transformation of an indirect to direct gap, which could be induced by relaxation of the k-selection rule in the quantum confinement regime. This interesting explanation remains to be proven since the possibility of impurity absorption in the tail region has to be rigorously excluded. Bulk chemical analyses (Galbraith Labs., Knoxville, TN) demonstrate that at shorter contact times of PH_3 (3 h or less) the Ga:P ratio is large (11:1, at 300 °C, 3 h) but at longer times (12 h) the ratio is reduced (0.4:1), indicating the presence of unreacted $(Me)_{3-x}Ga$ or phosphorus, respectively. X-ray diffraction patterns (both from a lab source and the synchrotron) of samples treated at 300 °C and below show no reflections other than those of the zeolite host (with greatly modified relative intensities due to the inclusion); however, at PH_3 treatment temperature of 400 °C, bulk GaP can be identified.[13]

For lower annealing temperatures, the formation of microdisperse GaP was monitored by ^{31}P MAS NMR. Figure 2 shows the spectra for four separate samples which had been exposed to $(Me)_3Ga$ by vapor transport and treated for 3 h in PH_3 at various temperatures. The sample annealed at 200 °C shows several distinct signals (attributed to molecular precursor complexes) superimposed on a broad resonance (assigned to microdisperse GaP). As the temperature is increased, the sharp peaks disappear, and only the broad resonance, dominated by a distribution of isotropic chemical shifts, remains. Most notably, the center of gravity of the broad resonance is found significantly upfield with respect to bulk GaP (−143 ppm vs 85% H_3PO_4)[14] and gradually shifts towards that position with increasing annealing temperature. For the 300 °C sample, the signal has sharpened significantly and resembles that of bulk GaP,[14-16] whereas the NMR spectrum of the 400 °C sample confirms the formation of the bulk material.

The EXAFS results,[17] for a sample treated at 300 °C with a short PH_3 contact time (i.e., 3 h), confirm the formation of small GaP clusters most likely located in the supercages of the zeolite.[18] Several different shells can be identified by fitting with adequate reference compounds. Ga is present in two distinct coordination environments. About 70% of the Ga is coordinated to the zeolite framework with an average Ga–O bond length of 2.04 Å. A peak at about 2.5 Å (uncorrected for phase shift) is interpreted as the corresponding Ga–Si/Al scattering from the host lattice. The second environment consists of GaP which is indicated in the EXAFS spectrum and the XANES (X-ray absorption near edge spectroscopy) region of the absorption edge. Three coordination shells of GaP were identified by the fitting procedure: a Ga–P shell at 2.37 Å (coordination number = 0.9), a Ga–Ga shell at 3.85 Å (CN = 1.1), and a second Ga–P contribution at 4.56 Å (CN = 1.5). These bond distances are consistent with those in bulk GaP. The small coordination numbers derived from the fit and the absence of any additional GaP shells indicate the formation of clusters with a size between 10 and 12 Å. Further EXAFS and X-ray diffraction experiments are in progress to better elucidate the structural nature of the species which are formed.

The results thus far indicate that we are able to synthesize small clusters of GaP within the pores of a zeolite and that we can change the optical properties by varying the synthetic conditions. The NMR results confirm the postulated chemistry and the suitability of this technique to monitor the transformation of microdisperse GaP during the synthesis. In conjunction with the UV–vis results and by analogy with the ^{77}Se NMR studies of colloidal CdSe[19] we interpret the chemical shift trend observed in Figure 2 in terms of a systematic change in the average excitation energy of Ramsey's paramagnetic chemical shielding contribution as a result of size quantization.[20] We therefore propose that, with proper calibration, solid-state NMR chemical shifts can be used to measure the average cluster sizes of such systems.

Acknowledgment. G.D.S. and J.E.M. acknowledge the Office of Naval Research and the duPont company for their financial support. Funding by the UCSB Academic Senate (to H.E.) is also gratefully acknowledged. The operational funds for NSLS beamline X-11A are supported by DOE Grant No. DE-AS0580ER10742.

Supplementary Material Available: Figure showing an EXAFS spectrum of sample GaP/NaY 300 °C, magnitude and imaginary parts, Fourier transformed with k^3 between 2.8 and 13.1 $Å^{-1}$ (1 page). Ordering information is given on any current masthead page.

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(13) J.C.P.D.S. Card Numbers: 12 191 and 32 397.

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(17) EXAFS measurements were performed at the National Synchrotron Lightsource at Brookhaven National Laboratories on beamline X-11A with a stored electron energy of 2.5 GeV and ring currents between 100 and 130 mA. Data were collected at the Ga K-edge of 10 367 eV at ~100 K in transmission mode using a Si(111) channel-cut monochromator. Harmonic contributions were eliminated by detuning the maximum signal ~30%. Samples and reference compounds were embedded in a 1:1 mixture of icosane/octadecane and stored under nitrogen. Thickness of materials was calculated to give a total absorption $\mu_x < 2.5$, and data were collected up to 1000 eV over the absorption edge with two scans/sample. Analyses were carried out according to published procedures. (See: Lee, P. A.; Citrin, P. H.; Eisenberger, P.; Kincaid, P. M. *Rev. Med. Phys.* **1981**, *53*, 769.)

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Trapping of the Low-Valent Nitrene Complex $(CO)_5W{=}NPh$ with PPh_3. Formation of the Phenylnitrene Transfer Product $PhN{=}PPh_3$

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We recently reported the formation of the zwitterion $(CO)_5WNPhNPhC(OCH_3)CH_3$ (**1**) as an isolable intermediate in the metathesis reaction of $(CO)_5W{=}C(OCH_3)CH_3$ with photochemically generated *cis*-azobenzene.[1] Decomposition of **1** under thermal or photochemical conditions resulted in formation of the organic metathesis product $PhN{=}C(OCH_3)CH_3$[2] and other compounds apparently derived from the low-valent tungsten nitrene complex $(CO)_5W{=}NPh$ (**2**).[3a] Many imido complexes have been reported in the literature.[4,5] However, although species such as the low-valent doubly bonded **2** have been invoked in reaction mechanisms,[3] they have not been directly observed. We now report that thermal decomposition of **1** in the presence of PPh_3 results in the trapping of nitrene complex **2** as its phosphine

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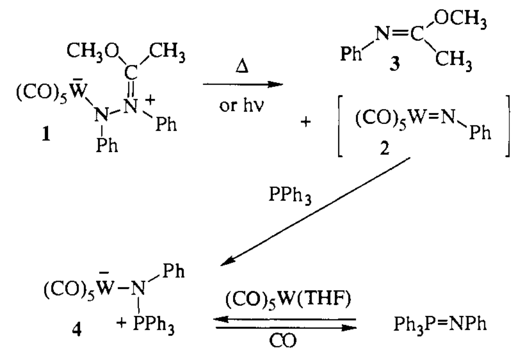
Scheme I



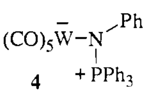
stabilized adduct (CO)$_5$W(Ph$_3$PNPh) (**4**).

In the absence of PPh$_3$, thermal or photochemical decomposition of zwitterion **1** in C$_6$D$_6$ gives rise to product mixtures that contain imidate **3** and a variety of nitrene-derived compounds that includes *trans*-azobenzene. In the presence of excess PPh$_3$, the major inorganic product is (CO)$_5$W(Ph$_3$PNPh).[6] The major organic product is imidate **3**. The properties of **4** are identical with those of an authentic sample prepared from (CO)$_5$W(THF)[8] and Ph$_3$P=NPh.[7]

Kinetics experiments demonstrate that the rate for disappearance of **1** is first order in [**1**] but shows no dependence on PPh$_3$ concentration.[9] These results are consistent with formation of complex **4** via rate-determining cleavage to (CO)$_5$W=NPh and imidate followed by trapping of **2** by the phosphine (Scheme I). The lack of [PPh$_3$] dependence allows direct attack of PPh$_3$ on zwitterion **1** to be ruled out. The intermediacy of free phenylnitrene in the disappearance of **1** has been excluded by carrying out the decomposition reaction in neat diethylamine. Although free phenylnitrene is known to form 2-(diethylamino)-3*H*-azepine upon reaction with Et$_2$NH,[10] the azepine could not be detected in the reaction mixtures.

Decomposition of zwitterion **1** gives rise to 2 equiv of NPh fragments. Under photochemical conditions these can all be accounted for in the reaction products. ^{1}H NMR of the reaction mixtures shows the yield of complex **4** from the primary photoprocess to be >95% (quantitative within experimental error). Complex **4** is stable to photolysis. The material balance of NPh's is completed by the organic products. Initially, the organic product is imidate **3**. Control experiments indicate imidate **3** undergoes reaction with PPh$_3$ to yield free Ph$_3$P=NPh.[11] If the light is Pyrex-filtered ($\lambda > 300$ nm), free phosphinimine reacts photochemically with W(CO)$_6$ that is present in **1** to give **4**, and the final yields are 131% **4** and 59% **3**. If longer wavelength light ($\lambda > 400$ nm) is used, W(CO)$_6$ does not photolyze, and the yield of **4** is exactly 100%. We interpret these results to mean that the source of excess **4** in the photochemical reaction is free Ph$_3$P=NPh and is not related to the trapping of nitrene **2** to give **4**.

Unstable metal–ligand multiply bonded complexes such as metal silylenes have been isolated as adducts in which a solvent lone pair stabilizes the reactive multiple bond.[12] The spectra of complex **4** suggest that this molecule should be viewed similarly. Its properties are more consistent with an ylide-type adduct of PPh$_3$ to nitrene **2** than with a coordinated phosphinimine that retains a phosphorus–nitrogen double bond. The values of ν_{CO} for the (CO)$_5$W unit of **4**[6] strongly resemble those for zwitterion **1** (2061, 1913, 1860 cm^{-1}) and carbene ylide **5**[13] (2051, 1950, 1909, 1871 cm^{-1}) suggesting similar amounts of electron density at the metal



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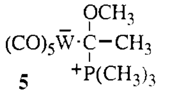

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in each case. Upon coordination of Ph$_3$P=NPh to (CO)$_5$W, the P=N stretch at 1344 cm^{-1}[14] disappears and is replaced by a strong band at 803 cm^{-1}. Weak bonding between phosphorus and nitrogen is suggested by the fact that this frequency is significantly lower than the 930 cm^{-1} reported for the bridging phosphinimine complex Mo$_2$(CO)$_6$(μ-Ph$_3$PNH)$_3$ in which the phosphinimine ligands have a zwitterionic structure.[15] For coordinated phosphinimines in which the double bond is retained, $\nu_{P=N}$ is found in the range 1100–1250 cm^{-1}.[16] An additional indication of P–N single bonding is found in the ^{31}P NMR shift of **4** (31.2 ppm) which lies in the 30–35 ppm range reported for Ph$_3$P$^+$–NHR compounds.[17]

Formation of adduct **4** upon addition of PPh$_3$ to nitrene complex **2** could be indicative of an interesting parallel between the chemistry of the low-valent nitrene complex and that of the related Fischer carbene (CO)$_5$W=C(OCH$_3$)CH$_3$ (**6**). Fischer carbenes are quite sensitive to nucleophilic attack at the carbene carbon,[18] as evidenced by the formation of ylide **5** from **6** and PMe$_3$.[13] The attack of nucleophilic PPh$_3$ on nitrene complex **2** and the similarity of adducts **5** and **4** suggests that the chemistry of low-valent metal nitrenes with nucleophilic species could be related to the chemistry of the Fischer carbenes.

It is also worth noting that this reaction is an example of arylnitrene transfer from the low-valent nitrene complex **2**. Free Ph$_3$P=NPh can be released from complex **4** by bubbling CO through the reaction mixtures (Scheme I). Formation of the free phosphinimine completes transfer of the NPh fragment from **2** to PPh$_3$. Although several cases of transfer of NX (X = tosyl, COCF$_3$) fragments from metal imido complexes to organic molecules have been reported,[19] this reaction is one of the first examples of transfer of a single aryl- or alkylnitrene moiety from a metal complex.[20,21] Additional nitrene-transfer reactions are under investigation.

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(6) ^{1}H NMR (CDCl$_3$) δ 6.84 (t, 1 H), 6.92 (d, 2 H), 7.07 (t, 2 H), 7.48 (m, 6 H), 7.61 (m, 9 H); ^{31}P NMR (C$_6$D$_6$) δ 31.2; IR (KBr) ν_{CO} 2060, 1966, 1909, 1866; $\nu_{P\text{-}N}$ 803 cm^{-1}; MS (FAB) M$^+$ 677 (isotope abundance for the molecular ion matched simulation for C$_{29}$H$_{20}$NO$_5$PW).

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(9) Kinetic data were obtained by monitoring the disappearance of the 440-nm absorption band of zwitterion **1** by UV. The initial concentrations of **1** were ca. 4 × 10^{-4} M, and the amount of PPh$_3$ ranged from 0 to 30 equiv. A new stock solution of **1** was prepared every three runs, leading to slight variations in the initial concentration of **1**. Additional kinetics experiments were performed by following the disappearance of the 1.64 and 2.45 ppm signals of **1** by ^{1}H NMR in the presence of 0–10 equiv of PPh$_3$.

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(11) Azobenzene, a product of the decomposition of **1** in the absence of PPh$_3$, also reacts slowly with PPh$_3$ to give free PhN=PPh$_3$. However, in the presence of PPh$_3$, the formation of azobenzene is suppressed.

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Acknowledgment. Funding was provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. 1, 118070-62-5; **3**, 55504-04-6; **4**, 122444-51-3; $Ph_3P{=}NPh$, 2325-27-1; $(CO)_5W(THF)$, 36477-75-5.

A Common Heterolytic Mechanism for Reactions of Iodosobenzenes, Peracids, Hydroperoxides, and Hydrogen Peroxide with Iron(III) Porphyrins

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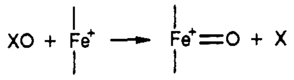
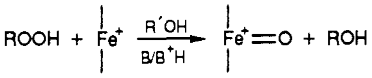
Received March 27, 1989

The isolation of high-valent iron porphyrin intermediates,[1,2] kinetic studies,[3] and product isolations[3,4] have demonstrated that the principal reaction of iron(III) porphyrins with iodosobenzenes and peracids is a two-electron oxidation to the iron(IV) radical cation (oxene) reaction 1.



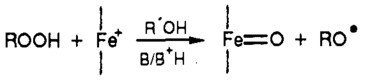
$$\mathrm{XO} + \mathrm{Fe}^{+} \longrightarrow \mathrm{Fe}^{+}{=}\mathrm{O} + \mathrm{X} \tag{1}$$

We find that the rate effects in reaction 2 upon changes in solvent acidity ($pK_{\mathrm{R'OH}}$),[5b] buffer concentration[3,5b] (R'OD vs R'OH),[6b] and leaving group acidity (pK_{ROH}) are essentially the same for peracids and hydroperoxides.[6] These findings are consistent with similarities in mechanisms and therefore heterolytic cleavage.



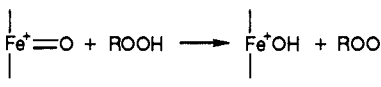
$$\mathrm{ROOH} + \mathrm{Fe}^{+} \xrightarrow[\mathrm{B/B^{+}H}]{\mathrm{R'OH}} \mathrm{Fe}^{+}{=}\mathrm{O} + \mathrm{ROH} \tag{2}$$

Bruice et al.[7] have found little effect of either buffer concentration (in water) or leaving group acidity and have concluded that hydroperoxides and hydrogen peroxide undergo homolytic cleavage under these conditions.



$$\mathrm{ROOH} + \mathrm{Fe}^{+} \xrightarrow[\mathrm{B/B^{+}H}]{\mathrm{R'OH}} \mathrm{Fe}{=}\mathrm{O} + \mathrm{RO}^{\bullet} \tag{3}$$

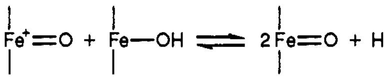
The reasons for these different results are not clear. However, available kinetic data do not provide conclusive evidence for mechanisms of cleavage. Evidence for the presence of alkoxy radicals and Fe=O, along with failures to observe hemin-catalyzed epoxidation, has also been interpreted in terms of homolytic cleavage (reaction 3).[8] However, alkoxy radicals are obtained through reactions of the oxene ($\mathrm{Fe^{+}{=}O}$) with hydroperoxides. This and other reactions produce Fe=O.



$$\mathrm{Fe}^{+}{=}\mathrm{O} + \mathrm{ROOH} \longrightarrow \mathrm{Fe}^{+}\mathrm{OH} + \mathrm{ROO}^{\bullet} \tag{4}$$

$$2\mathrm{ROO}^{\bullet} \longrightarrow 2\mathrm{RO}^{\bullet} + \mathrm{O_2} \tag{5}$$

$$\mathrm{RO}^{\bullet} \longrightarrow \mathrm{R'}^{\bullet} + \mathrm{R''_2CO} \tag{6}$$

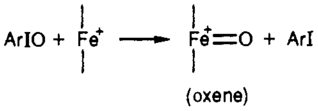


$$\mathrm{Fe}^{+}{=}\mathrm{O} + \mathrm{Fe{-}OH} \rightleftharpoons 2\,\mathrm{Fe}{=}\mathrm{O} + \mathrm{H}^{+} \tag{7}$$

Furthermore we have obtained good yields of epoxide using hydroperoxides at low concentrations where reactions 4 and 5 are minimized.

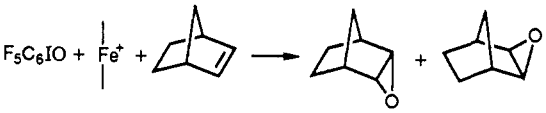
It is clear that the Fe(IV) and Fe(III) species are readily obtainable by electron-transfer reactions such as 4 or 7. However, production of the oxene $\mathrm{Fe^{+}{=}O}$ through the endothermic reversal of such electron transfers is highly unlikely. Therefore the identification of products exclusively derived from the oxene should serve as an indication of heterolytic cleavage in the first step.

We submit the following experiments as demonstrations of the presence of $\mathrm{Fe^{+}{=}O}$, assuming that the isolation of the oxene from reaction of iron(III) porphyrins with iodosobenzene[1] unequivocally establishes reaction 8.



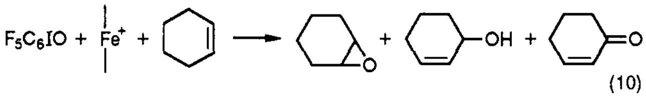
$$\underset{}{\mathrm{ArIO}} + \mathrm{Fe}^{+} \longrightarrow \underset{\text{(oxene)}}{\mathrm{Fe}^{+}{=}\mathrm{O}} + \mathrm{ArI} \tag{8}$$

We have found that the epoxidation of norbornene by use of the oxene from reaction 8 produces a mixture of products which is at once unlike that from any other epoxidation process and specific for the particular metalloporphyrin catalyst.[11] In particular, this is the only reaction which gives any appreciable endo product.



(9)

Among many other reactions which display product compositions specific for the *oxene* of a particular metalloporphyrin are the opening of hexamethyldewarbenzene[13] and epoxidation of cyclohexene.[12]



(10)

Thus, for example, with the catalyst iron(III) tetrakis(2,6-dichlorophenyl)porphyrin chloride (TDCPPFeCl) the product contains only 4–5% of alcohol or ketone.[12a] Other catalysts give different ratios, just as in the case of norbornene epoxidation.[12a,b] It is known that peroxy radicals give principally hydrogen abstraction from cyclohexene.[14]

We have therefore adopted known methods of producing alternatively the oxene, the oxo species, and peroxy radicals in the presence of these alkenes and compared the product compositions with those obtained from reactions of the same iron porphyrin

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(9) For example, although the "2,4,6-tri-*tert*-butylphenol trap" method,[3,10] for following the rates of reaction of hemins with ROOH, affords accurate kinetics with peracids, it often leads to inconsistent kinetic constants with hydroperoxides, especially in the absence of proximal imidazole or buffers.

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