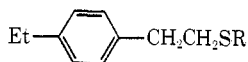


such as *p*-thiocresol and benzylmercaptan, the rate of disappearance of **1** was accelerated more than 10 times, indicating that $k_{-1}/k_2 \geq 10$ in the absence of the radical scavenger. Because the polarization in **1** was not observable under the above conditions, the radical responsible for the polarization in **1** or one equilibrating with it must have been efficiently trapped. *p*-Diethylbenzene and the addition product **5** were the major



5, R = *p*-CH₃C₆H₄ for *p*-thiocresol
= C₆H₅CH₂ for benzyl mercaptan

products. Thus, only **2** and **3** seem conceivable as the species in which the polarization arose.¹⁷ Indeed the thermal reactions of **1** investigated so far were all accountable in terms of the intermediacy of **2** and **3**.^{7,18} The possibility that the polarization was brought about through the dynamic behavior of the rather long-chain biradical **3**, however, is ruled out on the ground that spin-selection in a pair of equivalent radicals ($\Delta g = 0$) cannot give net polarization.^{1,2,19} Therefore the polarization would certainly be brought about through the dynamic processes of the singlet (thermally generated from ground state) biradical **2**.²⁰

According to the current theory, radical centers in a biradical must be separated to the distance where S-T₀ splitting $2J$ becomes the order of hyperfine interactions to give rise to (S-T₀) CIDNP. Therefore, unless the biradical is large enough to fulfill the above condition, no CIDNP effect is expected in its reaction. Recently Closs and Doubleday²¹ reported that the average S-T₀ splitting in the 1,7-biradical resulting from the photo- α -cleavage of cycloheptanone amounted to 1.87 cm⁻¹ (20 kG), which was *ca.* 10³ times the magnitude of a typical hyperfine interaction. Present results imply that even in **2**, the exchange interaction is sufficiently small to give rise to (S-T₀) CIDNP.

Some rather short-chain biradicals generated in the triplet state have been reported to exhibit CIDNP due to S-T₋ mixing.²¹⁻²³ CIDNP in **1**, however, is apparently not due to S-T₋ mixing because all the polarization should occur in emission or absorption in the (S-T₋) CIDNP spectrum.

CIDNP is a highly useful tool for the mechanistic investigations on the radical reactions. The results reported here show that CIDNP may be expected in the products derived from short-chain singlet biradicals in

(17) The biradical species formed reversibly by the reaction of **2** or **3**



with solvent may be rejected because the CIDNP effect was observed in solvents widely different in chemical properties: triglyme, *p*-dibromobenzene, and diphenyl ether.

(18) T. Tsuji and S. Nishida, *J. Amer. Chem. Soc.*, **95**, 7519 (1973).

(19) Even if $\Delta g \neq 0$, the polarization of olefinic protons whose hyperfine couplings in **3** should be small is difficult to explain; *cf.* J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3940 (1969).

(20) The distribution of odd electron density in the cyclohexadienyl radical has been reported to be 0.349 on C₁ and C₅, -0.103 on C₂ and C₄, and 0.506 on C₃: R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **38**, 773 (1963); **39**, 2147 (1963).

(21) G. L. Closs and C. E. Doubleday, *J. Amer. Chem. Soc.*, **95**, 2735 (1973).

(22) J. A. Berson, R. J. Bushby, J. M. McBride, and M. Tremelling, *J. Amer. Chem. Soc.*, **93**, 1544 (1971).

(23) G. L. Closs, *J. Amer. Chem. Soc.*, **93**, 1546 (1971); G. E. Closs and C. E. Doubleday, *ibid.*, **94**, 9248 (1972).

certain cases.²⁴⁻²⁶ We make this preliminary report because the present results promise to be of considerable importance, in view of current interests in the CIDNP phenomenon and the chemistry of short-chain biradicals.

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(24) Since S-T₀ mixing by the hyperfine interactions does not involve any change in the *z* components of nuclear spins, to observe CIDNP *via* spin selection, spin-independent competitive process is required. In the normal radical pair reactions, diffusive separation of the components generally provides such a process. In the biradical reactions, diffusive separation is absent. Closs and Trifunac¹ predicted that (S-T₀) CIDNP would not be observed in the biradical reactions because of the absence of diffusive process. However, (S-T₀) CIDNP is apparently observed as shown in this reaction and others.^{25,26} Rearrangement of **2** to **3** and subsequent solvent transfer reaction would provide the spin-independent process for **2** in this reaction.

(25) R. Kaptein, M. Frater-Schroeder, and L. J. Oosterhoff, *Chem. Phys. Lett.*, **12**, 16 (1971).

(26) T. Tsuji and S. Nishida, *Chem. Lett.*, 1335 (1973).

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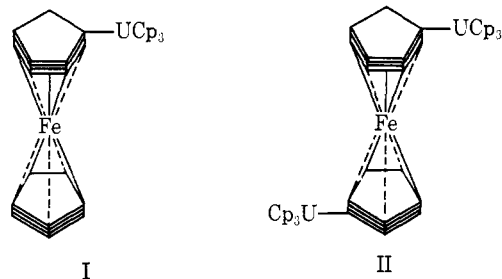
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Synthesis of a New Type of σ -Bonded Organouranium Compound. Mono- and Bis[tris(η^5 -cyclopentadienyl)uranium]ferrocene¹

Sir:

In recent years, there has been a growing interest in organoactinide chemistry, with particular emphasis on seeking evidence for covalency and possible 5*f* orbital participation in the bonding.² Two important types of compounds have been prepared and studied: the π -bonded "uranocenes"³ and (η^5 -C₅H₅)₃UR (R is a σ -bonded alkyl or aryl group).⁴ In our further studies of this latter class of compounds, we wish to report the preparation and some properties of two new novel derivatives, [tris(η^5 -cyclopentadienyl)uranium]ferrocene (I) and 1,1'-bis[tris(η^5 -cyclopentadienyl)uranium]ferro-



cene (II). These are the first compounds of the type η^5 -Cp₃UR (Cp = cyclopentadienyl) where R is an

(1) Organolanthanides and Organoactinides. VIII.

(2) (a) H. Gysling and M. Tsutsui, *Advan. Organometal. Chem.*, **9**, 361 (1970); (b) R. G. Hayes and J. L. Thomas, *Organometal. Chem. Rev., Sect. A*, **7**, 1 (1971).

(3) A. Streitwieser, Jr., U. Muller-Westerhoff, G. Sonnichsen, F. Mares, D. G. Morrell, K. O. Hodgson, and C. A. Harmon, *J. Amer. Chem. Soc.*, **95**, 8644 (1973), and references therein.

(4) (a) A. E. Gebala and M. Tsutsui, *J. Amer. Chem. Soc.*, **95**, 91 (1973); (b) T. J. Marks, A. M. Seyam, and J. R. Kolb, *ibid.*, **95**, 5529 (1973); (c) G. Brandi, M. Brunelli, G. Lugli, and A. Mazzei, *Inorg. Chim. Acta*, **7**, 319 (1973).

organometallic substrate and the first actinide compounds of any type to be coordinated in a η^1 rather than a η^5 fashion to the cyclopentadienyl moiety (from ferrocene). II is also the first example of a compound to contain two η^5 -Cp₃U moieties bound to the same ligand.

Compounds I and II are formed by the reaction in THF at -30° of $(\eta^5\text{-C}_5\text{H}_5)_3\text{UCl}^5$ with ferrocenyl-lithium⁶ or 1,1'-dilithioferrocenetetramethylethylenediamine,⁷ respectively. Both compounds are very sensitive to oxygen and moisture; II is a green crystalline solid formed in 60% yield and I is a brown solid, forming in 75% yield.⁸

II is nonvolatile, decomposing above 190° to give ferrocene and a brown intractable solid while I sublimes easily under vacuum above 180° . Mass spectra of I show several important peaks at m/e 618 (M^+), 553 ($\text{M} - \text{Cp}$), 433 (Cp_3U), 368 (Cp_2U), 186 (Cp_2Fe), and 121 (CpFe). The spectrum is completely consistent with a structure based on π -bonding of three of the Cp rings to the uranium and σ -bonding of a Cp ligand from ferrocene to uranium.

Infrared spectra⁹ of both I and II are also consistent with the proposed structures. Absorptions are present which are derived from both η^1 and η^5 coordinated cyclopentadienyl vibrations.¹⁰

The nmr data for I are also in accord with the above formulation. The 15 protons of the η^5 -Cp₃U group appear as a sharp singlet at $\delta -2.33$ ¹¹ which is in the region found for these protons by others.⁴ The five protons of the unsubstituted cyclopentadienyl ligand on ferrocene appear as a sharp singlet at $\delta -1.64$, a shift of over 5.7 ppm from free ferrocene. The signals for the four protons on the substituted ring which come much further upfield were found but could not be located exactly, coming roughly at $\delta -13$ and -30 . The furthest upfield signal is assigned to the two α protons. Marks^{4b} and Streitwieser¹² have explained these shifts in terms of large contact contributions. A mechanism which involves the bonding of the R groups (ferrocene here) to uranium is then seen as a covalent contribution from filled ligand MO's to vacant f orbitals.

No nmr data could be obtained for II due to its low solubility. It is insoluble in almost all organic solvents except THF, in which it is only very sparingly soluble.

Magnetic susceptibility data are listed in Table I. The susceptibility for the monosubstituted derivative is in the same range as other Cp₃UR derivatives.⁴ The susceptibility of II presents an interesting contrast. Preliminary results at variable temperatures indicate

Table I. Magnetic Susceptibility Data

Compound	$10^6\chi$	μ_{eff}
I ^a	2708	2.60
II ^b	5852	3.67

^a Data at 310°K . ^b Data at 288°K .

that, in the range from 300 to 60°K , there is continual increase in susceptibility as temperature decreases. It has been shown that other Cp₃UR derivatives display temperature-independent paramagnetism below 100°K . This phenomenon could be due to large spin-orbit coupling constants, strong ligand field splitting due to the ferrocene moiety, or perhaps to effects arising from having two Cp₃U groups bound in relatively close proximity to the same ligand.

Further studies with this type of compound are in progress to clarify the nature of the uranium-carbon σ bond, particularly with respect to f orbital involvement.

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Paramagnetic Rare Earth Ion Probes of Transfer Ribonucleic Acid Structure

Sir:

Numerous recent investigations¹⁻⁶ have demonstrated that chelated rare earth ions may be used as nmr shift reagents to study the structure of molecules in organic solvents. Recently, however, Williams, *et al.*,⁷ studied the binding of bare rare earth ions to the enzyme lysozyme in aqueous solution.⁸ In this communication we report the first use of bare lanthanide ions as nmr shift reagents in an investigation of the structure of tRNA molecules in H₂O. These molecules are very important biologically since they are responsible for translating the genetic code, and consequently, there is considerable interest in their structure in solution. We have already shown in a series of high resolution nmr studies that the cloverleaf model is the correct description of the base pairing structure of at

(5) L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 246 (1956).

(6) M. D. Rausch, G. A. Moser, and C. F. Meade, *J. Organometal. Chem.*, **51**, 1 (1973).

(7) J. J. Bishop, A. Davison, M. L. Katcher, D. W. Lichtenberg, R. E. Merrill, and J. C. Smart, *J. Organometal. Chem.*, **27**, 241 (1971).

(8) Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories. Calcd for I: C, 48.56; H, 3.90; U, 38.49; Fe, 9.03. Found: C, 47.56; H, 5.21; U, 38.13; Fe, 8.62. Calcd for II: C, 45.73; H, 3.64; U, 45.31; Fe, 5.32. Found: C, 45.52; H, 3.70; U, 45.52; Fe, 4.97.

(9) Mulls were prepared in a drybox and made with dry, deoxygenated Nujol and Fluorolube.

(10) F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **91**, 7281 (1969).

(11) The chemical shifts were calibrated using the upfield peak of the solvent THF, assumed to be 1.79 ppm.

(12) A. Streitwieser, Jr., D. Dempf, and G. N. LaMar, *J. Amer. Chem. Soc.*, **93**, 7343 (1971).

(1) C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).

(2) J. J. Uebel and R. M. Wing, *J. Amer. Chem. Soc.*, **94**, 8910 (1972).

(3) R. M. Wing, T. A. Early, and J. J. Uebel, *Tetrahedron Lett.*, **41**, 4153 (1972).

(4) W. D. Horrocks, Jr., and J. P. Sipe, III, *J. Amer. Chem. Soc.*, **93**, 6800 (1971).

(5) R. von Ammon and R. D. Fischer, *Angew. Chem., Int. Ed. Engl.*, **11**, 675 (1972).

(6) R. E. Sievers, Ed., "Nuclear Magnetic Resonance Shift Reagents," Academic Press, New York, N. Y., 1973.

(7) K. G. Morallee, E. Nieboer, F. J. C. Rossetti, R. J. P. Williams, A. V. Xavier, and R. A. Dwek, *Chem. Commun.*, 1132 (1970).

(8) W. D. Phillips, C. E. Looney, and C. K. Ikeda, *J. Chem. Phys.*, **27**, 1435 (1957).