anhydride or to react with $FeCl_2$ to form ferrocene[15] and from various spectroscopic data[16] on $(C_9H_7)_3UCl$. Other, indirect, evidence for covalency in $(C_5H_5)_4U$ is the Mössbauer study[17] of $(C_5H_5)_4Np$, a compound isostructural with $(C_5H_5)_4U$. The isomer shift found for Np indicated covalency in the Np–C bonds, but less than that found[11] for $(C_8H_8)_2Np$. Thus, while the eight-membered-ring sandwich configuration of $(C_8H_8)_2U$[18] appears particularly favorable for use of 5f orbitals in the bonding, chemical evidence for covalency in U(IV) compounds with other configurations, such as the one shown here, suggests that they too may have some participation of these orbitals in the organometallic bonding.

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Strategies for the Study of Structure Using Lanthanide Reagents

Sir:

Utilization of lanthanide complexes in solution structural studies has focused on the predicted $\langle(3\cos^2\theta - 1)r^{-3}\rangle$ dependence of the assumed dipolar or pseudocontact interaction.[1–9] Here θ is the angle between a real or time-averaged axis of symmetry and the metal nucleus vector, and r is the length of this vector. Although the dipolar mechanism appears to dominate the observed shifts in the majority of cases, recent evidence for sizable contact contributions in proton[10] as well as carbon-13[11,12] isotropic shifts introduces a disquieting degree of ambiguity in a solution structure deduced solely from the observed relative isotropic shifts.

Solution structures deduced from shift studies could, in principle, be severely tested by requiring a simultaneous fit to the relative line widths induced by the lanthanide ion, which in favorable cases can be shown to depend solely on relative values of $\langle r^{-6}\rangle$. The potentiality of this $\langle r^{-6}\rangle$ dependence of the line widths due to a "relaxation" reagent has been ignored generally. In isolated instances,[8,13] induced line widths with and without concomitant isotropic shifts have been employed. In the former case, the broadening rapidly leads to overlap[8] of the closely spaced unshifted resonances precluding an accurate determination of the line widths. In the latter case, the use of lanthanides[8,13] which possess sizable magnetic anisotropy results in line widths which have a more complex dependence[14] on r, θ, and the magnetic anisotropy than even the dipolar shift. We demonstrate here how the simultaneous use of a "shift" reagent (maximum shift with minimal broadening) and a "relaxation" reagent (severe broadening with negligible shift) can overcome both the resolution and interpretation problems of earlier studies and thereby provide a complementary, if not superior, method for effecting structural analyses.

The long electron spin relaxation time and highly isotropic magnetic moment of Gd^{3+} makes it the ideal lanthanide "relaxation reagent" with the desired $\langle r^{-6}\rangle$ line width dependence.[15] The magnetic isotropy of the $Gd(fod)_3$ complex is confirmed by noting that addition of only $Gd(fod)_3$ to the substrate causes broadening without observable shifts. The general procedure proposed is that of inducing large shifts between resonances by the addition of a shift reagent, *i.e.*, $Eu(fod)_3$, and then adding Gd(fod) to broaden the lines. This method readily allows the determination of a broadening of several hundred hertz, which would be impossible without the expanded chemical shift scale induced by the shift reagent. The line widths due solely to the relaxation reagent are obtained by correcting the observed line widths for minor paramagnetic relaxation due to the shift reagent and for broadening due to incompletely collapsed spin–spin multiplet structure in both the presence and absence of the relaxation reagent. Rapid relaxation of spins close to the metal may eliminate some multiplet structure;[16,17] residual multiplet structure may always be eliminated by using a second rf oscillator to effect instrumental decoupling.

Complicating factors, such as nonspecific relaxation in the second coordination sphere and the presence of multiple correlation times in substrates with internal motions, must be considered. The former effect, which is not very important in dilute solution, can be estimated by using a model noninteracting substrate (*i.e.*, benzene for pyridine). Multiple correlation times are not likely to arise in nonviscous media, and their presence can generally be established[18] experimentally.

The main advantage of analyzing relaxation data over shift data is that the $\langle r^{-6}\rangle$ interpretation of the relative line widths for Gd rests on firmer theoretical ground[15] than the $\langle(3\cos^2\theta - 1)r^{-3}\rangle$ interpretation of the shifts for Eu or Pr. Furthermore, the line width

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[1] Selected recent articles are given below.[2–9] The abbreviations dpm for dipivaloylmethanate and fod for 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate are used.

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ratios are expected to be less sensitive to the presence of multiple species than the shift ratios.[19] Although shifts can be measured more accurately than line widths, the $\langle r^{-6}\rangle$ dependence of the relaxation allows significant error in the measured line width without sacrificing acceptable accuracy in the determination of relative values for r.

The potential for this technique is reflected in the data for substituted pyridine in the presence of Eu(fod)$_3$ and Gd(fod)$_3$. The proton line widths, δ_i were obtained by frequency-swept spin decoupling and corrected for second coordination sphere effects.[23] The quantitative comparison of the observed $(\delta_i/\delta_j)^{-1/6}$ with the estimated r_i/r_j, is illustrated in Table I. The results are comparable in accuracy to those obtained by analyzing the relative shifts, $\Delta H_i/\Delta H_j$, in terms of the estimated geometric factors, which are also included in the table for comparison. We stress here that the proposed analysis of the line widths due to a relaxation reagent in the presence of a shift reagent is not intended so much as an alternative to the analysis of the assumed dipolar shifts as a complementary technique by which solution structures may be more critically examined. An important feature of our proposed technique is that it may provide an experimental test for the generally accepted $(3\cos^2\theta - 1)r^{-3}$ dependence of the observed isotropic shift in model lanthanide complexes. A simultaneous fit to both shift and line width data would significantly increase the confidence level of any structure determination. Analysis of line width data may also be at an advantage in cases where $(3\cos^2\theta - 1) \sim 0$, for ^{13}C spectra exhibiting contact shifts and in aqueous systems. A detailed evaluation of the method for solution structural determination and the factors contributing to the line widths is in progress.[24]

Table I. The Effect of Eu(fod)$_3$ and Gd(fod)$_3$ on the Pmr Spectrum of Some Pyridines

	3-H/2-H	4-H/2-H	3-Me/2-H	4-Me/2-H
$\Delta H_i/\Delta H_j$ py[a]	0.31	0.31		
$\Delta H_i/\Delta H_j$ 4-pic[b]	0.32			0.30
$\Delta H_i/\Delta H_j$ 3,5-lu		0.33	0.21	
$\langle(3\cos^2\theta - 1)/r^3\rangle$	0.38	0.32	0.23	0.21
$(\delta_i/\delta_j)^{1/6}$ 4-pic	0.64			0.54
$(\delta_i/\delta_j)^{1/6}$ 3,5-lu		0.60	0.58	
$\langle 1/r^6\rangle^{1/6}$ [c]	0.60	0.53	0.54	0.46

[a] Obtained in 100 MHz for a deuteriochloroform solution 0.20 M in pyridine, 0.05 M in Eu(fod)$_3$, and 0.002 M in Gd(fod)$_3$ at 30°; py = pyridine, pic = picoline, lu = lutidine. [b] ΔH(2-H) = 8.24 ppm; the uncorrected δ = 380 Hz. Using Eu(dpm)$_3$, ratios of 0.36 and 0.26 were obtained. [c] Assuming Eu–N and Gd–N bond lengths of 2.65 and 2.60 Å, respectively.

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(19) The line width ratios will be independent of the nature of the species in solution as long as the Gd-donor atom bond distance remains invariant; the dipolar shift ratios will be independent of the species only if the effective magnetic axis[20] coincides with the Eu-donor atom axis in all species.

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(23) The natural line widths (4-pic, 2-H, 6.1 Hz; 3-H, 1.7 Hz; 4-Me, 1.2 Hz) were determined by extrapolation of the observed line width with added Eu(fod)$_3$ to the slightly altered position in the presence of Gd(fod)$_3$ and Eu(fod)$_3$. Corrections of 1 Hz for the second coordination sphere relaxations were made using benzene.

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Evidence for a Norcaradiene–Bisnorcaradiene Rearrangement in a Di-π-methane System

Sir:

In a series of papers it has been shown that photolyses of diazocyclopentadiene (**1**) in benzene and its derivatives give spironorcaradienes (**2**)[1–5] (in equilibrium with their valence isomers **3**) which can be isolated if the photolysis is carried out with a long-wavelength filter (λ >360 nm) and if careful work-up procedures are applied.[1–3] With Pyrex filters (λ >290 nm) **2** $\rightleftarrows$ **3** rearrange to benzocycloheptatrienes **4** and their 5-H isomers (**5**).[6] Two possible mechanisms have been proposed for this rearrangement: (1) a mechanism that is tantamount to a symmetry-allowed[7] [1,7]-sigmatropic shift (to **9**) or (2) a di-π-methane rearrangement[8] (to **8**). In this communication we report the successful isolation and identification of **6**, a product which provides strong evidence for the intermediacy of the novel bisnorcaradiene **8**.

A reinvestigation of the irradiation of **1** in benzene[6] using a more powerful Hg high-pressure lamp (Hanovia 450 W, Pyrex filter) showed that in addition to the products **4** and **5** isolated before, another benzocycloheptatriene **6** could also be obtained. The new product was isolated by chromatography of the photolysate on silica gel (petroleum ether–benzene, 7–25%:93–75%). The total yield of **6a** + **4a** was 65%. Separation could also be achieved by recrystallization from ethanol in which **4a** is sparingly soluble.[9] The new benzocycloheptatriene **6a** has the following physical properties: mp 102°; uv $\lambda_{\max}$ (CH$_3$CN) 275 nm (ϵ 34,000); ir (KBr) 2930, 1600, 1495, 1450, 765, and 698 cm^{-1}; ^{1}H nmr (CDCl$_3$) τ 2.5–3.3 (m, 25 H), 4.63 (s, 1 H); mass spectrum m/e 446 (M$^+$, base peak). On the basis of the chemical shift of the saturated proton (heptaphenylcycloheptatriene shows a one-hydrogen resonance at τ 4.73[10]) **6a** appeared to be the most likely

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