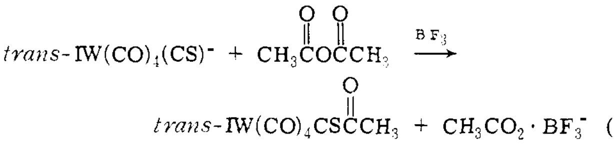
lized upon addition of diethyl ether and cooling. The complex reacts with methyl fluorosulfonate (eq 2) or triethyloxonium tetrafluoroborate to give neutral, pentane-soluble products.

$$\textit{trans}\text{-IW(CO)}_4\text{(CS)}^- + CH_3SO_3F \longrightarrow \textit{trans}\text{-IW(CO)}_4\text{(CSCH}_3\text{)} + SO_3F^- \quad (2)$$

These reactions differ from the reported reaction[9] of $IW(CO)_5^-$ with Et_3O^+ in which EtI is produced. The product of the methyl fluorosulfonate reaction in CH_2Cl_2 was isolated in low yield by removing the solvent at reduced pressure, extracting the residue with pentane, and crystallizing at −80°. The complex[10] is quite air-sensitive in solution but more stable in the solid state. The ν(CO) peaks occur at relatively high frequencies in the ir spectrum, and the thiocarbonyl ν(CS) absorption appears (Table I) as a sharp peak of medium intensity nearly 80 cm^{-1} lower than in the thiocarbonyl anion, **3**. The complex exhibits a singlet in its NMR spectrum at τ 7.40, and an abundant parent ion is observed in its mass spectrum.

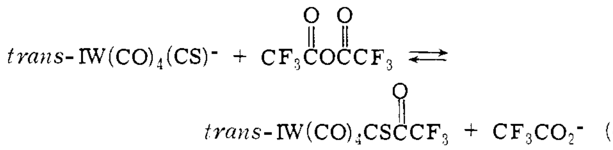
Although **3** does not react with acetic anhydride in CH_2Cl_2, the reaction does proceed in the presence of BF_3 (eq 3). The neutral *S*-acetylthiocarbonylium complex[11] has



$$\textit{trans}\text{-IW(CO)}_4\text{(CS)}^- + CH_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{BF_3} \textit{trans}\text{-IW(CO)}_4CS\overset{O}{\overset{\|}{C}}CH_3 + CH_3CO_2\cdot BF_3^- \quad (3)$$

ν(CO) bands (Table I) at higher frequencies than the methylated derivative, and the thiocarbonyl ν(CS) absorption is lowered by more than 110 cm^{-1} relative to that of **3**. The splitting seen in the strong ν(CO) E band and the appearance of a B_1 band suggest that the asymmetric acylthiocarbonylium ligand causes some distortion of the local C_{4v} symmetry of the complex.[12] Only a singlet at τ 7.60 is observed in its proton NMR spectrum at room temperature, and the acyl carbonyl ν(CO) absorption is seen as a sharp peak at 1753 cm^{-1}.

Trifluoroacetic anhydride also reacts with **3** to yield a similar product (eq 4). When carried out in CH_2Cl_2 the ir spectrum shows complete consumption of the starting complex, but removal of the solvent under reduced pressure also removes the trifluoroacetic anhydride, reversing the reaction and leaving mainly **3**. When the reaction is carried out in pentane, in which the trifluoroacetate salt product is insoluble, the solution may be concentrated and cooled to −80° to yield yellow crystals. This product is quite unstable, and the crystals darken even on standing in the mother liquor under N_2 at −80°. An elemental analysis was not attempted, but the high-resolution mass spectrum supports the assigned formula.[13] The acyl carbonyl exhibits a single band at 1737 cm^{-1}. Although the ν(CS) absorption could not be located because of the strong C-F absorption, its very high-frequency metal carbonyl ν(CO) bands[14] show that the *S*-trifluoroacetylthiocarbonylium ligand is a strong electron acceptor.



$$\textit{trans}\text{-IW(CO)}_4\text{(CS)}^- + CF_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CF_3 \rightleftarrows \textit{trans}\text{-IW(CO)}_4CS\overset{O}{\overset{\|}{C}}CF_3 + CF_3CO_2^- \quad (4)$$

Analogous *O*-alkylcarbonylium and *O*-acylcarbonylium complexes derived from metal carbonyl complexes are unknown.[16] That the reactions of *cis*-W(CO)(CS)(DPE)$_2$ with alkylating agents yield only the S-alkylated $W(CO)(DPE)_2(CSR)^+$ products shows that the sulfur of the CS group is more nucleophilic than the oxygen of the carbonyl. While the carbonyl groups in *cis*-W(CO)$_2$(DPE)$_2$ should be somewhat more nucleophilic than the CO in $W(CO)(CS)(DPE)_2$ (because of the greater π acidity of CS relative to CO), alkylating agents still do not react with a carbonyl oxygen but at the metal instead.

In metal carbonyl chemistry CO stretching frequencies or force constants are useful indicators of the electron density on the carbonyl oxygen atom.[17] The electron density on the sulfur of a metal thiocarbonyl complex is apparently influenced in much the same manner. Our results indicate that metal thiocarbonyl complexes with ν(CS) absorptions below approximately 1200 cm^{-1} will be reactive toward electrophiles such as those described in this and our preceding communication.[1] Complexes with ν(CS) frequencies above this value have been found not to react.

Acknowledgment. We are grateful for support of this research through a National Defense Education Act (Title IV) fellowship to B.D.D. and for a grant from the NATO Research Grants Program to R.J.A.

References and Notes

(1) B. D. Dombek and R. J. Angelici, *J. Am. Chem. Soc.*, **96**, 7568 (1974).

(2) Anal. Calcd for $[(DPE)_2(CO)W(CSCH_3)]SO_3F$: C, 56.60; H, 4.37; S, 5.49. Found: C, 56.35; H, 4.42; S, 5.71. All other new compounds reported, except $IW(CO)_4CSC(O)CF_3$, analyzed correctly for at least three elements.

(3) Anal. Calcd for $[(DPE)_2(CO)W(CSC_2H_5)]BF_4$: C, 57,53; H, 4.54; S, 2.74. Found: C, 57.72; H, 4.90; S, 2.27.

(4) J. Chatt and H. R. Watson, *J. Chem. Soc.*, 4980 (1961).

(5) K. Edgar, B. F. G. Johnson, J. Lewis, and S. B. Wild, *J. Chem. Soc. A*, 2851 (1968).

(6) F. L. Wimmer, M. R. Snow, and A. M. Bond, *Inorg. Chem.*, **13**, 1617 (1974).

(7) J. A. Connor, G. K. McEwen, and C. J. Rix, *J. Less-Common Met.*, **36**, 207 (1974).

(8) B. D. Dombek and R. J. Angelici, *J. Am. Chem. Soc.*, **95**, 7516 (1973).

(9) J. A. Connor, J. P. Day, E. M. Jones, and G. K. McEwen, *J. Chem. Soc., Dalton Trans.*, 347 (1973).

(10) Anal. Calcd for $IW(CO)_4(CSCH_3)$: C, 14.93; H, 0.62; I, 26.35. Found: C, 14.19; H, 0.7; I, 25.99. The $IW(CO)_4(CSEt)$ complex was characterized only by its analogous infrared spectrum.

(11) Isolated in 10% yield after three crystallizations from pentane. Anal. Calcd for $IW(CO)_4CSC(O)CH_3$: C, 16.47; H, 0.59; I, 24.90. Found: C, 16.15; H, 0.54; I, 25.70.

(12) J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 389 (1965).

(13) Calcd for $^{182}WI(CO)_4CSC(O)CF_3$: 561.7905. Found: 561.7924 ± 0.0028.

(14) For comparison, $IW(CO)_4C(C_6H_5)$ has infrared bands at 2119 m and 2037 vs cm^{-1}.[15]

(15) E. O. Fischer, G. Kreis, C. G. Kreiter, J. Müller, G. Huttner, and H. Lorenz, *Angew. Chem., Int. Ed. Engl.*, **12**, 564 (1973).

(16) Recently D. F. Shriver, D. Lehman, and D. Strope (*J. Am. Chem. Soc.*, submitted for publication) prepared $HFe_3(CO)_{10}(COCH_3)$ with an O-alkylated bridging carbonyl group.

(17) D. F. Shriver and A. Alich, *Inorg. Chem.*, **11**, 2984 (1972).

B. Duane Dombek, Robert J. Angelici*
Department of Chemistry, Iowa State University
Ames, Iowa 50010

Received December 4, 1974

Interaction of Paramagnetic Niobium(IV) Hydrides with Olefins. Electron Spin Resonance Studies of Metastable Intermediates

Sir:

We wish to describe a useful method to probe for *transient* species present during the reaction of paramagnetic metal complexes with olefins, involving the application of careful temperature modulation to electron spin resonance (ESR) techniques. Although a variety of catalytic reactions of olefins involve transition metal hydrides and alkyls as intermediates, due to their transitory existence little is known about the actual metal species participating in these reactions.[1] We have felt that metastable paramagnetic metal

Table I. ESR Parameters of Nb(IV) Species Derived from the Interaction of $(C_5H_5)NbH_2$ with Isobutylene, Propylene, and Ethylene

Species[a]	Structure [proposed]	Hyperfine splitting[b] (G)		Linewidth[c] (G)	$\langle g \rangle$[d]
		A_M	A_H		
I	$(C_5H_5)_2NbH_2$	45.9	11.7 (t)	6.0	2.0097
I	$(C_5H_5)_2NbD_2$	45.4	<2	7.6	2.0095
X	$[(C_5H_5)_2Nb]$	103		8.0	1.9894
II B[e]	$[(C_5H_5)_2NbH_2(=\!\!<)]$	68.1	10.5 (t)	4.0	2.0036
B[e]	$[(C_5H_5)_2NbD_2(=\!\!<)]$	68	nr	22	2.004
P[e]	$[(C_5H_5)_2NbH_2(=\!\!/)]$	69.2	10.8 (t)	5.4	2.004
E[e]	$[(C_5H_5)_2NbH_2(=)]$	~68	~10 (t)	j	j
III B[e]	$[(C_5H_5)_2NbH(:\!\!>\!\!-)]$	67.2	10.3 (d)	6.2	2.001
B[e]	$[(C_5H_5)_2NbD(:\!\!>\!\!-)]$	67	nr	22	2.001
P[e]	$[(C_5H_5)_2NbH(:\!\!>)]$	69.1	11.3 (d)	4.7	2.001
VP[f]	$[(C_5H_5)_2Nb(C_3H_7)_2]$	84	nr	14	1.997
g	$(C_5H_5)_2Nb(CH_3)_2$	88.8	6.3 (s)	3.7	1.9984
g	$(C_5H_5)_2Nb(C_6H_5)_2$	88.8	nr	9.0	1.9982
h	$[(C_5H_5)_2Nb(O\text{-}t\text{-}Bu)_2]$	127		20.0	1.95
g	$(C_5H_5)_2NbCl_2$	116.5		12.0	1.9970
i	$[(C_5H_5)_2Nb(Cl)H]$	97.6	12.8 (d)	11.0	j

[a] Key: B = isobutylene, P = propylene, and E = ethylene. [b] Key: t = 1:2:1 triplet, d = 1:1 doublet s = binomial septet, nr = not resolved. [c] Peak to peak. [d] Corrected to second order using the exact solution to the Breit–Rabi equation: ±0.0005, ±0.001, or ±0.01. [e] $(C_5H_5)_2 = (\eta^5\text{-}Cp)(\eta^3\text{-}Cp)$. [f] Footnote 10. [g] Footnote 4. [h] Footnote 5a. [i] Footnote 11. [j] Not measured.

complexes may play important catalytic roles.[2] The early transition metal complexes such as those derived from tantalum and niobium are effective catalysts[3] and applicable to mechanistic studies by ESR because they have large nuclear magnetic moments and nuclear spin quantum numbers, both of which give rise to well-resolved and characteristic splitting patterns (e.g., $I(^{93}Nb) = 9/2$).[4]

The paramagnetic $(C_5H_5)_2Nb^{IV}H_2$ species I, generated by abstraction of hydrogen from the diamagnetic $(C_5H_5)_2NbH_3$ with *tert*-butoxy radical,[4] has a half-life of at least 10 min in cyclopropane-benzene solutions at −70°. The ESR spectrum of I disappears within a few seconds on warming the solution to 0° and is replaced by what we believe is monomeric niobocene X (vide infra),[5] showing only resolved splitting to a single niobium nucleus.

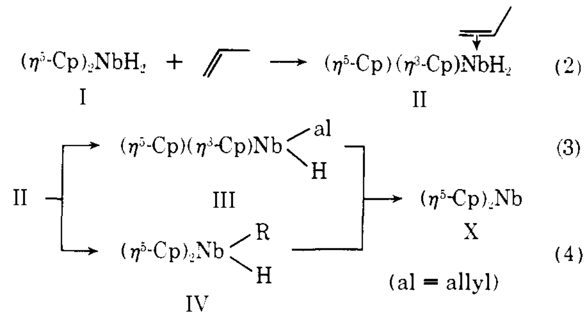
$$(C_5H_5)_2NbH_3 \longrightarrow \underset{\text{I}}{(C_5H_5)_2NbH_2} \longrightarrow \underset{\text{X}}{(C_5H_5)_2Nb} \qquad (1)$$

The same experiment carried out with isobutylene replacing cyclopropane also affords an intense spectrum of I as shown in Figure 1a. However, on raising the temperature of this solution (in the absence of irradiation), the spectrum of I disappears and is replaced by that of a second species IIB shown in Figure 1b having the same splitting pattern as I (i.e., a decet of triplets) but showing markedly different hyperfine constants (Table I). On further warming, the spectrum of IIB gradually disappears, and it is replaced simultaneously by that of a third species IIIB (decet of doublets in Figures 1c,d) and finally by the spectrum of X (shown in Figure 1e). The triplet splittings in both I and IIB and the doublet splittings in IIIB are clearly associated with couplings to two and one hydrogens, respectively, which were originally bonded to niobium, since no such splittings are observed when $(C_5H_5)NbD_3$ is treated under the same conditions.[6]

It must be emphasized that *tert*-butoxy radical provides only the means to generate high concentrations of I, and the observation of niobium(IV) species is not dependent on its presence. Thus, a thermal reaction between Cp_2NbH_3 and isobutylene themselves induces similar changes shown in Figure 2, and the observation has direct bearing on the importance of these paramagnetic species in catalytic reactions.

Ethylene and propylene react with $(C_5H_5)_2NbH_2$ significantly faster than isobutylene. Thus, the spectra of I and the ethylene adduct IIE can only be observed fleetingly at less than −100°. Similarly, propylene affords the propylene adduct IIP at −70°. The progression of spectral changes described above with each olefin (varying in facility), all finally terminate with the appearance of the spectrum of X.

Scheme I



The transient nature of the foregoing paramagnetic Nb(IV) intermediates preclude their isolation. However, the hyperfine splittings and *g* factors provide a basis for discussing their identity, and for purposes of stimulating further investigation we propose that the facile changes of I, II, III, etc. to X are due to coordination of olefin, rearrangement and reductive elimination as outlined in Scheme I.[7] According to this scheme the differences among olefins lie in equilibrium 2[8] but more importantly in the rates of the insertion-rearrangement steps 3 and/or 4. Isobutylene and propylene afford species III which we tentatively attribute to a hydrido(π-allyl)niobium(IV) species since it is absent with ethylene. The insertion product IV has not yet been observed probably due to a rapid reductive elimination.[9-11] The isotropic *g* factors provide a further basis for the structure assignment of these paramagnetic niobium(IV) species. Thus, the Nb and Ta hydride species in Table I all have *g* factors larger than those of the corresponding dialkyl species, roughly in proportion to the number of hydrido ligands.[12]

The confirmation of the structures presented here would require isolation of the intermediates. However, the ESR studies show the transitory nature of most of these species, and it is doubtful whether they would be isolable in pure form. For example, the species we have ascribed to niobocene has been isolated only as a diamagnetic dimer.[3] Although the ready dimerization of niobocene and its susceptibility to oxidative addition[15] is anticipated, we hope that

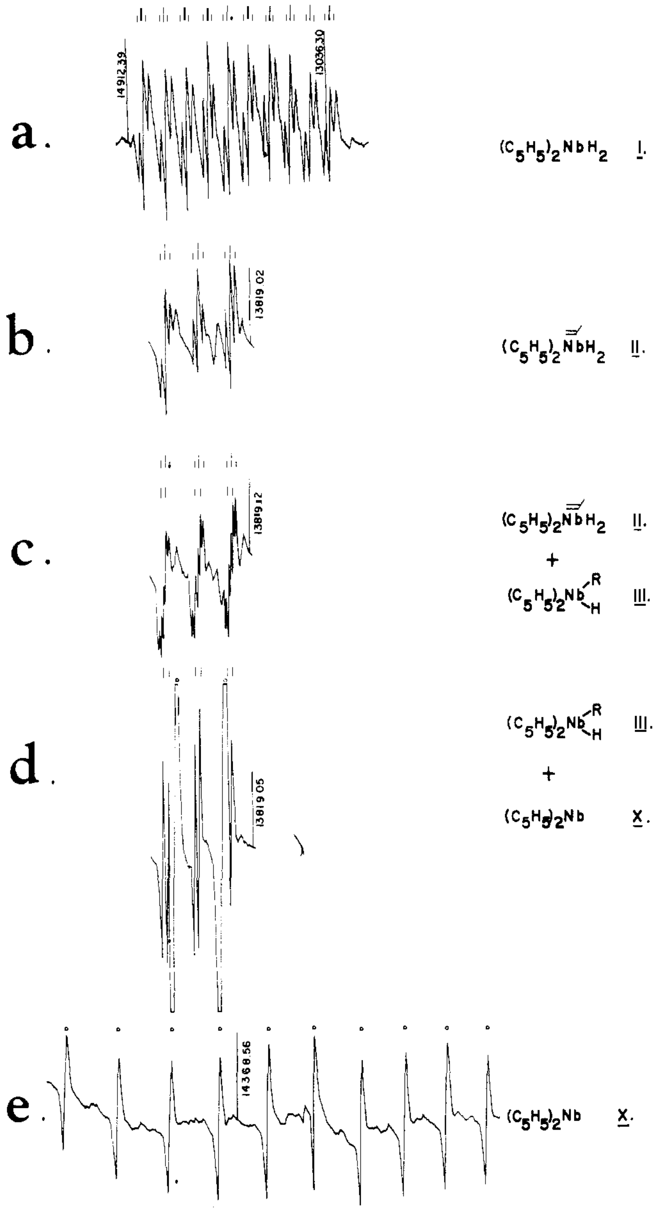


Figure 1. ESR spectral changes occurring during the reaction of $(C_5H_5)_2NbH_2$ with isobutylene at (a) −70°, (b) −37°, (c) −10°, (d) 25°, and (e) on standing. For clarity only selected lines corresponding to m_I = ½, ³⁄₂, and ⁵⁄₂ of the decet Nb splitting are shown in (b), (c), and (d). Sweep widths are the same in all the spectra. Proton NMR field markers are in kHz. In (d) and (e) lines marked with open circles are due to species X.

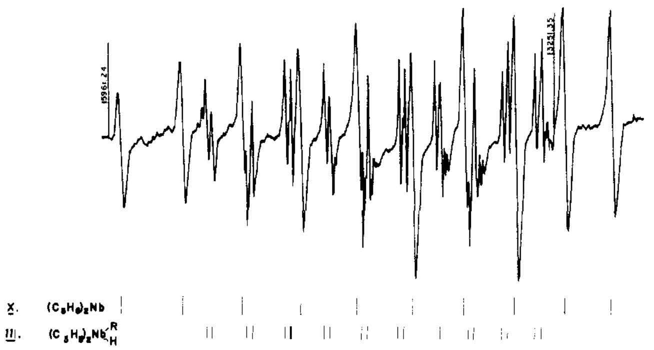


Figure 2. ESR spectrum obtained during the thermal reaction of Cp_2NbH_3 and isobutylene at 25° in cyclopropane-benzene solution. Two species clearly present are IIIb and X, in addition to minor amounts of other niobium(IV) species.

the information obtained from these ESR studies will provide us with optimum conditions for its eventual isolation, either as a crystalline substance or in an inert matrix.[16]

References and Notes

(1) J. Chatt, *Adv. Organometal. Chem.*, **12**, 1 (1974); H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, **72**, 231 (1972).
(2) J. K. Kochi, *Acc. Chem. Res.*, **7**, 351 (1974).
(3) F. N. Tebbe and G. W. Parshall, *J. Am. Chem. Soc.*, **93**, 3792 (1971); F. B. Tebbe, *ibid.*, **95**, 5823 (1973).
(4) I. H. Elson, J. K. Kochi, U. Klabunde, L. E. Manzer, G. W. Parshall, and F. N. Tebbe, *J. Am. Chem. Soc.*, **96**, 7374 (1974).
(5) (a) In addition to a species showing Nb splitting of 127 G (g = 1.95) formed only in the presence of di*tert*-butyl peroxide and assigned to $(C_5H_5)_2Nb(O\text{-}t\text{-}Bu)_2$ (vide infra). (b) The reversible addition of molecular hydrogen to titanocene and its analogs has been described by J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *J. Am. Chem. Soc.*, **94**, 1219 (1972).
(6) The unresolved deuterium splitting of ⅙. the proton splitting is within the linewidth (7.6 G).
(7) Depending on the location of the coordinated olefin in II, the pair of hydrogens attached to Nb will or will not be magnetically equivalent. Any differences in the latter case are not resolved within the spectral linewidths.
(8) We were unable to observe the corresponding equilibrium for $(C_5H_5)_2Nb(CH_3)_2$ and were unable to induce any such changes with ultraviolet radiation.
(9) Species III could be formed from II by loss of hydrogen. Deuterium labeling studies show that only one of the hydrogens attached to Nb is lost; the other may be lost from the allylic position of the olefin. However, except for slight differences in linewidths, the data are insufficient to distinguish III from IV rigorously. Since there is more precedence for the pathway via IV,[3] it may be necessary to change the spectral assignments from III to IV, if a choice is necessary. The failure to observe the species from ethylene may then be attributed to its instability.
(10) Propylene and I also produce a species V (which we ascribe to $CpNb(Pr)_2$ by comparison with the g factors of other $Cp_2Nb(alkyl)_2$ in Table I) derivable from IV by addition of a second propylene.
(11) The stability of alkyl- and dialkylniobium(IV) species was examined in the metathesis of $(C_5H_5)_2NbCl_2$ and alkyllithium reagents. Although the dimethyl derivative is sufficiently stable to isolate,[4] ethyl and *tert*-butyl analogs were not. Instead the reaction of $(C_5H_5)_2NbCl_2$ and *tert*-butyl Grignard or *tert*-butyllithium afforded a species with a single niobium and proton which could be $(C_5H_5)_2NbH(Cl)$, derived by β-elimination of the chlorobutyl intermediate.
(12) What is more significant is that the g factors for the hydrides of tantalum and niobium are greater than the free-spin value g_ε of 2.0023, whereas the g factor of the dimethyl species is less than free spin. Theoretically, the difference Δg (where $g_{obsd} = g_\varepsilon + \Delta g$) is inversely related to the difference in orbital energies.[13] The large positive deviation in Δg observed in the hydrides can be attributed, thus, to the mixing between the half-filled orbital and a bonding Nb–H σ orbital of *lower* energy. Such an interaction could lead to increased lability of the hydride ligands. On the other hand, the low g factors in the dialkyl and dichloro species is attributable to excitation of the odd electron into an empty orbital of *higher* energy and not into a bonding metal–alkyl or metal–chloro orbital. In this respect the behavior of tantalum and niobium differs markedly from that of the isoelectronic analogs of titanium.[14]
(13) (a) A. J. Stone, *Proc. R. Soc. London, Ser. A*, **271**, 424 (1963); (b) P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals", Elsevier, New York, N.Y., 1967.
(14) H. H. Brintzinger, *J. Am. Chem. Soc.*, **89**, 6871 (1967); J. E. Bercaw and H. H. Brintzinger, *ibid.*, **91**, 7301 (1969).
(15) The spectrum ascribed to niobocene X is not observed if organic halides and reactive peroxides are present. For example, in the presence of vinyl fluoride, vinylidene fluoride, tetrafluoroethylene, methyl chloride, and bis(trifluoromethyl) peroxide, the spectrum of X is not observed but is replaced by those of other paramagnetic species.
(16) Acknowledgment. We wish to thank the National Science Foundation for financial support and Dr. F. N. Tebbe for samples of Cp_2NbH_3 and Cp_2NbD_3.

Ian H. Elson, J. K. Kochi*
Department of Chemistry, Indiana University
Bloomington, Indiana 47401
Received October 29, 1974

A Synthesis of *d,l*-Muscone from Cyclododecanone

Sir:

We wish to disclose here an efficient synthesis of *d,l*-muscone (V) from the readily available cyclododecanone (I).[1] The ring expansion sequence employs consecutive two- and one-carbon ring homologations and allows the controlled introduction of substituents on the final macrocycle.