

cleavage of the oxirane at the *more* hindered site⁹ to form dihydrobenzopyran **6**: mp 146–147°; $[\alpha]^{25}_D -166^\circ$ (*c* 0.97, EtOH); δ (CCl₄) 6.37 (br, 1, vinylic), 6.20, 6.08 (AB, 2, *J* = 2 Hz, aromatics), 4.90 (br, 1, OH), 3.65 (s, 2, CH₂OH, 3 Hz band width at half-height), 3.23 (m, 1, C₃-H), 2.05 (br, 1, OH), 1.67 (br, 3, CH₃, vinylic), 1.00 (s, 3, C₈-CH₃), 0.90 (t, 3, ω -CH₃); mass spectrum (70 eV) *m/e* 330 (M⁺), 299 ([M - CH₂=OH]⁺, base peak), 231 and 193. Acetylation of **6** resulted in the facile formation of a diacetate (**9**) (δ (CCl₄) 6.48, 6.30 (AB, 2, *J* = 2 Hz, aromatics), 5.95 (br, 1, vinylic), 4.15 (s, 2, CH₂-OAc, 3 Hz band width at half-height), 3.03 (m, 1, C₃-H), 2.20 (s, 3, acetate), 2.03 (s, 3, acetate), 1.66 (br, 3, CH₃, vinylic), 1.06 (s, 3, C₈-CH₃), 0.88 (t, 3, ω -methyl); mass spectrum (70 eV) *m/e* 414 (M⁺), 371, 355, 295, and 231), which caused the expected downfield shift of the methylene adjacent to the asymmetric C₈. Although this methylene appears as a singlet, the nonequivalence of its protons can be demonstrated using benzene-*d*₆ as solvent: δ (C₆D₆) 4.17, 4.32 (AB, 2, *J* = 12 Hz). The assignment of the β -configuration to the C₈-hydroxymethyl substituent in **6** is based on the presence of a methyl signal at δ 1.00 and the absence of the lower field signal (δ 1.35–1.41) exhibited by the C₈- β -methyl group in various THC derivatives.¹⁰ Since no β -methyl isomers were isolated, the precursor epoxide **3** probably consisted of a single isomer indicating stereoselectivity during epoxidation of the 8,9-double bond.¹¹ This same selectivity would be expected in the formation of diepoxide **4**.

When **4** was treated with aqueous NaOH in MeOH the compound isolated in 60% yield showed: δ (CCl₄) 6.22 (s, 2, aromatics), 4.34 (d, 1, *J* = 9 Hz, C₂-H), 4.04, 3.38 (AB, 2, *J* = 13 Hz, CH₂-O), 3.3 (m, 1, C₃-H), 2.17 (br, 2, 2-OH), 1.30 (s, 3, CH₃), 1.22 (s, 3, CH₃), 0.88 (t, 3, ω -CH₃); mass spectrum (70 eV) *m/e* 346 (M⁺), 290, 285, 218, and 214. The same material (by glc) could be obtained from **7** via epoxidation and alkaline hydrolysis. Although two exchangeable protons are apparent in the nmr, silylation could not be achieved. The structure in concert with the data is the novel tetracyclic ether **10** comprising the dihydrobenzoxepin ring system. Compound **10** is formed by dual phenolate anion attack at the less highly substituted oxirane sites.

The selectivity of these cyclizations indicates that in the intramolecular base-induced cleavage of epoxides ring size is more important than substitution. While both ring size and steric factors favor furan ring formation in **5**, ring size prevails in the cyclization of **3**, in spite of an adverse substitution pattern, to give a pyran (**6**) rather than an oxepin. Formation of the oxepin ring in **10** probably occurs only after initial closure to the furan ring. Furan formation places severe steric constraints on the subsequent cyclization, thus effectively eliminating the possibility of pyran formation. These findings, together with the observation that both compounds **11**^{2a} and **12**^{2b} give dihydrobenzofurans under basic conditions, suggest that the entropy of ring formation is the major factor in determining the product of an intramolecular epoxide cleavage.¹²

(-)-8 β -Hydroxymethyl- Δ^1 -THC (**6**) exhibited THC-like overt CNS symptomatology in rodents at 1.0 mg/kg iv (equivalent to that of Δ^1 -THC) and is of interest as a possible metabolite of Δ^1 -THC. Cannabielsoin (**5**) and the tetracyclic ether (**10**) showed no CNS activity up to 10 mg/kg iv.

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Paramagnetic Hydride and Alkyl Complexes of Niobium(IV) and Tantalum(IV)

Sir:

Transition metal hydrides are recognized as important intermediates and catalysts in a variety of reactions including hydroformylation, hydrogenation, olefin isomerization, and hydrogen exchange.¹ Electron spin resonance (esr) spectroscopy represents one of the best available techniques for the study of paramagnetic hydrides; however, only a few are extant.² The recent synthesis³ of the early transition metal hydrides of niobium and tantalum, which are involved in H-D exchanges,⁴ coupled with the development of esr techniques for the study of transient paramagnetic species,⁵ provide an excellent opportunity to generate and to study metal-centered radicals, particularly those with nuclear magnetic moments, e.g., ⁹³Nb with *I* = 9/2 and ¹⁸¹Ta with *I* = 7/2, both present in 100% natural abundances.

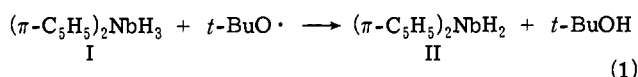
We wish to report the observation by esr of dicyclopentadienylniobium(IV) dihydride produced in solution by abstraction of a single hydrogen from the diamagnetic dicyclopentadienylniobium trihydride (π -C₅H₅)₂NbH₃ (I).³ Thus, a rigorously degassed solution of I in a mixture of benzene and cyclopropane containing di-*tert*-butyl peroxide (DTBP) on photolysis at -80° in the cavity of an esr spec-

Table I. Hyperfine Coupling Constants for Dicyclopentadienyl Metal Alkyls and Hydrides

Radical	Hyperfine coupling constant (G) ^a		Line width (G)	$\langle g \rangle^{d,h}$	Ref
	$\langle a_M \rangle$	$\langle a_H \rangle$			
$(\pi\text{-Cp})_2\text{NbH}_2$	45.9	11.7	6.0	2.0097	<i>b</i>
$(\pi\text{-Cp})_2\text{NbD}_2$	45.4	<2	7.6	2.0095	<i>b</i>
$(\pi\text{-Cp})_2\text{NbH}(t\text{-Bu})^{e,f}$	68.5	11.6	6.2	2.001	<i>b</i>
$(\pi\text{-Cp})_2\text{Nb}(\text{CH}_3)_2$	88.8	6.3	3.7	1.9984	<i>b</i>
$(\pi\text{-Cp})_2\text{Nb}(\text{CD}_3)_2$	88.3	<1	7.6	1.9989	<i>b</i>
$(\pi\text{-Cp})_2\text{Nb}(\text{C}_6\text{H}_5)_2$	88.8	n. r.	9.0	1.9982	<i>b</i>
$(\pi\text{-Cp})_2\text{Nb}(\text{Cl})_2$	116.5		12.0	1.9770	<i>b</i>
$[(\pi\text{-Cp})_2\text{TiH}_2]^-$	6.5	~ 7		1.992	<i>c, d</i>
$[(\pi\text{-Cp})_2\text{Ti}(\text{CH}_3)_2]^-$	9.6	~ 4.2		1.990	<i>c, d</i>
$(\pi\text{-Cp})_2\text{TaH}_2^g$	66	n. r.	30	2.006	<i>b</i>
$(\pi\text{-CH}_3\text{Cp})_2\text{Ta}(\text{CH}_3)_2$	93	n. r.	17	1.993	<i>b</i>
$(\text{DMPE})_2\text{TaH}_4^g$	106.3	32.9 ^g	18	1.992	<i>b</i>
$(\pi\text{-Cp})_2\text{Ta}(\text{C}_6\text{H}_5)_2$	93.6	n. r.	25	1.988	<i>b</i>

^a Hyperfine coupling constants and isotropic g factors are all corrected to second order using the Briet-Rabi equation. ^b This work. ^c H. Brintzinger, ref 9. ^d J. G. Kenworthy, J. Myatt, and P. F. Todd, *J. Chem. Soc. B*, 791 (1970). ^e Assignment uncertain. ^f See ref 11. ^g ³¹P quintet. ^h ± 0.0005 or ± 0.001 .

trometer,^{5,6} affords the spectrum shown in Figure 1. The



triplet hyperfine structure arises from coupling between the electron and two hydrogen nuclei, further split into ten lines by one niobium nucleus as verified by the accompanying computer-simulated spectrum. Furthermore, the triplet splitting is readily assigned to the two equivalent protons attached to the niobium nucleus, since it is absent in the esr spectrum of the deuterium analog generated from Cp_2NbD_3 under the same conditions as listed in Table I. The esr spectrum of the transient paramagnetic dihydride, II disappears upon shuttering the light at 0°, but the species is significantly longer lived at lower temperatures. The intensity of the spectrum decays quite rapidly on further irradiation. In both cases, the resonance is gradually replaced by others, all resulting from species containing a single niobium nucleus.⁷ Although the spectrum of II may be expected to show small coupling to the cyclopentadienyl hydrogens,⁸ they are probably unresolved due to the rather large quadrupole moment of niobium leading to line broadening. In the absence of DTBP, no reaction is observed at room temperature over a period of days.

A thermal reaction which also produces paramagnetic niobium-containing species is observed when isobutylene is mixed with a solution of I in benzene and cyclopropane at room temperature in a sealed tube. The ready formation of paramagnetic species by this simple perturbation of I clearly shows that one-electron processes are facile and can compete with other (two-electron) processes.¹⁰ The esr spectrum of the transient niobium species III obtained under these conditions consists of a coupling to a single niobium nucleus ($a_{\text{Nb}} = 68.5$ G) and a single proton ($a_{\text{H}} = 11.6$ G). We were also able to generate the same species by reaction of I with *tert*-butylmagnesium bromide as shown in Figure 2. Believing that III might be dicyclopentadienyl-*tert*-butylniobium hydride, we were prompted to investigate the synthesis and stability of the corresponding dialkyl derivatives V from dicyclopentadienylniobium dichloride IV.¹¹

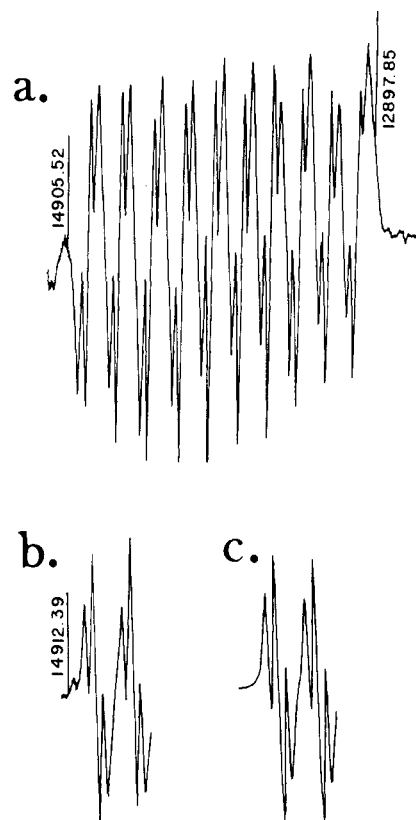
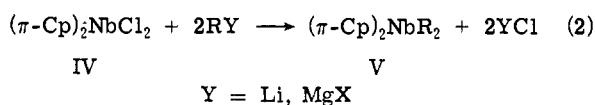


Figure 1. (a) ESR spectrum of Cp_2NbH_2 obtained during the reaction of Cp_2NbH_3 with *tert*-butoxy radicals at -80° , (b) $m_{\text{Nb}} = \frac{1}{2}$ and $\frac{3}{2}$ lines under higher resolution, (c) computer simulation of (b). Proton nmr field markers are in kilohertz.

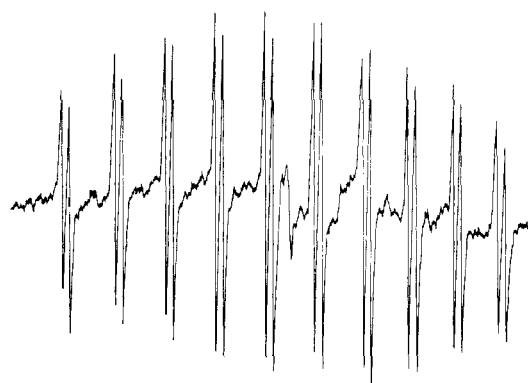


Figure 2. ESR spectrum obtained during the reaction of Cp_2NbH_3 with *tert*-butylmagnesium bromide at ambient temperatures.

Indeed, upon adding methyllithium or methylmagnesium bromide to an ethereal solution of IV, the esr spectrum disappears and is immediately replaced by a new spectrum shown in Figure 3, which shows hyperfine splitting to one niobium nucleus and six equivalent protons due to two methyl groups as indicated by the correct binomial intensity ratio in the simulated spectrum. Furthermore, the same behavior was observed using perdeuteriomethylithium, although the deuteron splittings were unresolved.¹² The esr spectra are unambiguously assigned to V [$\text{R} = \text{CH}_3$ or CD_3], since $(\pi\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CH}_3)_2$ can be isolated from the reaction mixture as a dark red crystalline solid which shows the same spectrum.¹³ The niobium splitting of 88.8 G in the corresponding diphenyl analog, $(\pi\text{-Cp})_2\text{Nb}(\text{C}_6\text{H}_5)_2$,¹⁴ which is readily generated in a similar manner from phenyllithium, is in accord with the methyl derivatives, although the couplings to the protons in the phenyl ring were unre-

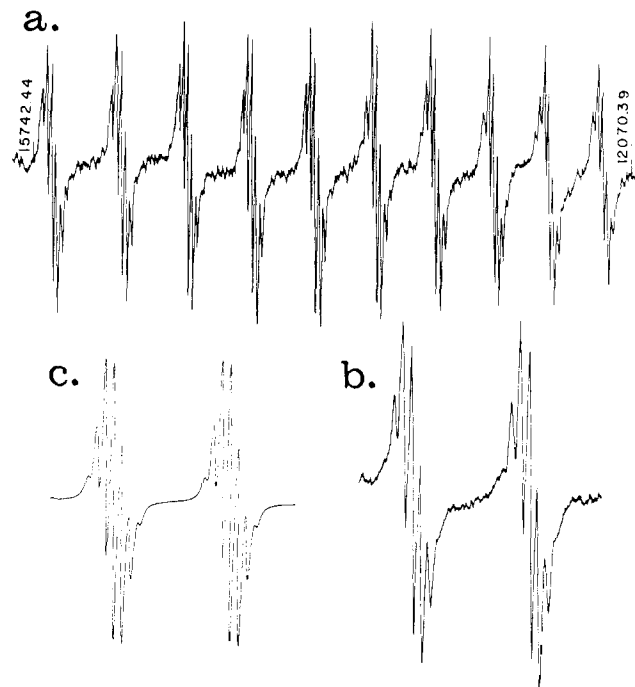


Figure 3. (a) ESR spectrum of $Cp_2Nb(CH_3)_2$ from Cp_2NbCl_2 and methylolithium, (b) central multiplet ($m_1 = \pm 1/2$) at higher resolution, (c) computer simulation of (b).

solved. In contrast to these observations, the addition of an ethyl or *tert*-butyllithium or Grignard reagent to a solution of $(\pi-C_5H_5)_2NbCl_2$ readily collapsed the esr signal of IV without the appearance of a new spectrum corresponding to that of a dialkyniobium(IV) species. We conclude that the expected dialkyl species are quite unstable as shown previously for similar alkyl derivatives of dicyclopentadienylniobium(III) susceptible to β -elimination.^{9,15}

The tantalum analogs to the niobium species described above showed similar behavior, but were generally less reactive. Thus, photolysis of a solution of $(\pi-C_5H_5)_2TaH_3$ and DTBP at -50° , afforded a spectrum consisting of eight lines ($a_{Ta} = 66$ G), but the line widths of 30 G precluded the observation of smaller hyperfine splittings. By analogy with the niobium compounds it is reasonable to assign the spectrum to that of a paramagnetic tantalum(IV) dihydride. Similarly the esr spectrum of $(\pi-CH_3C_5H_4)_2Ta(CH_3)_2$, a dark red solid, afforded a spectrum showing only tantalum hyperfine coupling. Unfortunately the line width of 17 G obscured any further splittings.

Finally, treatment of $[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2TaH_5$ ³ with photochemically generated *tert*-butoxy radicals afforded an esr spectrum showing hyperfine coupling to one tantalum nucleus and a quintet due to coupling with four equivalent nuclei with $I = 1/2$. The magnitude of the splitting suggests that the quintet arises from the phosphorus coupling.

The esr parameters for the niobium(IV) and tantalum(IV) compounds are summarized in Table I along with those of the analogous titanium(III) compounds. It can be seen that an increase in the metal hyperfine splitting in going from the dihydride to the dimethyl species is common for the three metals. A description of the bonding in these interesting species in the light of the Fenske-Hall model for MO calculations¹⁶ will be deferred.¹⁷

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- (11) Subsequent studies suggest that III is a different derivative of dicyclopentadienylniobium(IV). Unpublished results (I. H. Elson).
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Structure Control in Organic Metals. Synthesis of Tetrathiofulvalene and Its Charge Transfer Salt with Tetracyano-*p*-quinodimethane¹

Sir:

Considerable interest has been shown recently in the study of highly conducting organic charge transfer salts.² The most attractive of these systems is the salt formed between tetrathiofulvalene (TTF, **1**) and tetracyano-*p*-quinodimethane (TCNQ, **2**), which displays exceptional electrical conductivity ($\sigma_{max, 58^\circ K}$ ca. 10^4 (Ω cm)⁻¹) and metallic-like behavior over a wide temperature range.^{3,4} Further, a few "anomalous" crystals of TTF-TCNQ have been reported to exhibit a giant conductivity maxima.^{4,5} Attempts have been made to enhance the metallic properties of the tetrathiofulvalenium radical cation by substitution of electron releasing substituents.⁶ However, such substitution distorts the original TTF-TCNQ crystal structure in an unpredictable way,⁷ obscuring the electronic effect of the substituent on the solid state properties. In order to improve upon the metallic properties of fulvalenium systems in a more definable and controllable fashion, we have synthesized tetrathiofulvalene (TSeF, **3**) and its charge transfer salt with