to a dry methylene chloride solution of **3** results in appearance of a species with absorption maxima at 409 (ϵ 1.80 × 10^5 M^{-1} cm^{-1}), 522, and 558 nm (Figure 1d). This new species presumably is $Co^{III}(ROH)_2OEPClO_4^-$ [13] as its optical characteristics are identical with those of typical Co^{III} porphyrin spectra;[14] i.e., the Soret peak is red-shifted by ~20 nm compared with that of **1**, and the relative intensities of the visible bands are decreased. The effect of "wet" solvent is reversible: if the solvent of the 409-nm species is evaporated to dryness and the residue is redissolved in dry CH_2Cl_2, the 376-nm species reappears. It seems that an authentic $Co^{III}OEPClO_4^-$ species, stripped of other coordinating solvents or ligands, does not exist.

3 is ESR silent.[15a,16] This indicates that the unpaired electron of low-spin Co^{II} in the d_{z^2} orbital of **3** is spin-coupled with the porphyrin unpaired electron.[17] The magnetic susceptibility of **3**[15b] at 50 K indicates a magnetic moment of 0.215 μ_B, most of which is likely to arise from contaminants,[16] and supports the quenching of the unpaired spins in **3**. This value may be contrasted with our measured values of 2.53 μ_B for **1** and 1.84 μ_B for **4** at this temperature.

Figure 2 shows the resonance Raman (RR) spectra of species **1**–**4** excited at 363.8 nm.[15c] Scattering from **1**, Figure 2a, is typical of Soret excited metalloporphyrin spectra and is dominated by totally symmetric vibrational modes.[18] The spectrum of **2**, Figure 2b, shows the effects of oxidation at the metal center. The high-frequency bands (above 1400 cm^{-1}) remain essentially unchanged in frequency, indicating little change in the core size of the ring.[19] Interestingly, ν_2,[20] occurring at 1599 cm^{-1} in **1**, is barely visible in **2** at 363.8 nm but is seen at 1596 cm^{-1} in spectra excited at 406.7 nm (not shown). The oxidation-state marker, ν_4, increases from 1379 to 1383 cm^{-1}, reflecting depopulation of porphyrin π^* orbitals caused by oxidation of the metal center.[18b] Except for some changes in the relative intensity of several of vibrational bands, the Raman spectra of **3** and **4** are essentially identical and radically different from RR spectra of **1** and **2** with unoxidized porphyrin rings. The most intense band in the RR spectra of both the π-cation species, Figure 2c,d, occurs at ~1362 cm^{-1} and is tentatively assigned to ν_4. The 20-cm^{-1} difference between this value and the value of ν_4 for **1** and **2** is presumably consistent with depopulation of the porpyrin a_{2u} π orbital.[15c,21] The IR spectra of **3** and **4**[15d] display bands at 1576 ± 5 and 1554 ± 5 cm^{-1}, respectively, diagnostic of porphyrin π-cation radicals.[22] The similarity between the vibrational spectra of $Co^{II}OEP^{+\bullet}ClO_4^-$ and of the authentic π-cation radical $Co^{III}OEP^{+\bullet}2ClO_4^-$ provides strong evidence that the former is also a π-cation radical.

The $AgClO_4/CH_2Cl_2$ oxidation method appears to be applicable in the preparation of other metalloporphyrin π-cation radicals such as $ZnTPP^{+\bullet}ClO_4^-$ (TPP = tetraphenylporphyrin), $ZnOEP^{+\bullet}ClO_4^-$, $CuOEP^{+\bullet}ClO_4^-$, and OEP itself. However, it fails to react with $Co^{II}TPP$, or $Cu^{II}TPP$, to give the corresponding divalent metal porphyrin radical. Assuming that this is due to the difference in the oxidation potential between OEP and TPP, the oxidizing power of the $AgClO_4/CH_2Cl_2$ is limited to ~+0.9 V (SCE).

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(12) (a) Electrochemical oxidation of $Co^{II}OEP$ carried out in CH_2Cl_2 and CH_3CN yields very different optical spectra; in CH_2Cl_2 it has features similar to that of **3** (Fujita, E.; Fajer, J., private communication). (b) Setsune et al. recently observed the 376-nm species but no assignment was made: Setsune, J.-i.; Ikeda, M.; Kishimoto, Y.; Kitao, T. *J. Am. Chem. Soc.* **1986**, *108*, 1309. (c) Sholz et al. have also suggested that oxidation of $Co^{II}TPP$ leads to a π-radical, $Co^{II}TPP^{+\bullet}SbCl_6^-$: Scholz, W. F.; Reed, C. A.; Lee, Y. A.; Scheidt, W. R.; Lang, G. *J. Am. Chem. Soc.* **1982**, *104*, 6791.

(13) Our preliminary optical and RR data (not shown) favor this assignement; nevertheless, the mixed diaxial Co^{III} $(CH_3OH)(ClO_4^-)OEP$ is not yet ruled out.

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(15) (a) The ESR spectra were recorded on a Varian E-4 spectrometr, 298–173 K in CH_2Cl_2. The *g*-value calibration and spin quantitation were performed by using Fremy's salt. (b) Magnetic susceptibility was obtained on an SHE SQUID susceptometer at a field of 5 KG. (c) Raman spectra were measured with a Spex 1877 Triplemate and OMA II electronics (Oertling, W. A.; Babcock, G. T. *J. Am. Chem. Soc.* **1985**, *107*, 6406–6407). Laser emission at 363.8 nm was provided by a Coherent Innova 90-5 Argon Ion Laser. (d) Infrared spectra of compounds **1**, **3**, and **4** were examined as KBr disks by using a Perkin-Elmer 599-IR Spectrophotomer.

(16) A residual ESR signal was often detected in the preparation, amounting to 3–4% of the spin density of **4**; however, it was verified to be due to contaminants for the following reasons. (a) Upon conversion by addition of methanol of **3** into **2**, which is a diamagnetic d^6Co^{III} species, the signal persisted with the same intensity. (b) Increasing the initial ratio of $AgClO_4$ to **1** resulted in a higher signal intensity. (c) The intensity of residual contaminant diminished upon repeated evaporating–redissolving **3** in CH_2Cl_2.

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Nuclear Spin Coherence Transfer in Photochemical Reactions

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The idea of labeling nuclear spin magnetization in the study of chemical reactions dates back to the famous saturation transfer experiment of Forsen and Hoffman.[1] This experiment, designed for chemically exchanging systems, has seen many applications, recently, for instance, in ^{31}P NMR studies of cell metabolism.[2] The two-dimensional analogue of it has been proposed by Jeener et al.[3] (2D exchange spectroscopy). Sagdeev and co-workers have applied radiofrequency labeling techniques to thee study of one-sided chemical reactions.[4] All these experiments involve *z*-magnetization labeling either through saturation or inversion of nuclear spins.

We propose here a two-dimensional experiment, whereby use is made of *xy*-magnetization labeling of nuclear spins. It can be used to study one-sided chemical reactions where the chemical change is brought about in a pulsed fashion, such as in flash photolysis. Comparison with a similar 2D experiment based on *z*-magnetization transfer shows that the coherence transfer experiment is inherently more sensitive. Furthermore a comparison of both may be particularly informative in situations where dephasing occurs (e.g., in the presence of paramagnetic intermediates), since the decay of *xy*-magnetization may be quite different from that of *z*-magnetization. In the latter case the two methods provide complementary information.

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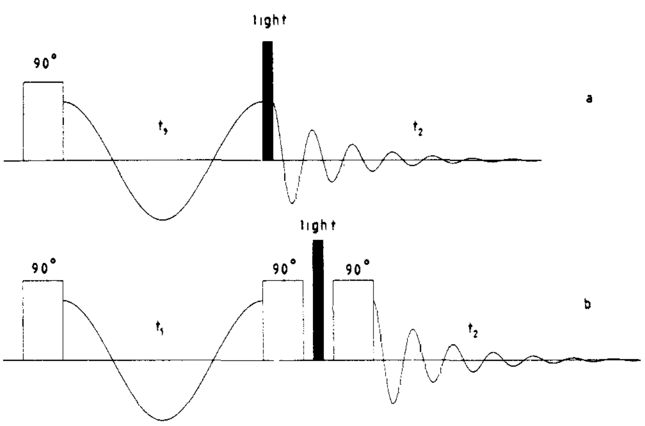


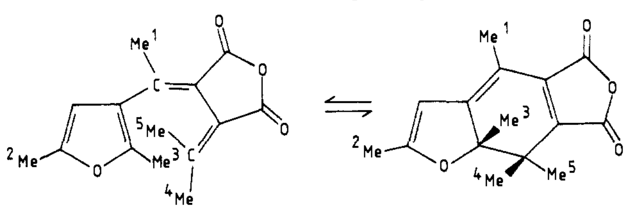
Figure 1. Pulse sequences for nuclear spin coherence transfer (a) and longitudinal magnetization transfer (b) in photochemical reactions. In (a) a 90° rf pulse excites nuclear spins in the precursor molecules, while the laser pulse converts these to products. Free induction decays are recorded in t_2 for various t_1 values as is usual in 2D NMR. Experiment b is very similar to a 2D exchange or 2D NOE experiment, where the "mixing time" is now replaced by a laser pulse.

The pulse sequence for the coherence transfer experiment is extremely simple and involves just one rf pulse and one light pulse as shown in Figure 1a.[5] A related sequence for z-magnetization transfer is shown in Figure 1b.

Consider a simple photochemical reaction of type

$$A \xrightarrow{h\nu} B$$

and let molecule A contain a proton resonating at frequency ω_A, while the same proton in molecule B resonates at ω_B. When a 90° rf pulse is applied on the A spins, xy-magnetization is created, precessing at frequency ω_A. A laser pulse then partially converts A to B and the xy-magnetization now processes at frequency ω_B. After double Fourier transformation of the free induction decays recorded in t_2 the 2D NMR spectrum contains diagonal peaks at frequencies ω_A and ω_B of unreacted A and accumulated B, respectively, and off-diagonal cross peaks at ω_A in the ω_1 dimension and at ω_B in the ω_2 dimension. In the case of more protons a map is then created in which each resonance in the photoproduct is coupled to the corresponding resonance in the starting compound. The z-transfer experiment of Figure 1b is analogous to the 2D exchange or 2D NOE sequence,[3] where a laser pulse is applied in the "mixing time", which can therefore be very short. The second rf pulse now generates chemical shift labeled z-magnetization, which is (partially) transferred to B by the light pulse and converted to observable xy-magnetization by the third rf pulse. Like in two-dimensional CIDNP spectroscopy,[6] these experiments lead to asymmetric 2D spectra, since magnetization transfer takes place from A to B but not vice versa.



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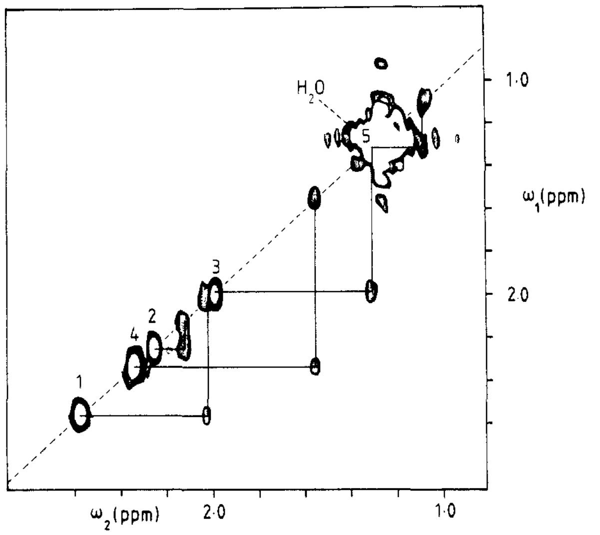

Figure 2. Two-dimensional ^1H NMR spectrum, 360-MHz, of the photoreaction of a 0.2 mM solution of **1** in $CDCl_3$ taken by the coherence transfer sequence of Figure 1a. The methyl group region is shown with numbering for the methyl groups in **1**. Laser pulses, 30 mJ, of 10-ns duration at 351 nm (XeF excimer laser) were used. FID's, 2K, were collected for 64 t_1 values ranging from 10 μs to 40 ms corresponding to a spectral width of 800 Hz; 32 FID's were accumulated for each t_1 value. Before Fourier transformation the data were weighted by a sine bell function in both dimensions; an absolute value mode presentation is shown.

As an illustration we studied the photocyclization of **1**.[7] Irradiation at 351 nm (XeF emission of a Lambda Physik EMG 101 excimer laser) yields **2** with a quantum yield of 0.2.[8] The reaction can be reversed by visible light and can be used as a chemical actinometer.[8c] In order to obtain constant reaction conditions during the full 2D experiment, we used a flow system. The laser light was focused on a flat bottom NMR tube, through which a 0.2 mM solution of **1** in $CDCl_3$ flows at a rate of 1.5 mL/min. Application of the pulse sequence of Figure 1a resulted in the 2D NMR spectrum shown in Figure 2. The methyl group region is shown. The assignment of the methyl groups of **1** (indicated in the figure) was independently obtained from NOE measurements except for the methyl groups 1 and 2, which had been assigned earlier on the basis of selective deuteration.[8b] The cross-peak connectivities immediately yield the methyl group assignments in the product **2**. These, however, do not agree with previously reported assignments of these methyl groups.[8b] Thus, the experiment gives the chemical shift relationships of protons in product and precursor in a very direct way. Alternatively, when the shift assignments are known independently, information on the reaction mechanism is obtained (in the present case the conrotatory nature of the cyclization is confirmed).

The longitudinal magnetization transfer experiment of Figure 1b gave rise to a very similar 2D spectrum (not shown), although the sensitivity was lower. This is because an extra 90° pulse, for instance, along the x-axis selects the y-component of the rotating frame magnetization (contributions from the x-component are suppressed by phase cycling). An advantage of the latter experiment is that higher resolution can be obtained due to phase-sensitive processing of the data, which is not possible for the coherence transfer experiment.

Potentially these experiments could give valuable mechanistic information in reactions in which paramagnetic intermediates occur. Specifically, nuclear spin coherence is expected to dephase due to the interaction with unpaired electrons. This would manifest itself as a decrease in cross-peak intensities dependent on hyperfine coupling and lifetime of the paramagnetic intermediates. Experiments designed to explore these effects are in progress.

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Determination of Metal Particle Size of Highly Dispersed Rh, Ir, and Pt Catalysts by Hydrogen Chemisorption and EXAFS[†]

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Chemisorption of gaseous molecules, especially hydrogen, is extensively used to estimate the dispersion of group VIII (groups 8–10) metal catalysts.[1-7] Chemisorption methods are especially important for highly dispersed catalysts, because of the difficulty to establish their dispersion by other techniques, such as X-ray diffraction or electron microscopy.[1] When hydrogen chemisorption data are used to calculate metal surface areas, often a hydrogen-to-metal stoichiometry of one is assumed. However, H/M values exceeding unity have been obtained for supported Pt,[2,3] Rh,[4,5] and Ir[6,7] systems. In these cases the dispersions cannot be calculated straightforwardly from the chemisorption results, because of the uncertainty in the adsorption stoichiometry. To solve this problem we used the EXAFS technique to determine the average metal–metal coordination number in the metal particles, which is related to the particle size. From the combined results of the chemisorption and EXAFS measurements we have been able to conclude that the high H/M values are due to the fact that more than one hydrogen atom can be attached to a surface metal atom and that the trend in stoichiometry is analogous to that observed in metal polyhydride complexes.

The results of hydrogen chemisorption[8] and EXAFS measurements[9] were compared for several Pt, Rh, and Ir catalysts supported on SiO$_2$, Al$_2$O$_3$, and TiO$_2$[10] (Figure 1). Although a variety of supports and pretreatments was used,[11] their effect on the hydrogen-to-metal stoichiometry appeared to be minor, since straight lines were obtained independent of the support used. A large difference was observed between the three metals and for a fixed coordination number H/Pt < H/Rh < H/Ir was observed.

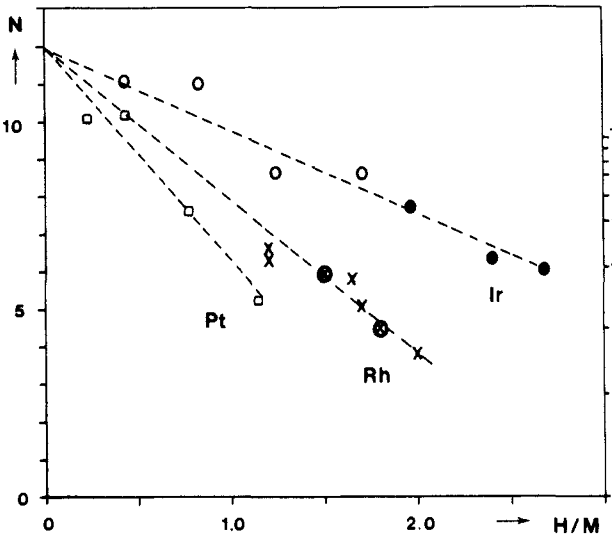

Figure 1. Metal–metal coordination number N, determined with EXAFS, and metal particle size D (expressed in metal atom diameters), determined from N using model calculations,[11] vs. H/M for Pt/Al$_2$O$_3$ (□), Rh/Al$_2$O$_3$ (×), Rh/TiO$_2$ (⊗), Ir/SiO$_2$ (○), and Ir/Al$_2$O$_3$ (●) catalysts.

Several explanations have been proposed for high H/M values. A common explanation is that part of the hydrogen is supposed to be adsorbed by the support through hydrogen spillover from the metal particles.[15,16] Since in the case of spillover differences are expected between the supports used, and not between the metals used, spillover cannot explain our observations. Our results have to be explained by an adsorption stoichiometry larger than one. Subsurface hydrogen seems to provide an opportunity for high stoichiometries.[17-19] However, subsurface adsorption cannot explain H/M values higher than one either, because subsurface adsorption sites need subsurface metal atoms in order to exist. Therefore multiple adsorption on exposed metal atoms, especially at edge or corner positions, must be the main reason for the observed high H/M values.

To explain the observed differences in adsorption stoichiometry for Pt, Rh, and Ir, we have taken the view that the small metal particles (d < 15 Å) can be considered as transition-metal polyhydride complexes. These very small particles consist of too few atoms to be truly metallic. This fact has also been observed by Sanz and Rojo[20] in ^{1}H NMR of hydrogen on Rh/TiO$_2$ (P(H$_2$) > 40 kPa). They found chemical shifts very similar to those of transition-metal hydride compounds. Although transition-metal

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[†] In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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(9) Catalyst samples were measured at liquid nitrogen temperature as thin self-supporting wafers in H$_2$, after in situ reduction. The Rh and Pt measurements were performed on beamline I-5 at the Stanford Synchrotron Radiation Laboratory (SSRL) at the Rh K-edge (23 220 eV) and Pt L_{III}-edge (11 564 eV), respectively. The Ir measurements were done on station 9.2 at the Synchrotron Radiation Source (SRS) at the Ir L_{III}-edge (11 215 eV). The data were analyzed by using reference compounds.[11-14] The uncertainty in the metal–metal coordination number N is ±10%.[12,13]

(10) The catalysts were prepared from RhCl$_3$ and IrCl$_3$ via the incipient wetness technique, from Pt(NH$_3$)$_4$(OH)$_2$ and Rh(NO$_3$)$_3$ via the ionexchange technique, and from IrCl$_3$ via the urea method. γ-Al$_2$O$_3$, SiO$_2$, and TiO$_2$ (anatase) were used as supports. Metal loadings were in the range 0.5–7.0 wt %.

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