electrochemical methods, to furnish 38–52% yields of a blue-green intermediate **6**. The optical spectrum [λ_{max} 303 (ϵ 15 300), 380 (45 300), 646 (inf; 8000), 704 nm (9300)] was almost identical with that of the previous intermediate; the greatly simplified proton NMR spectrum showed three methine peaks (6.26, 5.35, 5.00 ppm), two NHs (13.84, 13.22 ppm), nine methyl resonances (2.03–1.77, 1.40 ppm), and an AB quartet [2.98, 2.52 ppm (each d, J_{AB} = 15.3 Hz)] (Figure 3). Insert A in Figure 3 shows the methine protons of the intermediate from the unsymmetrical *a,c*-biladiene **3** and demonstrates the presence of unequal amounts of two isomeric structures depending upon which of the two terminal methyls in **3** forms the macrocyclic bridging carbon. Irradiation of the methyl singlet in **6** at 1.40 ppm gave a nuclear Overhauser enhancement at the upfield doublet (2.52 ppm) and also at a methyl resonance (1.77 ppm). On the basis of this evidence, we propose structure **6** for the intermediate, with proton NMR assignments as annotated. High resolution FAB mass spectrometry[16] confirmed the expected molecular weight.

The mechanism shown in Scheme I is proposed for the decamethyl-*a,c*-biladiene **5** electrocyclization; following deprotonation[17] the conjugated tetrapyrrole suffers two-electron oxidation and macrocyclization to give the intermediate **6**. Nucleophilic attack,[18] presumably by the electrolyte, causes formation of the phlorin **7** which undergoes spontaneous oxidation[19] to give porphyrin. Thin-layer spectroelectrochemistry (not shown) indicates that the order of the nucleophilic attack/oxidation steps may be reversed in the electrochemical conversion of **6** into porphyrin.

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(16) Mass spectra were measured on a VG Analytical ZAB-HS-2F instrument by using fast atom bombardment and a tetraethylene glycol matrix. Compound **6**, found 438.2787. Calcd for $C_{29}H_{34}N_4$ 438.2784.

(17) The precise order of deprotonation and oxidation steps cannot be defined at this point in time.

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Para Hydrogen Induced Polarization in Hydrogenation Reactions Catalyzed by Ruthenium–Phosphine Complexes

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Para hydrogen induced polarization (PHIP) leading to enhanced ^{1}H NMR absorptions and emissions has recently been reported for hydrogenation and hydrogen addition reactions.[1,2] The basis of PHIP, which was presented initially by Weitekamp, involves pairwise transfer of para-enriched H_2 to substrate.[1,3] If this happens fast relative to proton relaxation, then the transferred protons will reflect initially the nuclear spin populations of the starting dihydrogen and give rise to polarized or enhanced transitions for the product resonances. The occurrence of PHIP is thus definitive evidence for pairwise hydrogen transfers. In this paper, we describe studies including the observation of PHIP for hydrogenation reactions catalyzed by ruthenium phosphine complexes.

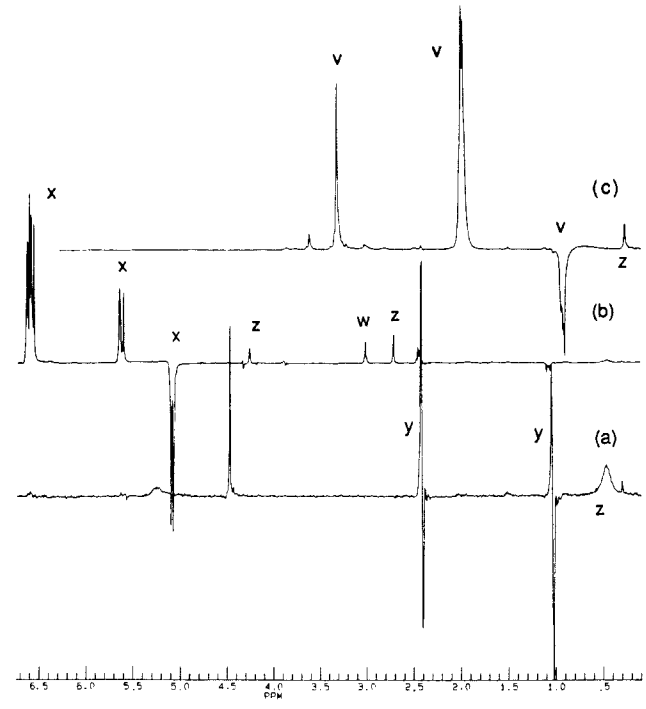

Figure 1. PHIP in the ^{1}H NMR spectra of $RuH_4(PPh_3)_3$-catalyzed hydrogenations in C_6D_6 under ~3 atm para-enriched H_2 at room temperature for (a) styrene-d_8, (b) phenylacetylene, and (c) methyl acrylate: v = $CH_3CH_2COOCH_3$, w = PhC≡CH, x = PhCH=CH_2, y = $C_6D_5CDHCHD_2$, and z = solvent impurities. The resonance at δ 4.45 ppm corresponds to H_2 (while para H_2 is NMR silent, ortho H_2 is not).

The tetrahydride species $RuH_4(PPh_3)_3$ is a known hydrogenation catalyst which readily exchanges H_2 and has recently been shown to be a dihydrogen complex.[4] When $RuH_4(PPh_3)_3$ is used to catalyze hydrogenation of styrene-d_8 in benzene-d_6 under 2–3 atm of para-enriched hydrogen, a strong absorption/emission pattern characteristic of PHIP is seen in the ^{1}H resonances of the $C_6D_5CHDCHD_2$ product as shown in Figure 1a.[5] The polarization is observable for up to 2 min and decays exponentially with a first-order rate constant of ~0.044 s^{-1}. During this period the broad hydride resonance of $RuH_4(PPh_3)_3$ at δ −7.52 ppm is observable and remains unchanged. Hydrogenation of C_2D_4 using $RuH_4(PPh_3)_3$ under these conditions also yields para hydrogen induced polarization in the CHD_2CHD_2 product identical with that reported previously.[2]

When methyl acrylate and the alkynes PhC≡CH, *t*-BuC≡CH, and $MeOCH_2C$≡CH are employed as the substrate in these hydrogenations, the nature of the polarization changes dramatically. This is shown for PhC≡CH and CH_2=CHCOOMe in Figure 1 (parts b and c, respectively), in which the initial product resonances (styrene in part b and methyl propionate in part c

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(3) (a) Weitekamp suggests the acronym PASADENA for "parahydrogen and synthesis allow dynamically enhanced nuclear alignment". We prefer the shorter, less geographically specific PHIP. (b) The term "pairwise" means that both transferred hydrogen atoms originate from the same H_2 molecule. Pairwise transfer need not be concerted or synchronous; for PHIP it must be short relative to loss of spin correlation (relaxation) and requires that the protons maintain coupling throughout the hydrogenation process.

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(5) These experiments were carried out in 5-mm NMR tubes equipped with a Teflon valve. Solvents (0.5 mL) and substrates (10 μL) were vacuum transfered to an NMR tube containing ~3 mg of the ruthenium complex. The tubes were stored at −196 °C. Para enriched hydrogen (prepared by storing H_2 over a Fe_2O_3/silica/C catalyst at −196 °C for 3–4 h) was added just prior to thawing the tube and insertion into the magnetic field.

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(Figure 1)) exhibit "net" polarization with individual resonances entirely in emission or enhanced absorption. The basis for this change in polarization is a magnetic field dependent effect recently discussed by Weitekemp[1c] which arises when transfer of para H_2 to substrate occurs outside the field of the NMR spectrometer followed shortly thereafter by transport into the probe. Since hydrogenation reactions involving styrene-d_8, methyl acrylate, and the alkyne substrates are performed under virtually identical conditions with sample placement into the NMR probe immediately after thawing of the frozen C_6D_6 reaction solutions, the difference in polarization reflects the fact that methyl acrylate and alkynes hydrogenate more rapidly with $RuH_4(PPh_3)_3$ than does styrene.

When the $RuH_4(PPh_3)_3$-catalyzed hydrogenation of styrene-d_8 using para-enriched H_2 is carried out in halogenated solvents ($CDCl_3$ or CD_2Cl_2), the intensity of PHIP is greatly diminished. Concurrently, the solution changes from colorless to purple-red, and the hydride resonance of $RuHCl(PPh_3)_3$ is observed to grow in. Thus in halogenated solvents, the nature of the catalyst system changes to that of $RuHCl(PPh_3)_3$.

The complex $RuHCl(PPh_3)_3$ is purportedly a very active homogeneous hydrogenation catalyst,[6-8] and while its mechanism of catalysis is not established definitively, it is thought to function via phosphine loss, olefin coordination, insertion into Ru–H, and hydrogenolysis (H_2 addition and alkane reductive elimination).[7] In this mechanism, the two hydrogen atoms transferred to substrate originate on different H_2 molecules. Therefore, catalysis by $RuHCl(PPH_3)_3$ would be anticipated to produce no PHIP. However, when $RuHCl(PPh_3)_3$ is used to catalyze hydrogenation of styrene-d_8 in $CDCl_3$ or CD_2Cl_2 under para H_2, A/E polarization of the $C_6D_5CHDCHD_2$ resonances occurs similar to, but much weaker than, that seen using $RuH_4(PPh_3)_3$.[9] The polarization decays within 90 s but can be regenerated by evacuation and addition of more para-enriched H_2. This cycle can be repeated for up to 15 min of total reaction time. With ethylene-d_4 as substrate, polarization of the CHD_2CHD_2 product resonances is also seen. The occurrence of PHIP in these reactions establishes that for at least some fraction of product, hydrogenation takes place with pairwise transfer of H_2 to substrate. In these experiments, the hydride resonance of $RuHCl(PPh_3)_3$ exhibits no evidence of polarization, unlike the case using $RhCl(PPh_3)_3$.[1b]

To probe further the mechanism of hydrogenation using $RuHCl(PPh_3)_3$, the hydride resonance of this complex was examined under different reaction conditions as shown in Figure 2. Under N_2, $RuHCl(PPh_3)_3$ exhibits a hydride resonance which is a sharp quartet in either CD_2Cl_2 (δ −18.22; J_{PH} = 26 Hz) or $CDCl_3$ (δ −17.85; J_{PH} = 26 Hz). At low temperature this resonance shifts to −18.55 ppm in CD_2Cl_2 and appears as a doublet of triplets with couplings of 34 and 22 Hz. Under H_2 at 298 K, the hydride resonance of $RuHCl(PPh_3)_3$ appears broad and without coupling, while under D_2 (~3 atm), it disappears within seconds, indicative of facile exchange.

When examined under hydrogenation catalysis conditions, the hydride resonance shows strikingly different behavior. In the presence of styrene in CD_2Cl_2 under ~3 atm H_2 or D_2, the hydride resonance appears as a quartet similar to that of the complex under

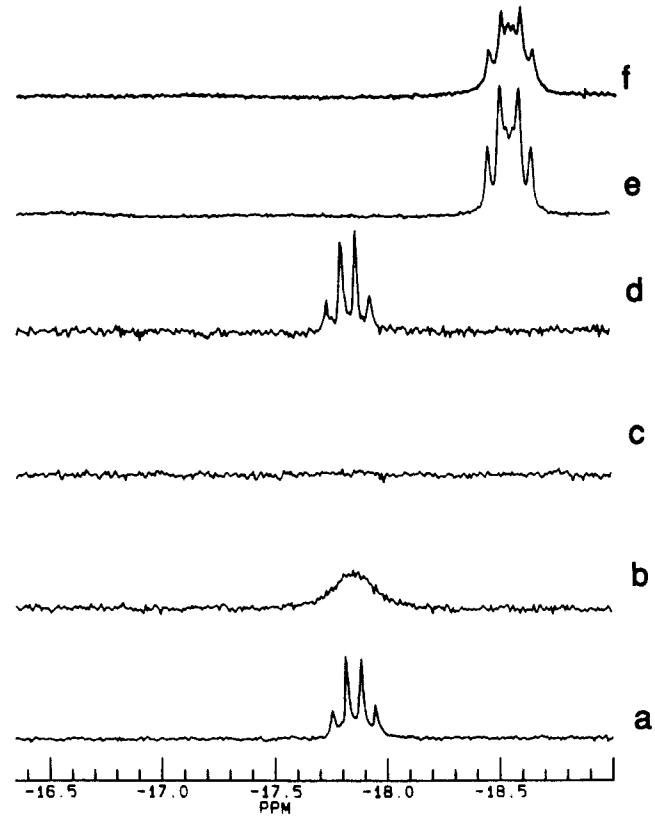

Figure 2. Hydride resonances of $RuHCl(PPh_3)_3$: (a) under N_2 in $CDCl_3$, (b) under ~3 atm H_2 in $CDCl_3$, (c) under ~3 atm D_2 in $CDCl_3$, (d) during the hydrogenation of styrene-d_8 under ~3 atm para-enriched H_2 in $CDCl_3$, (e) in CD_2Cl_2 at −66 °C, and (f) in CD_2Cl_2 containing 27 mM styrene-d_8 at −66 °C.

N_2 (Figure 2d). Moreover, in the experiment using D_2 there is no reduction in hydride intensity for up to 2 h during which several turnovers of ethylbenzene-d_2 are noted. It is only *after* styrene has been consumed that loss of the hydride resonance is observed. It thus appears that substrate suppresses hydride/H_2 (or D_2) exchange seen under H_2 (or D_2) alone. Suppression of exchange, however, does not occur by formation of a coordinatively saturated $RuHCl(PPh_3)_3$(olefin) complex. The ^1H NMR spectrum of $RuHCl(PPh_3)_3$ + substrate (styrene-d_8, methyl acrylate, or 1-hexene) in CD_2Cl_2 at ~ −66 °C shows the same hydride resonance as seen in the absence of substrate under N_2 (cf., Figure 2, parts e and f, for styrene-d_8). While these results—i.e., substrate suppresses hydride/H_2 exchange and substrate does not bind to $RuHCl(PPh_3)_3$—appear at first contradictory, they indicate that $RuHCl(PPh_3)_3$ is not the active hydrogenation catalyst nor is it connected to the active catalyst(s) by equilibria rapid on the NMR time scale.

A species capable of hydrogenation by pairwise hydrogen transfer and therefore of yielding PHIP is $RuH_2(PPh_3)_3$ which forms readily from $RuH_4(PPh_3)_3$ and can be generated by dehydrohalogenation from $RuHCl(PPh_3)_3$. This latter pathway has in fact been proposed previously,[10] and the species $RuH_2(PPh_3)_3$ has been invoked as an intermediate in $RuH_4(PPh_3)_3$-catalyzed hydrogenations.[3b,e] We therefore suggest that even in halogenated solvents, if PHIP is observed, a small and undetectable amount of $RuH_2(PPh_3)_3$ is present as an active catalyst. The qualitative differences in the magnitudes of PHIP, large for $RuH_4(PPh_3)_3$ catalysis in C_6D_6 and weak for $RuHCl(PPh_3)_3$ in halogenated solvents, support this notion. While PHIP establishes a mechanism based on pairwise H_2 transfer, at least one other mechanism for the $RuHCl(PPh_3)_3$ catalyst precursor system exists. When olefins with electron-withdrawing groups such as acrylonitrile and tet-

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(9) $RuHCl(PPh_3)_3$ was synthesized and isolated from $RuCl_2(PPh_3)_3$ + H_2 + Et_3N in refluxing toluene.[6c,8h]

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racyanoethylene are hydrogenated using $RuHCl(PPh_3)_3$, the reaction solutions change color rapidly, the Ru-H resonance disappears within 15 s, and hydrogenation is observed after 15 min, but no PHIP is detected.

While the present study does not resolve the complexities of the $RuHCl(PPh_3)_3$ catalyst system, it does show that a pairwise hydrogen transfer pathway exists, most probably via $RuH_2(PPh_3)_3$. In addition, the change in polarization with change in substrate using $RuH_4(PPh_3)_3$ in C_6D_6 suggests that PHIP may be useful in establishing relative rates. This aspect is under continuing study.

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Registry No. $RuH_4(PPh_3)_3$, 31275-06-6; $RuHCl(PPh_3)_3$, 55102-19-7; ethylene-d_4, 683-73-8; styrene-d_8, 19361-62-7; phenylacetylene, 536-74-3; methyl acrylate, 96-33-3.

Anion Radicals of Porphycenes: First ESR and ENDOR Characterization

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It has been established that porphyrinoid systems are essential chromophores in many photochemical and photobiological processes. This includes a new class of porphyrin isomers, named porphycenes (Figure 1), which have been recently synthesized and characterized.[1,2] Investigations of their role in photophysical and photochemical processes have been started.[3-5] The difference in molecular design and symmetry between porphyrins and porphycenes leads to different spectroscopic behavior as found in recent studies on the photoexcited singlet and triplet states.[3-5] The doublet state radical ions of porphycenes should also be of considerable interest in comparison with those of analogous porphyrins

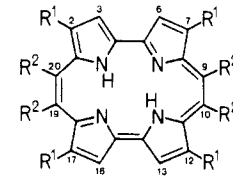

Figure 1. Porphycenes; D_{2h} symmetry on the ESR and NMR time scale: H_2PC1 (parent compound), $R_1 = R_2 = H$; H_2PC2, $R_1 = C_3H_7$, $R_2 = H$; H_2PC3, $R_1 = H$, $R_2 = C_3H_7$; PdPC2, the two central H's are replaced by Pd, $R_1 = C_3H_7$, $R_2 = H$.

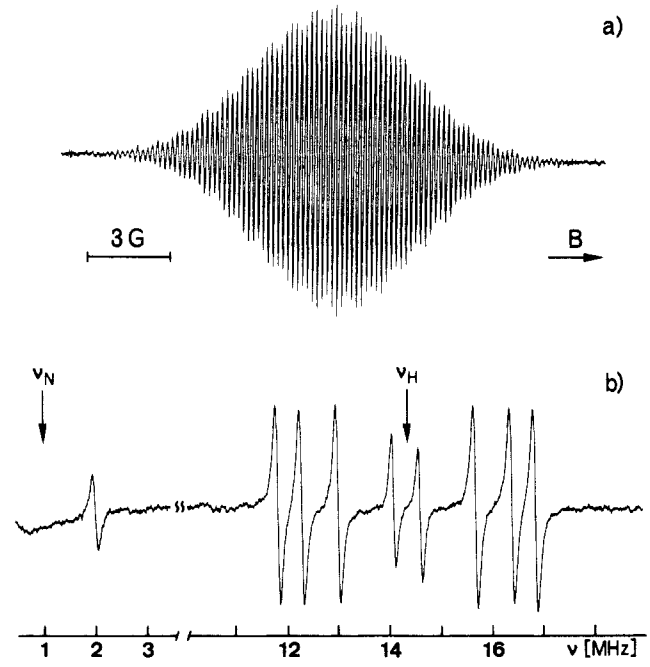

Figure 2. (a) ESR spectrum of $H_2PC1^{\bullet-}$ in THF at 240 K. (b) ^{14}N- and H-ENDOR spectrum of $H_2PC1^{\bullet-}$ in THF at 193 K; experimental conditions: see note b of Table I.

in view of anticipated relationships between electronic structure and reactivity of these compounds.

In this communication we report on liquid phase ESR, electron nuclear double resonance (ENDOR), and electron nuclear nuclear triple resonance (TRIPLE) measurements of isotropic interaction parameters such as g factor and H- and ^{14}N-hyperfine coupling constants (hfc's) of the unsubstituted free-base porphycene (H_2PC1) anion radical. An extended study on the other porphycenes shown in Figure 1 will be presented in a forthcoming publication.

The anion radicals of the porphycenes were prepared chemically by reduction with sodium metal under high vacuum conditions.[6] Tetrahydrofuran (THF) was used as a solvent, and the porphycene concentration was about $5 \cdot 10^{-4}$ M. The radicals were shown to be stable over at least several weeks. The anion radicals of H_2PC1 were also generated by potentiostatically controlled electrolysis in THF by using tetra-*n*-butylammonium perchlorate (TBAP) as the supporting electrolyte.[7] In this case the porphycene concentration was 10^{-3} M. Optical spectra of the neutral and anion radical porphycenes were measured in a 3-mm flat cell.

The ENDOR and TRIPLE experiments were performed with a self-built computer-controlled X-band spectrometer,[8,9] while for ESR a commerical spectrometer (Bruker ER 200D) was used. The UV-vis spectra of H_2PC1 were recorded with a Cary-219 spectrophotometer.

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