promote ion pairing with the dianionic COT moiety of the trianion thus slowing the intramolecular electron transfer process. These parameters are currently under study.

The anion radical of (II) at 10 °C in HMPA–THF solution again indicates that the unpaired electron resides exclusively in one of the COT moieties. Esr spectral data clearly indicates that $-Si(CH_3)COT$ acts as an electron withdrawing group. This is probably the reason why the electron does not exchange between the COT's, since the unpaired electron resides primarily in a COT molecular orbital which has a node in the substituted position. Interestingly, an esr signal for $COT^{-\cdot}$ is observed simultaneously with that of the compound. This signal grows as a function of time, suggesting that there is slow decomposition of one of the C–Si bonds. Experiments are underway to generate the trianion radical of (II) at low temperatures to see if electron transfer can be detected. Ion pairing perturbations will be also investigated.

Compound (III) has been recently synthesized. Electron transfer between COT moieties in (III$^{-\cdot}$) is definitely expected. The transfer rate will be investigated as a function of both temperature and ion pairing parameters.

Electron Spin Relaxation in the Study of Boundary Layers at the Liquid–Solid Interphase

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The electron spin relaxation of transition metal ions is largely sensitive towards structural changes of the complex and towards mobility alterations of the solvent. In the case of Cu(II) (S = 1/2), structural changes influence both the magnetic parameters (*g* and *A* tensors) and the line width as a consequence of the relaxation mechanisms dominating in solution (spin-rotation and *A* and *g* anisotropies modulation). Solvent mobility variations also alter the line width, at low and high temperature, in opposite ways. In the case of Mn(II) (S = 5/2), structural changes influence the zero-field splitting term, thus effecting the line width, without appreciably modifying the line position (static term in the spin Hamiltonian). Decreased solvent mobility increases the correlation time for the motion and therefore the line width (dynamic term in the spin Hamiltonian).

The liquid mobility at the solid–liquid interface is expected to be decreased and to induce large effect on the line width of paramagnetic probes in the boundary layers. From a line width analysis, the correlation times for the motion can be calculated as a function of the distance from the surface.

The above procedure is applied to liquid–solid interphases in which SiO_2, Al_2O_3, TiO_2, and carbon were the porous solid supports, and water, NaOH water solution, and organic fluids were the liquids. The probes used were $Mn(H_2O)_6^{2+}$, $Cu(H_2O)_2^{2+}$, $Cu(OH)_4^{2-}$, and $Cu(acac)_2$.

Diastereomeric Electron-Donor–Acceptor Complexes

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An electron–donor acceptor (EDA) interaction has been assumed to contribute, besides hydrogen bonding, to the formation of certain diastereomeric complexes [1]. We have now shown, for different molecular systems, the existence of diastereomeric complexes which seem to be held together by EDTA attraction *exclusively*.

Among others, carbazole derivatives were chosen as π-donors and fluorenone derivatives as π-acceptors [2] (*e.g.* Fig. 1). The ^1H NMR signals of racemic

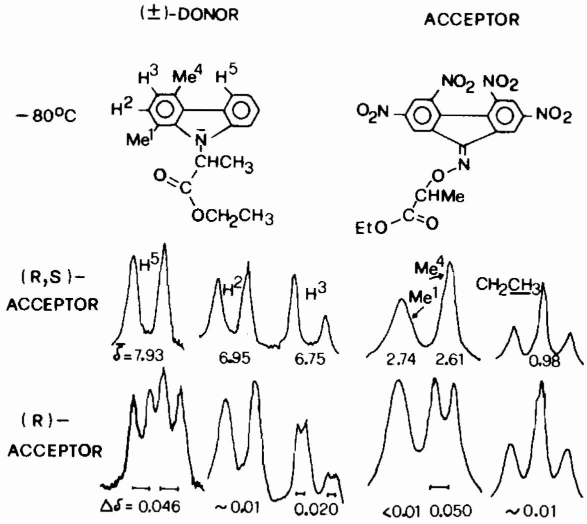

Fig. 1. ^1H NMR in [D_6]acetone of a racemic donor in the presence of 1.10 equivalents of (R,S)- or (R)-acceptor, respectively. Δδ: Shift difference between protons of (+)- and (−)-donor, determined from splittings or estimated from linewidths.

donors show additional splittings Δδ in the presence of *optically active* acceptors (Fig. 1, bottom) which are absent (Fig. 1, top), if *racemic* acceptors are applied [2]. Similarly, the signals of racemic acceptors are split in the presence of optically active donors. In some cases, assignments of individual lines to specific diastereomeric complexes have been achieved by using a *nonracemic* mixture of one component and a pure enantiomer of the other component [3].

The comparison of ^{1}H NMR shifts $\bar{\delta}$ for the mixtures with those of the pure components [4] as well as the temperature dependence [2] of $\bar{\delta}$ for the mixture provide further evidence of association. These relative shifts are caused predominantly by the diamagnetic anisotropy of the partner in the complex. They enabled us to propose a model for the *orientation* (Fig. 2) of the components for some of the complexations studied. The magnitudes of the above splittings Δδ (*e.g.* Fig. 1) give some support to this proposal.

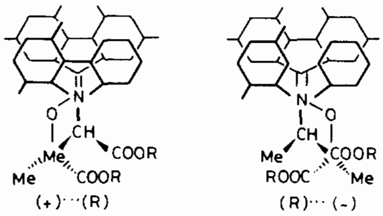

Fig. 2. Average diastereomeric 1:1 complexes between (R)-2-(N-carbazolyl)-propionic esters and (±)-2-(2,4,5,7-tetranitro-9-fluorenylideneaminoxy)-propionic esters.

Results [5] with chiral or prochiral cations and optically active anions will be mentioned. In this case, similar ^{1}H NMR effects are brought about by *cation–anion attraction.* Possible applications for the measurement of enantiomeric purity [6] will be discussed.

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^{31}P and ^{1}H NMR Characterization of Stereoisomeric Macrocyclic Nickel(II) Complexes with a Tetraphosphane Ligand

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Several studies on metal complexes formed by macrocyclic ligands have shown that these compounds provide stimulating examples for studying the conformational properties of the molecules. Recent synthetic developments in this laboratory have provided some ideal ligands for investigating the configurational properties of polyphosphane macrocyclic complexes. As an example, the results of ^{31}P and ^{1}H NMR investigations on some stereoisomeric nickel(II) derivatives of the 4,7,13,16-tetraphenyl-1,10-dioxa-4,7,13,16-tetraphosphacyclooctadecane {|18|aneP$_4$O$_2$} are here reported.

The |18|aneP$_4$O$_2$ ligand can exist in five basic structural forms (Fig. 1), as determined by the distribution of phosphorus atom configurations with respect to the aliphatic chains spanning the phosphorus atoms themselves. Three of these forms [(a), (b), and (c)] are nonenantiomeric, whereas (d) and (e) forms exist together their respective enantiomers. The five forms are interconvertible diastereoisomers; however, because of their high temperature of

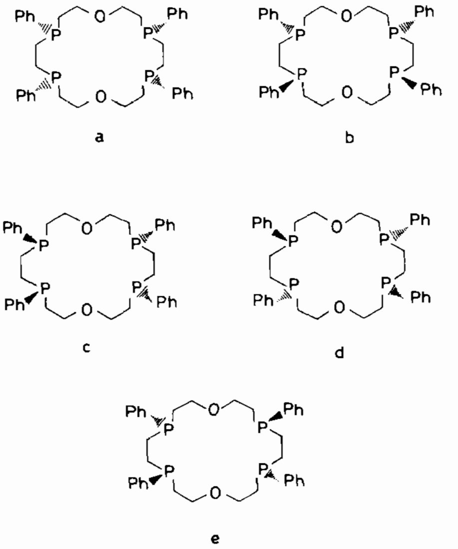

Fig. 1. The five possible diastereoisomers of |18|aneP$_4$O$_2$ ligand.