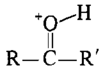
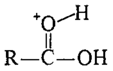
Table I. Relative Ion Stabilities and ^{13}C Chemical Shift of the Carbonyl Carbon in Protonated Ketones and Carboxylic Acids

R	R′	pK^a	ΔH_{R_1} (kcal/mol)^b	$\delta_{^{13}C}$, RCOR′^{c}	$\delta_{^{13}C}$, $RC(={}^+OH)R'^d$
					
Me	Me	−7.2	−19.1 ± 0.1	−12.3	−55.7
Me	C_6H_5	−6.2 (−4.32)^e	−18.9 ± 0.2	−3.2	−25.8
C_6H_5	C_6H_5	−6.2 (−4.97)^e	−16.9 ± 0.3	−2.4	−15.4
					
Me		−6.10^f		15.6^g	1.6^g
C_6H_5		−7.38^f		19.7^g	12.0^g

[a] Data from E. M. Arnett, *Prog. Phys. Org. Chem.*, **1**, 223 (1963). [b] Data from ref 8. [c] J. B. Stothers and P. C. Lauterbur, *Can. J. Chem.*, **42**, 1563 (1964). [d] In parts per million from $^{13}CS_2$; data from ref 2b,c. [e] Data from ref 6. [f] Data from M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957). [g] In parts per million from $^{13}CS_2$; data from G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, 89, 7072 (1967).

Table II. Relative Ion Stability and ^{13}C Chemical Shifts for the Acyl Carbon in $R{-}{}^+C{\equiv}O$

R	ΔH^a (kcal/mol)	$\delta_{^{13}C}$,^{b} RCOCl	$\delta_{^{13}C}$, $R{-}{}^+C{\equiv}O^c$
Me	−21.3 ± 0.2	23.8	44.3
C_6H_5	−15.9 ± 0.3	25.0	40.0

[a] Heat of transfer from CCl_4 to 11.5 mol % SbF_5 in FSO_3H_2, both at 25 °C, measured calorimetrically as before: J. W. Larsen, P. A. Bouis, M. W. Grant, and C. A. Lane, *J. Am. Chem. Soc.*, **93**, 2067 (1971); E. M. Arnett and J. W. Larsen, "Carbonium Ions", Vol. 1, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N.Y., 1968. [b] In parts per million from CS_2; data from ref *c* (Table I). [c] In parts per million from CS_2; data from reference in *g* (Table I).

least stable. The $\delta_{^{13}C}$ (or $\Delta\delta_{^{13}C}$) indicates that the highest charge density on the carbonyl carbon is to be found in protonated acetone, the most stable ion. The ion with the lowest charge density and presumably the greatest amount of charge delocalization is the least stable. The picture is complicated somewhat if pK values for the ketones are used. These give the same basicity for acetophenone and benzophenone, both being more basic than acetone. The basicity order expected from the ^{13}C measure of charge delocalization ($C_6H_5COC_6H_5$ > $C_6H_5COCH_3$ > CH_3COCH_3) is not observed. However, a recent very careful determination shows that acetophenone is slightly more basic than benzophenone.[6] The difference between these values and the older ones is a good illustration of the experimental difficulties encountered. From Arnett's work,[7] one expects pK and ΔH to show the same behavior. There are two possible explanations for the discrepancy. One is the notorious difficulty in measuring accurate pK values for simple ketones using acidity function techniques.[8] The other is large solvation differences resulting in a large variation in the entropy of protonation. We feel the calorimetric data are more reliable. The same trends are seen with protonated carboxylic acids and acylium ions. The acyl cation data led Olah to state "This positive charge is better delocalized in the benzoyl than in either the acetyl or propionyl systems". It makes no difference whether the $\delta_{^{13}C}$ or $\Delta\delta_{^{13}C}$ on ion formation is used, the results are still the same.

These data do not indicate which of the generalizations is breaking down. The effect of solvent in these systems may be important and a comparison of gas phase and solution behavior would be most interesting, albeit complicated by the possibility of protonating the aromatic ring in the gas phase.[9] Discussion of this will be deferred to a full paper now in preparation.

The notion that charge delocalization results in increased stability stands near to the heart of organic chemistry. Likewise, the use of $\delta_{^{13}C}$ has proved a very powerful tool for investigating charge densities in a variety of molecules, one which is being used with increasing frequency and circumspection. It is clear that some rather stringent limitations will have to be placed on one of these.

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Nonaqueous Reductive Lanthanide Chemistry. 1. Reaction of Lanthanide Atoms with 1,3-Butadienes[1]

Sir:

The known chemistry of the lanthanide elements is rather limited when compared with the chemistry of the transition metals. The variety of ligands found in complexes of the lanthanide metals is small,[2] and nearly all the chemistry centers on the +3 oxidation state.[3] In efforts to demonstrate experimentally a broader chemistry for the lanthanide metals, we have begun an investigation of the nonaqueous reductive chemistry of these elements. Specifically, we wish to determine if lower oxidation states are accessible in insolable complexes or obtainable transiently in reactions centering on these metals. We anticipate that the lanthanide metals in lower oxidation states will display unusual and perhaps unique chemistry which can be exploited in general synthetic schemes as well as in the synthesis of lanthanide complexes.

The metal atomization technique has been shown to be a useful method for the synthesis of low and zero valent transition metal complexes of low stability[4,5] and we describe here the use of this technique to make a new class of organolanthanide complexes. Metal atomization has previously been employed preparatively with lanthanide metals to synthesize the trivalent molecules $Nd_2^{3+}(C_8H_8^{2-})_3$,[6] $Ln^{3+}(acac^-)_3$,[7] and

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Table I

	Elemental anal., %			Magnetic susceptibility		
	Metal	C	H		$10^6\chi_M$, cgs	μ_{eff} (295 K)
				$Er(C_4H_6)_3$ (I)		
Calcd	50.76	43.74	5.51	Typical[a] for Er^{3+}		9.4-9.6
Found	50.56	43.47	5.60	found for I	35 500	9.1
				$Er[(CH_3)_2C_4H_4]_2$ (II)		
Calcd	50.46	43.49	6.08	Typical for Er^{3+}		9.4-9.6
Found	50.09	43.15	6.14	found for II	37 500	9.4
				$Nd(C_4H_6)_3$ (III)		
Calcd	47.06	47.02	5.92	Typical for Nd^{3+}		3.3-3.7
Found	47.29	47.18	6.10	found for III	5 700	3.7
				$Sm(C_4H_6)_3$ (IV)		
Calcd	48.09	46.10	5.80	Typical for Sm^{3+}		1.4-1.7
Found	47.88	45.73	5.90	found for IV	1 800	2.1
				$La[(CH_3)_2C_4H_4]_2$ (V)		
Calcd	45.82	47.53	6.65	Typical for La^{3+}		0
Found	45.39	*b*	*b*	found for V	930	1.6

[a] Observed in $Ln_2(SO_4)_3{\cdot}8H_2O$, Ln_2O_3, $Ln(C_5H_5)_3$, etc.[3] [b] Carbon and hydrogen analyses were incomplete for V, the least stable of the series.[9,13]

$Ln^{3+}(C_5H_5^-)_3$[8] from the metal and cyclooctatetraene, acetylacetone, and cyclopentadiene, respectively.[9] We were interested in organic reactants which were not readily reducible to anions familiar in organolanthanide chemistry[14] and have isolated and investigated the products of reactions with 1,3-butadiene and its 2,3-dimethyl-substituted derivative.

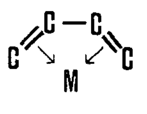
Cocondensation of 1,3-butadiene with erbium metal at −196 °C in a reactor of the Timms' design[15] produces a matrix of brown solids which upon warming is only slightly soluble in the excess diene present. Following removal of excess butadiene in vacuo, extraction of the reaction mixture with toluene and tetrahydrofuran (THF) gives two distinct brown products. The major product (I), isolated in 20% yield (based on Er vaporized), is the THF-soluble complex which by combustion analysis has empirical formula $Er(C_4H_6)_3$ (Table I). When erbium is cocondensed with dimethylbutadiene, three compounds can be differentiated by their solubility in pentane, toluene, and THF. The major product (II) is again the THF-soluble complex, but in this case a 2:1 stoichiometry is found by elemental analysis: II analyzes for $Er[(CH_3)_2C_4H_4]_2$.

We have synthesized a variety of such lanthanide organometallics, including $Nd(C_4H_6)_3$ (III) and $Sm(C_4H_6)_3$ (IV), from 1,3-butadiene and the appropriate metal, and $La[(CH_3)_2C_4H_4]_2$ (V), from 2,3-dimethyl-1,3-butadiene and lanthanum. With the exception of the thermally less stable lanthanum complex (V) we have been able to obtain complete analytical data for this new series of lanthanide compounds, a feature which is somewhat unusual for organolanthanides.[16,17] Our preliminary studies on other unsaturated organic substrates as well as other metals suggest that this synthetic approach will be of general use in obtaining new classes of isolable complexes of the f orbital metals.

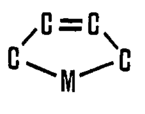
The complexes I-V are oxidatively and hydrolytically very unstable. The brown-colored solutions of these complexes in THF decolorize immediately on exposure to air with subsequent polymerization. The volatile products of hydrolytic decomposition include 2-butenes, 1-butenes, and octadienes, with the 2-butene usually predominating. For example, room temperature hydrolysis of $Er[(CH_3)_2C_4H_4]_2$ produces 2,3-dimethyl-2-butene (60%) with smaller amounts of tetramethyloctadiene (20%).[18] 2,3-Dimethyl-2-butene is also the primary volatile product of the thermal decomposition of II, which begins to occur at 120 °C in vacuo.[20,21]

The near-infrared and visible spectra of complexes I-V do not contain the usual sharp absorption bands characteristic of trivalent lanthanide ions. Instead a broad intense band with maximum beyond the ultraviolet region extends into the visible region of each spectrum and dominates any other absorptions.[22] Similarly, the room temperature magnetic susceptibilities of I-V (Table I) are not entirely consistent with susceptibilities previously measured for trivalent lanthanide species. The most striking differences are observed for $Sm(C_4H_6)_3$ and for $La[(CH_3)_2C_4H_4]_2$ which we believe to be the first reported paramagnetic organolanthanum complex. Neither NMR[23] nor mass spectroscopy[24] has been useful in characterizing these complexes.

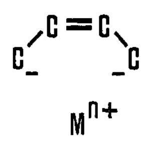
Examination of previously reported metal butadiene complexes shows that the lanthanide species I-V are unique. Three possible descriptions (A-C) of the metal-butadiene interaction are shown.



A



B



C

The purely ionic structure (C) is often postulated in alkali metal[25] or alkaline earth[26] polymerizations of butadiene. Such a structure can be eliminated for I-V since these complexes are stable to polymerization in the presence of excess diene, and since sharp free ion optical spectra are not observed.

Both structure A, in which the metal is formally zero valent, and structure B, which contains a dialkyl moiety coordinated to a metal with formal positive charge, have been used to describe metal-diene bonding in simple transition metal-butadiene complexes, $M(C_4H_6)_x$. Tentative bonding arguments, based on hydrolytic decomposition reactions, suggest that $Ni(C_4H_6)_2$ is best described by A since butadiene is released upon hydrolysis,[27] and that $Cr(C_4H_6)_3$ has more dialkyl character since it forms primarily 1-butene upon hydrolysis.[19,28] $Al(C_4H_6)_3$ similarly forms 1-butene when hydrolyzed.[29] The lanthanide-butadiene complexes are singular in that 2-butenes are prominent hydrolysis products. On this basis, type B bonding might seem appropriate, but structures involving purely type B bonding cannot readily be assigned to I-V since the stoichiometry would require a lanthanide metal with a formal charge of +4 for the dimethylbutadiene complexes and +6 for the butadiene derivatives.[30] Knowledge of the precise mixture of type A and type B bonding in I-V as well as the degree of oligomerization will require an x-ray crystallographic determination. It is clear, however, that these lanthanide–butadiene complexes represent a new class of organolanthanide compounds.

These results suggest to us that a variety of organic species previously thought to be of little use as ligands for lanthanide metals will interact with these elements to form isolable complexes. Moreover, we expect the ligand chemistry to be observed will be distinct from that found for other organometallic systems. We are actively pursuing these ideas.

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(1) Presented in part at the Second Joint Conference of the Canadian Institute of Chemistry and the American Chemical Society, Montreal, June 1, 1977.

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(17) Analytical data were obtained from A. Bernhardt Microanalytical Laboratory, D-5250 Engelskirchen, West Germany, and Pascher Microanalytical Laboratory, D-Buschstrasse 54, 5300 Bonn, West Germany.

(18) Approximately 10% conversion at room temperature; cf. 16% conversion for transition metal–butadiene complexes.[19] Hydrolytic decomposition product mixtures vary depending on the decomposition temperature, e.g., at 0 °C a higher proportion of 1-butene is observed.

(19) P. S. Skell, D. L. Williams-Smith, and M. J. McGlinchey, *J. Am. Chem. Soc.*, **95,** 3337 (1973).

(20) Decomposition of other lanthanide–diene complexes is initially observed at the following temperatures: $Nd(C_4H_6)_3$, 175 °C; $Nd[(CH_3)_2C_4H_4]_2$, 190 °C; $Er(C_4H_6)_3$, 100 °C; $Sm(C_4H_6)_3$, 130 °C; $La[(CH_3)_2C_4H_4]_2$, 80 °C.

(21) Hydrogenation of $Er[(CH_3)_2C_4H_4]_2$ in THF solution with 10% palladium on charcoal for 16 h at 3.5 atmH_2 decomposes only 20% of the compound producing ~60% C_6 species and 30% higher molecular weight products. Hydrogenation of 2,3-dimethyl-1,3-butadiene in THF solution under the same conditions produces complete conversion to 2,3-dimethylbutane within 3 h.

(22) $Er[(CH_3)_2C_4H_4]_2$ (II): 800 nm (ϵ60), 600 (200), 400 (1300), no maxima. For several of these complexes, some small broad bands are observed in the visible and near-infrared regions superimposed on the intense band. These small bands are displaced from 10–30 nm from the position of 4f–4f transitions observed for the corresponding $Ln(C_5H_5)_3$, $LnCl_3$, etc., and are considerably broader. Sharp trivalent absorptions are observed upon partial decomposition/reaction of the complexes with appropriate reagents. Broad absorption spectra have previously been described for organolanthanides but only in the visible region of the spectrum.[16c]

(23) NMR spectroscopy is usually useful for the characterization of organolanthanide complexes of diamagnetic La^{3+} and paramagnetic Nd^{3+} and Sm^{3+} (R. G. Hayes and J. L. Thomas, *Organomet. Chem. Rev., Sect. A.*, **7,** 1 (1971)). For the diene complexes of these metals, however, we have not observed any comparably sharp, assignable resonances over a 300-ppm range by FTNMR spectroscopy. This result is consistent with the other unusual physical properties displayed by these complexes and is not due to limited solubility.

(24) These complexes are insufficiently volatile for mass spectral analysis.

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(30) Structures in which the metal is trivalent can be envisioned if the butadiene ligands oligomerize. Such structures require very low coordination numbers for the metal centers, which is inconsistent with the thermal stabilities of I–V.

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Nonaqueous Reductive Lanthanide Chemistry. 2. Conversion of *cis,cis*-1,5-Cyclooctadiene to Cyclooctatetraenyl Dianion by Reduced Praseodymium and Potassium

Sir:

We recently have described the synthesis of a new class of organolanthanide complexes obtained from 1,3-butadienes and vaporized lanthanide metal atoms as part of a general investigation of the nonaqueous reductive chemistry of the lanthanide elements.[1] Concurrently with the metal vaporization studies we have endeavored to develop solution syntheses of lanthanide complexes in which a reduced oxidation state of the metal is involved. Since our previous results suggested that a variety of unsaturated organic molecules would be useful in organolanthanide chemistry, we have continued with such reactants in our solution studies. We report here preliminary results of an investigation of the reductive chemistry of $PrCl_3$ which has led to a facile laboratory-scale synthesis of the cyclooctatetraenyl dianion, $C_8H_8^{2-}$, from the readily available *cis,cis*-1,5-cyclooctadiene (1,5-C_8H_{12}).

Anhydrous $PrCl_3$[2,3] (2.5 g, 10 mmol) is reduced by potassium (1.2 g, 30 mmol) in tetrahydrofuran (THF) at reflux in ~4.5 h to form a black slurry. Removal of THF from this slurry by filtration[4] gives a gray powder which reacts with 1,5-C_8H_{12}[5] (45 mL, 366 mmol) over a period of several days at room temperature. After removal of excess 1,5-C_8H_{12}, the reaction residue is extracted with THF to give an intensely colored red-brown solution from which ~1.0 g[6] of a red-brown solid, I, is isolable. I is not particularly stable, decomposing slowly in an inert atmosphere at room temperature. Spectral, magnetic, and analytical data on I were not definitive owing to this decomposition; hence simple chemical decomposition was examined to minimally identify carbon fragments present. Oxidative decomposition of I in benzene-d_6 gave almost exclusively 1,3,5,7-cyclooctatetraene, C_8H_8[7]! Soxhlet extraction with diethyl ether of samples of I which are partially decomposed gives yellow solids which have infrared and NMR spectra[8] which match those reported for $K_2C_8H_8$,[9] but which by elemental analysis[10] contain praseodymium, possibly as $K[Pr(C_8H_8)_2]$.[11,12] In further confirmation of the presence of $C_8H_8^{2-}$, I is observed to slowly react with UCl_4 at room temperature to form uranocene, $U(C_8H_8)_2$.[13,14] Although the mechanisms of formation of I and its subsequent decomposition

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