a mechanism that probably involves dyhydrogen, dihydride, or monohydride intermediates and that requires *cis* coordination on one face of the metalloporphyrin. The catalytic activities of these supported ruthenium(II) porphyrins are diminished by the presence of ligating functionalities on the surface of the supporting matrix. In addition, although extremely slow, these electron-deficient Ru(II) porphyrins catalytically activate the C−H bonds of methane and aromatic hydrocarbons at room temperature.

Experimental Section

General. Manipulations of oxygen-, water-, and nitrogen-sensitive compounds were performed in an argon-filled Vacuum Atmospheres Co. inert atmosphere glovebox. Oxygen levels (≤1 ppm) were monitored by a Vacuum Atmospheres Co. trace oxygen analyzer. Air- and moisture-sensitive materials were also handled on a vacuum line and in Schlenkware flasks and tubes equipped with J. Young valves and O-ring adapter fittings.

NMR spectra were recorded on a Varian XL-400 Fourier transform spectrometer using benzene-d_6, toluene-d_8, or chloroform-d_1 as a solvent. Resonances were referenced versus the residual ^{1}H signal of the deuterated NMR solvent and are reported relative to tetramethylsilane. UV−vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer with 2 nm resolution. IR spectra were recorded at 1 cm^{-1} resolution and signal averaged over 32 scans on a Mattson Research Series 1 FTIR spectrometer. Mass spectra were recorded at the Mass Spectrometry Facility of the University of California at San Francisco.

Separation and quantitation of H_2, HD, and D_2 were achieved according to modified literature procedures[4e,17] by utilizing an HP 5890 gas chromatograph equipped with a thermal conductivity detector (TCD).

UV photolysis experiments were conducted by using a Conrad-Hanovia 450 W medium-pressure mercury vapor UV lamp with an Ace Glass one-piece, water-cooled 200 mL borosilicate photochemical reaction vessel. Irradiation was conducted under a moderate, steady sparge of argon.

Commercially available solvents and chemical reagents were purchased and used as received unless otherwise noted. All solvents for use in the inert atmosphere boxes were purified prior to use. Toluene and benzene were distilled from sodium benzophenone ketyl solutions under nitrogen or argon. The solvents were subsequently transferred into the inert atmosphere box in sealed flasks and sparged with nitrogen or argon to remove residual oxygen. Reagent grade acetonitrile was distilled over calcium hydride under argon, transferred into the inert atmoshpere box, and sparged with N_2 or Ar. Often, for use with particularly air- or water-sensitive compounds, these reagents were redistilled by vacuum transfer over their respective drying agents followed by repetitive freeze−pump−thaw cycles prior to reintroduction to the inert atmosphere box. Benzene-d_6 and toluene-d_8 were vacuum transfered from sodium/potassium benzophenone ketyl solutions to a Schlenk flask. After repeated freeze−pump−thaw cycles, the solvent was then transferred into an inert atmosphere box.

Flash chromatographic silica gel (60 H, E. Merck, EM Science) and alumina (neutral, activity I, 80−200 mesh) for use in the inert atmosphere boxes were dried at 200 °C under vacuum (10^{-2} Torr) for at least 24 h prior to introduction into the inert atmosphere box.

H_2/D_2 Exchange Reactions. Catalyst syntheses and sample preparations were handled exclusively under a purified argon atmosphere with the use of standard Schlenk or glovebox techniques.

Methods and Materials. Carbon supports were dried under vacuum at 200 °C for 2 days prior to their transfer to the glovebox. Catalysts were adsorbed onto the carbon supports, at loadings of 1−5% (w/w), by slow evaporation of dilute benzene solutions, and the supported catalysts were dried under low vacuum for 4 h at 100 °C. After cooling to room temperature, supported catalysts were then loaded into a quartz flow reactor and removed from the inert atmosphere box under argon. The reactor, containing supported catalyst, was mounted on an RXM-100 catalyst characterization and gas-handling system (Advanced Scientific Designs, Inc.), where catalyst pretreatments (*vide infra*)—including the introduction of exogenous ligands, chemisorption experiments, and rate measurements—were performed.

Surface Polarity of Carbon Supports. Temperature-programmed desorption (TPD) analyses of both carbon supports employed in this study were done as follows. Carbon support (3−5 mg) was placed in a quartz U-shaped microreactor, and the sample was evacuated at ambient temperature until a base pressure of 0.10 μTorr was reached. The sample was then heated linearly from 30 to 1100 °C at a temperature ramp of 10 °C/min with direct evacuation of desorbed gases into a chamber containing a UTI 100C quadrupole mass spectrometer. Masses 28 and 44 were monitored and quantified as a function of temperature.

H_2/D_2 Turnover Frequencies. Turnover frequencies (TOFs) for H_2/D_2 exchange were calculated from the measured percent conversion

---

(17) (a) Yasumori, I.; Ohno, S. *Bull Chem. Soc. Jpn.* **1966,** *39,* 1302. (b) Paonessa, R. S.; Prignano, A. L.; Trogler, W. C. *Organometallics* **1985,** *4,* 647.

to HD in the effluent from a flow reactor containing a known amount of supported catalyst (typically ca. 50−250 mg) and the flow rate of H_2 and D_2.[18] Reactant gases were passed into the reactor at equivalent rates and controlled to within ± 0.1 cm^3 min^{-1} with the use of electronic mass flow controllers. The reactant gases were passed through liquid nitrogen traps upstream of the sample to remove trace oxygen and water. Reactant flow rates were varied between 10 and 100 cm^3 min^{-1} to keep the percent conversion of reactants between 5 and 15%. The effluent gas mixture was analyzed with a Leybold Inficon Quadrex 200 mass spectrometer tuned and calibrated to give accurate relative amounts of H_2, HD, and D_2.

CO Chemisorption Measurements. Carbon monoxide chemisorption was measured by using a volumetric, two-isotherm experiment. First, the total *(reversible + irreversible)* adsorption isotherm was measured over a pressure range of 20−80 torr. The sample was then evacuated at room temperature for 10 min to remove any reversibly adsorbed CO, after which a physical *(reversible only)* adsorption isotherm was measured over the same pressure range. The chemisorption *(irreversible only)* isotherm was determined by subtraction of the second isotherm from the first.[19]

Qualitative Studies. In a glovebox under an argon atmosphere, a 5 mL flask was charged with 1 mL of a 1 mM benzene solution of the catalyst and a stir bar. The vial was sealed with a Teflon-lined cap, briefly exposed to low vacuum to evacuate the headspace, and charged with 1 atm of H_2/D_2 (50/50). The sample was stirred, and, at appropriate intervals, 100 μL of headspace was withdrawn via a gas-tight syringe and analyzed for H_2, HD, and D_2 by gas chromatography. Qualitative catalytic studies on the molecular solids were performed as before, in the absence of benzene solvent.

H_2 Exchange into Deuterated Solvents. In a glovebox under an argon atmosphere, a 5 mL flask was charged with a 1 mL solution of the catalyst in benzene-d_6 or toluene-d_8 and a stir bar. The vial was sealed with a Teflon-lined cap, briefly exposed to low vacuum to evacuate the headspace, and charged with 1 atm of H_2. The sample was stirred, and after 6 days the headspace was analyzed for H_2, HD, and D_2 by gas chromatography. Neither H_2 nor HD was detected in the headspace over catalyst solutions in benzene-d_6 or toluene-d_8 stirred for 1 week in the absence of exogenous H_2; thus, catalyst molecules were not the source of exchangeable hydrogen.

D_2 Exchange into Methane. A 5 mL flask was charged with catalyst (2 mg) and a stir bar. The vial was sealed with a Teflon-lined cap, exposed to low vacuum to evacuate the headspace, and charged with 1 atm of CH_4/D_2 (90/10). The sample was stirred, and, at appropriate intervals, 100 μL of headspace was withdrawn via a gas-tight syringe and analyzed for H_2, HD, and D_2 by gas chromatography. To eliminate the solid catalysts as the source of exchangeable hydrogen atoms, catalyst (2 mg) was stirred under D_2 for 6 days with no observed production of HD.

Synthesis and Characterization of Metalloporphyrin Complexes. The metalloporphyrin complexes discussed herein were synthesized from well-characterized monomeric porphyrin and cofacial diporphyrin free bases. Known complexes, whether synthesized by the original synthetic method or by independent methods, were identified by comparison with the published characterization data. All new complexes were characterized by the similarity of their characterization data to the published data for related known complexes. New complexes were characterized by a variety of spectroscopic techniques, including ^{1}H NMR, UV−vis, IR, and mass spectrometry. ^{1}H NMR spectroscopy of these highly symmetric porphyrin complexes is particularly powerful for their characterization; however, two cofacial metallodiporphyrin species, Ru_2(DPAHM) and RuNi(DPAHM), were characterized by their reactivity, which mimics that exhibited by related monomeric porphyrins (*vide infra*). The limited quantities of these complexes and their inherent reactivity (including the formation of weak complexes with solvent) preclude characterization by other methods.

Ni[1-(10,15,20-trimesityl-5-porphyrinyl)-8-formylanthracene]. Nickel was inserted into 1-(10,15,20-trimesityl-5-porphyrinyl)-8-formylanthracene according to modified literature procedures.[20] Free-base porphyrin (200 mg) was dissolved in 40 mL of *o*-dichlorobenzene. The dark purple solution was sparged for 40 min with argon and brought to reflux under positive argon pressure. A deoxygenated, saturated, methanolic solution of $Ni(OAC)_2 \cdot (H_2O)_4$ was added slowly. Methanol was allowed to evaporate out of the reaction flask through a needle, and within 10 min the solution became bright red. After 1 h at reflux, the reaction mixture was cooled to room temperature, filtered over Celite, and eluted with CH_2Cl_2. Solvent was removed under vacuum, and the red residue was chromatographed over flash silica (3 × 22 cm). The column was packed and loaded in hexanes/toluene (2/1), and the product was eluted as a bright red band in hexanes/toluene (1/3). Solvent was removed under vacuum, yielding a red solid (209 mg): mass spectrum *m/e* 924.4 (M^+); ^{1}H NMR (C_6D_6) δ 9.67 (s, 1H), 9.15 (s, 1H), 8.79 (dd, 4H), 8.64 (br s, 4H,), 8.29 (s, 1H), 8.07 (d, 1H), 7.93 (d, 1H), 7.75 (d, 1H), 7.50 (dd, 1H), 7.11 (s, 1H), 7.07 (s, 1H), 7.05 (s, 2H), 7.00 (s, 2H), 6.98 (obscured d, 1H), 6.89 (dd, 1H), 2.40 (s, 3H), 2.34 (s, 6H), 1.94 (s, 3H), 1.92 (s, 6H), 1.84 (s, 3H), 1.80 (s, 3H); UV−vis (CH_2Cl_2) λ_{max} (nm) 416 (Soret), 526.

Ni(H_2DPAHM). A second 10,15,20-trimesitylporphyrin was condensed onto Ni[1-(10,15,20-trimesityl-5-porphyrinyl)-8-formylanthracene] by employing modified Lindsey[9] conditions, in a manner analogous to that used to synthesize nonmetalated derivatives.[8] Ni[1-(10,15,20-trimesityl-5-porphyrinyl)-8-formylanthracene] (200 mg), mesitaldehyde (384 mg), and pyrrole (203 mg) were dissolved in 285 mL of chloroform. After argon sparging for 1 h, enough $BF_3(OEt)_2$ was added via syringe to result in a solution that was 3.3 mM in catalyst. After 70 min of stirring in the dark, oxidation of the porphyrinogen was effected by the addition of DDQ (485 mg). Workup of the reaction mixture and crude purification were as described by Collman and coworkers for nonmetalated cofacial diporphyrins.[8] Final purification of the mononickel cofacial diporphyrin was effected by chromatography over flash silica (3.5 × 23 cm). The column was packed and loaded, and tetramesitylporphyrin monomer was eluted in hexanes/CH_2Cl_2 (4/1). A broad, red-brown band that contained the desired product was eluted in 2/1 hexanes/CH_2Cl_2. Evaporation of solvent under vacuum yielded 94 mg (28% yield based on the nickelated, bridged porphyrin): mass spectrum *m/e* 1558.7 (M^+); ^{1}H NMR (C_6D_6) δ 9.21 (s, 1H), 8.78 (s, 1H), 8.59 (d, 2H), 8.36 (dd, 4H), 8.24 (d, 2H), 8.16 (d, 2H), 8.11 (d, 2H), 7.97 (d, 2H), 7.76 (d, 2H), 7.34 (t, 2H), 7.29 (t, 2H), 7.07 (s, 1H), 7.04 (s, 1H), 6.97 (s, 3H), 6.89 (s, 3H), 6.64 (s, 2H), 6.23 (s, 2H), 2.35 (s, 9H), 2.31 (s, 3H), 2.29 (s, 6H), 2.02 (s, 6H), 1.79 (s, 6H), 1.78 (s, 6H), 1.52 (s, 3H), 0.39 (s, 6H), 0.38 (s, 3H), −0.46 (s, 6H), −2.52 (br s, 2H); UV−vis (CH_2Cl_2) λ_{max} (nm) 412 (Soret), 520, 592.

Red crystals of Ni_2(DPAHM) for X-ray analysis were grown by vapor diffusion of methanol into a methylene chloride solution of the compound followed by slow evaporation of the solvent. Due to the presence of disordered solvent molecules in a number of sites in the crystal lattice, refinement of the crystal structure was limited to R = 10.9. The porphyrin itself is well defined (esd ≅ 0.010 Å for the 24-atom core of each of the constituent porphyrins). We consider this only a preliminary structure determination; thus, a thorough presentation of the data and analysis of the structure will not be presented.

Ni(DPAHM)Ru(CO)(CH_3OH). Ruthenium was inserted into Ni(H_2-DPAHM) according to a modified literature procedure.[21] Ni(DPAHM)-H_2 (70 mg) was dissolved in (30 mL) *o*-dichlorobenzene. Solid $Ru_3(CO)_{12}$ (60 mg) was added, and the reaction mixture was sparged with argon. Under an argon atmosphere, the dark purple mixture was heated to reflux for 3 h, during which time the solution turned dark red. The extent of reaction was monitored by UV−vis spectra (CH_2Cl_2) or TLC (SiO_2/toluene). When no starting material remained, the solution was cooled to room temperature and 10 mL of methanol was added under argon. The reaction mixture was filtered through a Celite pad and eluted with CH_2Cl_2/CH_3OH (5/1), and the solvent was removed under vacuum. The residue was chromatographed over flash silica (3.5

---

(18) Gu, Y.; Brenner, A. *J. Catal.* **1992**, *136*, 222.

(19) Data analysis was performed by using the program Chemisorption Data Analysis v.4.06 (Copyright 1990−1994, Advanced Scientific Designs, Inc.).

(20) *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier Scientific Publishing Company: New York, 1975; and references cited therein.

(21) (a) Rillema, D. P.; Nagle, J. K.; Barringer, L. F.; Meyer, T. J. *J. Am. Chem. Soc.* **1981,** *103,* 56. (b) Venburg, G. D. Ph.D. Dissertation, Stanford University, Stanford, CA, 1990.

× 18 cm). The column was packed and loaded in hexanes/CH_2Cl_2 (6/1 + 0.5% methanol). The solvent polarity was gradually increased, and the desired product was eluted as a broad, red-orange band in 2/1 hexanes/CH_2Cl_2 + 0.5% methanol. The product was recrystallized from methanol over CH_2Cl_2 followed by slow evaporation. Red crystals were harvested, washed with cold methanol, and dried under vacuum to yield 70 mg of a red-purple solid: mass spectrum (Ru^{102}, Ni^{57}) *m/e* 1686.5 (cluster, $M^+ - CH_3OH$); ^1H NMR (C_6D_6) indicates the presence of a mixture of diamagnetic species; UV−vis (CH_2Cl_2) λ_{max} (nm) 408 (Soret), 528; IR (KBr) 1934 cm^{-1} (br).

Ni(DPAHM)Ru(CH_3CN)$_2$. Ni(DPAHM)Ru(CH_3CN)$_2$ was synthesized by using a modification of the standard procedures for photolysis of ruthenium porphyrin carbonyl complexes.[5,10b,d,21] Ni(DPAHM)Ru(CO)(CH_3OH) (70 mg) was dissolved in benzene (50 mL) and acetonitrile(100 mL), placed in a water-cooled, borosilicate photochemical reaction vessel, sparged with argon, and subjected to UV irradiation under a steady argon sparge. After 2 h, the solution, now visibly darker, was transferred under argon to a Schlenk flask via cannula. Solvent was evaporated under vacuum, and the flask containing the product, now a purple solid, was transferred to an argon-filled glovebox. The residue was run through an alumina plug (neutral, activity I) using toluene containing a trace of acetonitrile as solvent. The dark orange-brown eluent was collected and dried under vacuum to yield 65 mg of purple solid: ^1H NMR (C_6D_6) diporphyrin resonances δ 9.22 (s, 1H), 8.79 (s, 1H), 8.28 (d, 2H), 8.43 (d, 2H), 8.36 (d, 2H), 8.35 (d, 2H), 8.25 (d, 2H), 8.24 (d, 2H), 8.17 (d, 2H), 8.12 (d, 2H), 7.82 (d, 2H), 7.50 (dd, 1H), 7.11 (s, 2H), 7.08 (s, 2H), 7.05 (s, 1H), 6.99 (s, 2H), 6.97 (s, 1H), 6.88 (s, 1H), 6.71 (d, 1H), 2.47 (s, 6H), 2.40 (s, 6H), 2.29 (s, 3H), 1.95 (s, 6H), 1.94 (s, 3H), 1.83 (s, 3H), 1.69 (s, 6H), 1.65 (s, 3H), 1.46 (s, 6H), 1.40 (s, 3H), 0.91 (s, 6H), 0.57 (s, 3H); acetonitrile resonances δ −1.61 (s, 3H), −3.76 (s, 3H); UV−vis (C_6H_6) λ_{max} (nm) 400 (Soret), 528; IR (KBr) no CO stretch.

Ni(DPAHM)Ru. Ni(DPAHM)Ru(CH_3CN)$_2$ (40 mg) was lyophilized from benzene. The amorphous red-purple solid was then pyrolyzed according to general literature procedures,[5,10d,22] at 225 °C, under vacuum (10 μTorr) for 3.5 h. Ni(DPAHM)Ru could not be definitively characterized spectroscopically (*vide infra*). The ^1H NMR (C_6D_6) spectrum exhibited broad resonances in both the aromatic and aliphatic regions. Upfield signals corresponding to bound acetonitrile ligands were *not* observed. UV−vis (C_6H_6) λ_{max} (nm): 406 (Soret), 530.

Ru_2(DPAHM)(CO)$_2$(CH_3OH)$_2$. H_4DPAHM (80 mg) was ruthenated according to the same procedure used to insert ruthenium into Ni(H_2DPAHM). Final purification was effected in the following manner. The reaction mixture was filtered through a celite pad and eluted with CH_2Cl_2/CH_3OH (5/1), and the solvent was removed under vacuum. The residue was chromatographed over flash silica (3 × 25 cm). The column was packed and loaded in hexanes/CH_2Cl_2 (6/1 + 0.5% methanol). The solvent polarity was gradually increased, and the desired product was eluted as a broad, red-orange band in 3/1 hexanes/CH_2Cl_2 + 0.5% methanol. The product was recrystallized from methanol over CH_2Cl_2 followed by slow evaporation. The purple-red crystals were harvested, washed with cold methanol, and dried under vacuum to yield 80 mg: mass spectrum (Ru^{102}) *m/e* 1822.6 (cluster, $M^+ - 2CH_3OH$); ^1H NMR (C_6D_6) δ 8.73 (s, 1H), 8.35 (d, 4H), 8.37 (d, 4H), 8.21 (d, 2H), 7.93 (d, 4H), 7.88 (d, 4H), 7.45 (s over d, 3H), 7.36 (dd, 2H), 6.96 (s, 2H), 6.77 (s, 4H), 2.41 (s, 6H), 2.33 (s, 12H), 1.87 (s, 6H), 1.59 (s, 6H), 1.37 (s, 12H), 1.21 (s, 12H), −1.8 (br s, 6H); UV−vis (CH_2Cl_2) λ_{max} (nm) 406 (Soret), 530 (br); IR (KBr) 1937 cm^{-1}.

Ru_2(DPAHM)(CH_3CN)$_4$. Ru_2(DPAHM)(CH_3CN)$_4$ (70 mg) was photolyzed using the method described earlier for synthesis of Ni(DPAHM)Ru(CH_3CN)$_2$. After photolysis, the solvent was stripped, and the residue was transferred to an argon-filled glovebox. The residue was run through an alumina plug (neutral, activity I) using toluene, containing a trace of acetonitrile, as solvent. The dark orange-brown eluent was collected and dried under vacuum to yield 65 mg: ^1H NMR (C_6D_6) porphyrin resonances δ 9.30 (s, 1H), 8.77 (s, 1H), 8.29 (d, 4H), 8.26 (d, 4H), 8.21 (d, 2H), 8.18 (d, 4H), 8.10 (d, 4H), 7.95 (d, 2H), 7.46 (t, 2H), 7.21 (s, 4H), 7.09 (s, 2H), 7.04 (s, 4H), 2.44 (s, 12H), 2.40 (s, 6H), 2.03 (s, 6H), 1.82 (s, 12H), 1.59 (s, 6H), 1.57 (s, 12H); acetonitrile resonances, in and out δ −1.73 (s, 6H), −2.12 (s, 6H); UV−vis (C_6H_6) λ_{max} (nm) 398 (Soret), 528 (br); IR (KBr) no CO stretch.

Ru_2(DPAHM). Ru_2(DPAHM) was synthesized by solid state vacuum pyrolysis of amorphous Ru_2(DPAHM)(CH_3CN)$_4$ using the general procedure described earlier. Ru_2(DPAHM)(CH_3CN)$_4$ (30 mg) was carefully lyophilized from benzene. The amorphous red-purple solid was then pyrolyzed under vacuum (230 °C, 10^{-5} Torr) for 4 h to yield a shiny red-purple solid quantitatively. Ru_2(DPAHM) could not be definitively characterized spectroscopically. The ^1H NMR (C_6D_6) spectrum exhibited broad resonances in both the aromatic and aliphatic regions. Upfield signals corresponding to bound acetonitrile ligands were *not* observed. UV−vis (C_6H_6) λ_{max} (nm) 406 (Soret), 528.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged. We thank the Mass Spectrometry Facility at the University of California at San Francisco, supported by NIH Division of Research Grant RR01614 and by NSF Grant DIR8700766. We are grateful to Dr. Larry Ito at Dow Chemical Company, Midland, MI, for performing the TPD analyses on both carbon supports employed in this study. We thank Professor T. Daniel P. Stack at Stanford University for assistance with acquisition and refinement of the preliminary crystal structure.

IC951495+

---

(22) Collman, J. P.; Barnes, C. E.; Woo, L. K. *Proc. Natl. Acad. Sci. U.S.A.* **1983,** *80,* 7684.