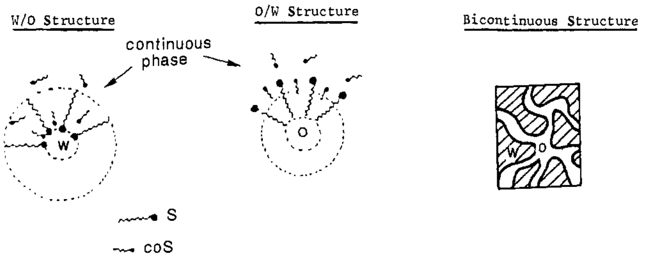

Figure 1. Structures of the microemulsions (**O** = oil, **W** = water, **S** = surfactant, **CoS** = cosurfactant).

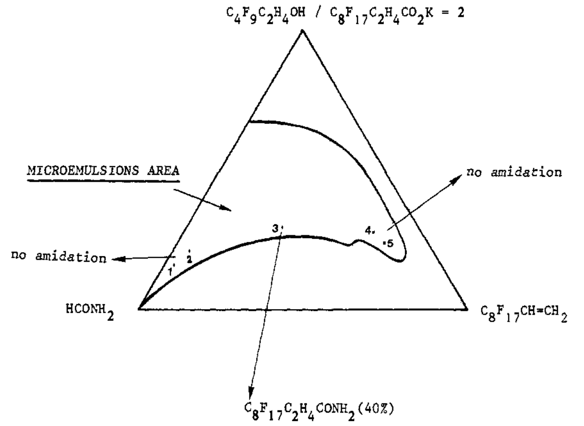

Figure 2. γ radiolysis at 25 °C of microemulsion system ($HCONH_2$, C_8F_{17}-$CH{=}CH_2$, $C_4F_9C_2H_4OH/C_8F_{17}C_2H_4CO_2K = 2$).

Table I. Self-Diffusion Coefficients of $HCONH_2$ (D1) and $C_8F_{17}CH{=}CH_2$ (D2) in the Microemulsions at 25 °C[a]

	microemulsions (% wt)					
no.	F	O	S	CoS	$D1$	$D2$
1	87	7	2	4	3.62	0.54
2	78	10	4	8	3.37	0.60
3	44	44	4	8	0.85	1.21
4	12	61	9	18	0.60	2.89
5	10	66	8	16	0.60	2.98
pure $HCONH_2$					5.21	
pure $C_8F_{17}CH{=}CH_2$						5.32

[a] F = $HCONH_2$, O = $C_8F_{17}CH{=}CH_2$, S = $C_8F_{17}C_2H_4CO_2K$, CoS = $C_4F_9C_2H_4OH$. Unit for $D = 10^{-10}$ $m^2 \cdot s^{-1}$ ± 0.08 × 10^{-10} $m^2 \cdot s^{-1}$.

emulsions analogous to aqueous systems.

Amidation of $C_8F_{17}CH{=}CH_2$ by γ Radiolysis. The following results were obtained (cf. Figure 2). (i) In microemulsions 1, 2, 4, and 5, the olefin does not react, and only the oxamide $CONH_2$–$CONH_2$ is obtained in low yield (≈5% with respect to the starting formamide).[8] (ii) The amidation reaction only takes place in microemulsion 3. The terminal amide $C_8F_{17}CH_2CH_2CONH_2$ is isolated in a 40% yield with respect to the starting olefin which is the limiting reactant.[8] The oxamide $CONH_2$–$CONH_2$ is also obtained in low yield (≈5% with respect to the starting formamide).

These results can be interpreted in terms of the general mechanism of an amidation reaction.[9]

Initiation

$$HCONH_2 \xrightarrow{\gamma} {}^{\bullet}H + {}^{\bullet}CONH_2$$

Propagation

$$C_8F_{17}CH{=}CH_2 + {}^{\bullet}CONH_2 \rightarrow C_8F_{17}CH^{\bullet}CH_2CONH_2$$

$$C_8F_{17}CH^{\bullet}CH_2CONH_2 + HCONH_2 \rightarrow C_8F_{17}CH_2CH_2CONH_2 + {}^{\bullet}CONH_2$$

Termination

$$2{}^{\bullet}CONH_2 \rightarrow CONH_2\text{–}CONH_2$$

In the reverse microemulsions 4 and 5, formamide is confined to the droplets, as demonstrated by the self-diffusion measurements, the carbamoyl radicals diffuse little being restrained in a micellar cage, and only the oxamide is formed.

On the other hand, in the direct microemulsions 1 and 2, the olefin is confined in the micelles. The self-diffusion measurements show that the olefin in fact diffuses little into the medium, and so does not interact greatly with the carbamoyl radicals.

However, in microemulsion 3 with a bicontinuous structure, the constituents (also reactants) diffuse together (Table I), and suitable contact between formamide and the olefin can take place hence enabling reaction.

These results show the potential of the relatively orderless bicontinuous phase as a medium for chemical reactions. These structures, which favor simultaneous diffusion of reactants, enable reactions to be carried out that would be impossible in a strictly micellar medium. These results also confirm the similarity between formamide and aqueous microemulsions, with a first demonstration of a bicontinuous structure in a nonaqueous medium.

Acknowledgment. We thank the U.S. Army for financial support and Atochem who kindly supplied the fluorinated compounds.

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[8] The fluorinated derivatives (99% pure) were a generous gift of Atochem. Formamide (Aldrich 99% pure) was kept on a molecular sieve and contained less than 1% water (Karl-Fisher). The following reaction conditions were employed: 50 mL of degassed microemulsion were irradiated for 70 h at 9.1.10^5 $cm^{-3} \cdot rad \cdot h^{-1}$ in a Gammacell 220 apparatus containing a ^{60}Co source emitting γ radiation at 1.33 and 1.17 MeV. The reaction was followed by GLC (SE30 column with 10% silicone on Chromasorb PAW 80/100 mesh). The amide $C_8F_{17}C_2H_4CONH_2$ and the oxamide were the only products. The oxamide, insoluble in the microemulsion, was filtered off at the end of the irradiation. The amide $C_8F_{17}C_2H_4CONH_2$ was recovered as a solid after precipitation in the microemulsion diluted in a 5-fold volume of water. The products were identified by ^1H (and ^{19}F) NMR and elemental analysis.

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INEPT in a Chemical Way. Polarization Transfer from Parahydrogen to ^{31}P by Oxidative Addition and Dipolar Relaxation

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Parahydrogen induced polarization (PHIP) leading to enhanced ^1H NMR absorptions and emissions arises in hydrogenation and hydrogen addition reactions when H_2 enriched in the para state is added pairwise to substrate.[1,2] If this addition occurs fast relative to proton relaxation, then the transferred protons reflect initially the nuclear spin populations of the starting dihydrogen and yield polarized transitions for the product resonances. In this paper we report that the inverted ^1H nuclear spin populations

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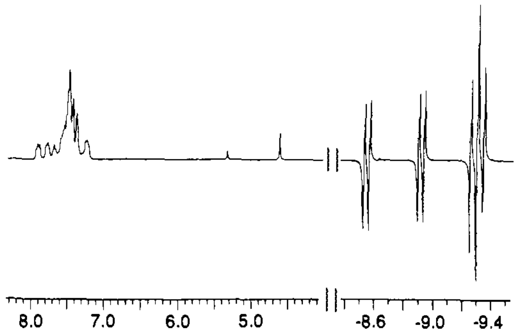
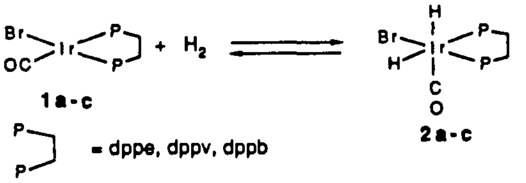


Figure 1. ^1H NMR spectrum at 400 MHz of $IrH_2Br(CO)(dppb)$ formed in the reaction of **1c** with para enriched H_2 in CD_2Cl_2 at 48 °C ~60 s after thawing from storage at −196 °C. The resonances at δ 5.32 and 4.58 ppm correspond to $CHDCl_2$ and dissolved H_2, respectively.

achieved chemically using para H_2 can be selectively transferred to other nuclei such as ^{31}P giving substantial enhancement of their signals. The spectra so obtained are strikingly similar to those produced by using the INEPT pulse sequence though the physical process leading to polarization is that of the nuclear Overhauser effect.[3]

The reaction chemistry used to develop our "chemically INEPT" results is shown in eq 1 corresponding to the oxidative addition



(1)

of H_2 to iridium(I) complexes of the type $IrX(CO)(\widehat{P\,P})$, **1**, where $\widehat{P\,P}$ = $Ph_2PCH_2CH_2PPh_2$ (dppe), *cis*-$Ph_2PCH{=}CHPPh_2$ (dppv), and *o*-$(Ph_2P)_2C_6H_4$ (dppb). This reaction, which has been described previously for the dppe complex **1a**, proceeds under kinetic control to form the isomer shown as **2a** stereoselectively.[4] The oxidative addition is reversible, and, while a slow isomerization to a more stable dihydride isomer occurs subsequently, it is unimportant in the present study. The complexes IrBr(CO)(dppv), **1b**, and IrBr(CO)(dppb), **1c**, are prepared identically to the dppe analogue[5,6] and show similar reaction chemistry with H_2. All three complexes react immediately upon contact with H_2 to form isomer **2**.

When eq 1 for IrBr(CO)(dppb) is carried out under a para enriched H_2 atmosphere in CD_2Cl_2 at 48 °C, the ^1H NMR spectrum shown in Figure 1 is observed within 1 min of thawing and mixing the sample.[7] The resonances for the hydride trans to P and the hydride trans to CO are seen at δ −8.73 and −9.32 ppm, respectively. Each of the ^{31}P coupled lines exists as an E/A (emission/absorption) doublet with a peak separation (3.7 Hz) corresponding to H–H coupling which is usually unresolved in these systems. The phase of the doublets (E/A rather than A/E) indicates that J_{HH} is negative as has been noted before.[2a] In Figure 1 the vertical scale is unchanged between the hydride and phenyl regions of the spectrum, and, from integration, signal enhancement of the hydride resonances can be estimated as 12-fold. After the sample is thawed and shaken, the polarization lasts for ~3 min at 48 °C and up to 6 min at 23 °C. This is beyond what is expected for decay due solely to relaxation of the Ir hydrides, for which T_1's are found to be 1.49 and 0.73 s for the low and high field protons, respectively.[8] In light of this and the reversibility of H_2 addition to yield **2c**, the polarization decay may best be described as a combination of proton relaxation, the formation of newly polarized **2c** by eq 1 and depletion of the para enrichment of H_2 present in solution.

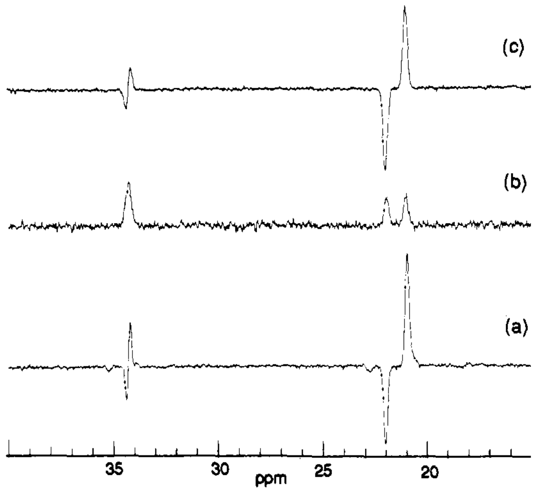


Figure 2. ^{31}P NMR spectra at 162 MHz of $IrH_2Br(CO)(dppb)$ formed in the reaction of **1c** with ~3 atm para enriched H_2 in CD_2Cl_2 at 48 °C: (a) 1 minute after thawing from −196 °C, 16 scans; (b) 2 min later, 16 scans; (c) INEPT spectrum of the same sample with room-temperature equilibrium of ortho and para H_2, 64 scans with J = 148 Hz for $1/4J$ delay in pulse sequence.

Equilibration of ortho and para H_2 above the solution occurs even more slowly, as evidenced by simply shaking the NMR sample tube after which nearly identical polarization is reestablished in the NMR spectrometer. Eventually all polarization is lost as reversible H_2 oxidative addition/reductive elimination and gas/solution mixing act to restore the 298 K equilibrium distribution of ortho and para H_2 above the solution. The results found for the other Ir(I) complexes IrBr(CO)(dppe) and IrBr(CO)(dppv) are virtually identical.

The transfer of polarization to phosphorus is dramatically seen when ^{31}P NMR spectroscopy is used to monitor eq 1 performed with para enriched H_2. The result for the dihydride complex $IrH_2Br(CO)(dppb)$, **2c**, is shown in Figure 2, trace (a). The two ^{31}P resonances show antiphase polarization with a signal enhancement of ~7.4 estimated from integration relative to the normal spectrum of **2c**, trace (b), taken several minutes later. The ^{31}P polarization decays over a period of ~3 min similar to the ^1H polarization decay seen above.

For the P trans to one hydride and cis to the other, phosphorus-proton coupling would be expected to yield a doublet of doublets, or if J_{PH}cis is unresolved, a doublet of broad resonances. Trace (a) of Figure 2 shows that this resonance at δ 21.3 ppm exhibits strong E/A polarization with a peak separation corresponding to the sum of $^2J_{PH}$trans + $^2J_{PH}$cis (148.0 and 14.8 Hz). The two inner lines of this doublet of doublets are absent and, as described below, are not expected to show polarization. The other ^{31}P resonance at δ 34.2 ppm for the phosphorus cis to both hydrides exists as a weaker E/A pattern with a separation of 34 Hz or ca. twice $^2J_{PH}$cis of 18 Hz. In this multiplet polarization, only the outer lines of the expected triplet are seen with the central line absent.

For the other dihydride complexes **2a** and **2b** formed with para H_2, the polarization transfer to ^{31}P yields similar results, with the

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(6) For complex **1b**: IR (KBr) ν_{CO} 1981 cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 39.73 and 24.28 (d, J_{PP} = 17 Hz). For **1c**: IR (KBr) ν_{CO} 1994 cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 52.31 and 42.60 (d, J_{PP} = 16 Hz).

(7) These experiments were carried out in 5 mm NMR tubes equipped with a Teflon valve. Solvents (0.5 mL) were vacuum transferred to an NMR tube containing ~6 mg of the iridium 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. NMR spectra were recorded on a Bruker WH-400 spectrometer operating at 400 MHz for ^1H and 162 MHz for ^{31}P.

(8) T_1 values were measured by using the inversion recovery procedure, (180–τ–90) pulse sequence.

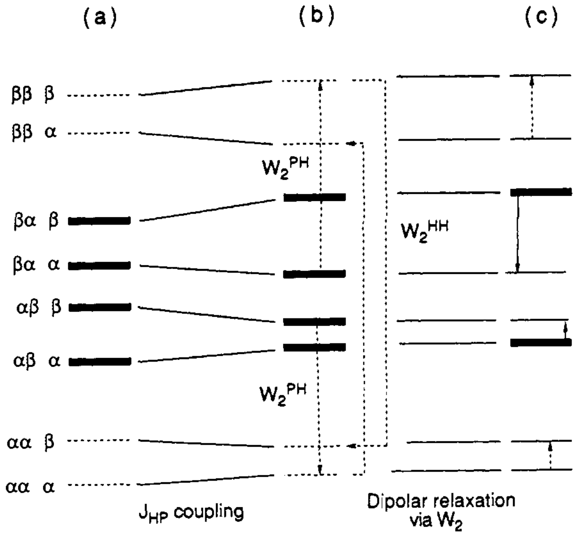

Figure 3. Energy levels for the HH'P (AMX) spin system with individual spin designations in the order of $H_{trans}H_{cis}P$. Energies are not to scale. (a) No ^{31}P–^{1}H coupling. Only the ^{1}H $\alpha\beta$ and $\beta\alpha$ levels are overpopulated from para H_2 addition, with underpopulations indicated by dotted lines. (b) After introduction of couplings with J_{PH}trans > 0 and J_{PH}cis < 0, dipolar relaxation occurs between levels connected by dotted lines. (c) Populations after dipolar relaxation with enhanced transitions shown as solid arrows.

more pronounced effect being observed in the resonance for the phosphorus trans to one of the hydrides. All examples show an E/A phase, a peak separation of $^{2}J_{PH}$trans + $^{2}J_{PH}$cis, and an estimated signal enhancement of 6–10-fold. Coincidentally, the spectrum generated by using para H_2 (Figure 2, trace (a)) can be duplicated with the ^{1}H–^{31}P INEPT pulse sequence.[3] This is shown as trace (c) in Figure 2. In INEPT the hydride ^{1}H populations are selectively inverted, and these population differences are transferred onto the ^{31}P transitions. In the present study, the ^{1}H populations are perturbed chemically, with the population differences transferred to ^{31}P by dipolar relaxation.

The observed polarization in the resonance of P trans to H can be understood in terms of the energy level diagrams of Figure 3 for the HH'P (AMX) spin system with individual level spin functions designated in the order $H_{trans}H_{cis}P$. In Figure 3a only the ^{1}H $\alpha\beta$ and $\beta\alpha$ levels are overpopulated as a result of the oxidative addition reaction using para H_2. Upon introduction of coupling with J_{PH}trans > 0 and J_{PH}cis < 0, the level ordering is modified to that of Figure 3b. Since dipolar relaxation via two-quantum transitions (W_2) is distance dependent, it occurs preferentially through cis partners as shown by the dotted lines on Figure 3b for H_{cis}–P and H–H leading to the population modifications shown in 3c. Only two levels, $\alpha\beta\ \alpha$ and $\beta\alpha\ \beta$, remain unaffected and, by virtue of para H_2 addition, overpopulated. The ^{31}P NMR transitions in enhancement are shown in 3c by the solid arrows, while those which are absent are indicated by dotted arrows.

The above results thus demonstrate that spin overpopulations generated by oxidative addition of para H_2 can be transferred effectively to ^{31}P nuclei resulting in NMR signal enhancement and polarization. Other systems including Vaska's complex, $IrCl(CO)(PPh_3)_2$, show similar results regarding polarization transfer in H_2 addition products, and initial investigations have yielded polarization transfer to ^{13}C nuclei in ^{13}C NMR spectra of hydrogenation products.[9] Because potential population inversions using para H_2 are larger than are obtainable through pulse sequences, we think this procedure, where appropriate, will prove valuable for signal enhancement and spectroscopic analysis.

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The Generation of 2-Vinylcyclopentene-1,3-diones via a Five-Component Coupling in the Coordination Sphere of Chromium

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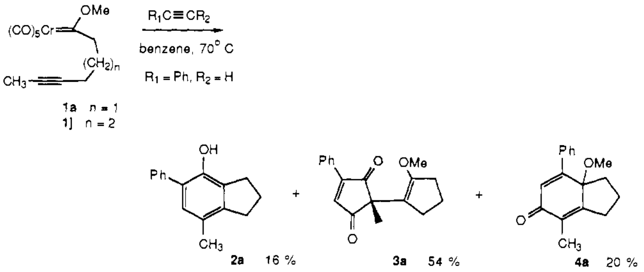
The chemistry of Fischer carbene complexes and alkynes is extremely fertile and is known to produce 4-alkoxyphenols, phenols, furans, cyclopentadienes, cyclobutenones, vinylketenes, cyclohexadienones, 1,3-dienes, pyrones, and cyclopentenones.[2-4] A year ago we communicated the first examples of the intramolecular reactions of alkyne carbene complexes of the type **1** involving the annulation of the carbene complex **1** with a number of alkynes.[5,6] In the case of phenylacetylene, the only product that could be isolated from the reaction in acetonitrile was the two-alkyne phenol **2a** in 52% yield.



The reactions of carbene complexes with acetylenes are known to be sensitive to solvent,[2c,7] and the reaction of **1a** with phenylacetylene proved to be no exception. The reaction of **1a** with phenylacetylene in nonpolar, noncoordinating solvents such as benzene produces two new structural types, the 2-vinylcyclopentene-1,3-dione **3a** and the cyclohexa-2,5-dienone **4a**, both of which are unprecedented from the reaction of carbene complexes and acetylenes. Final assignment of the structure of **3a** was made by X-ray diffraction.[8] Pyrones having one alkyne and two carbon monoxides[9] and phenols having two alkynes and one carbon monoxide[9b,10] have both been observed, but there has never been

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