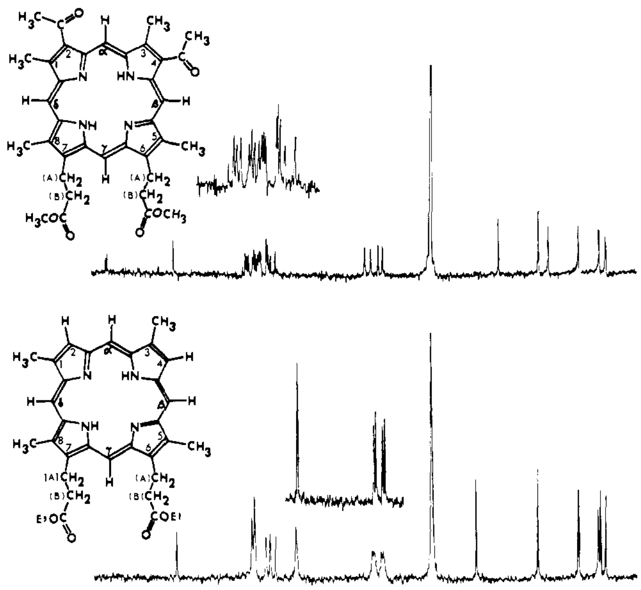

Figure 1. Proton-decoupled natural-abundance carbon-13 Fourier transform nmr spectra at 42° and 15.08 MHz of chloroform solutions of: top, 2,4-diacetyldeuteroporphyrin IX dimethyl ester (**3**) (0.15 *M* and 2886 scans) with the proton decoupling frequency set at about 4 ppm in the proton spectrum (insert, expansion of the region for the nonprotonated carbons of the pyrrole rings); bottom, deuteroporphyrin IX diethyl ester **2** (0.31 *M*, 530 scans) with the proton decoupling frequency set at about 4 ppm in the proton spectrum (insert, same as the bottom spectrum but with the proton decoupling frequency set at about 1 ppm in the proton spectrum). All spectra were recorded with a 90° pulse recycle time of 5.43 sec. The region shown is from −11.5 to 193.0 ppm from neat carbon disulfide. The intense resonance at 115.4 ppm is from the solvent.

information in support of this proposal is apparent from an inspection of the spectrum of the pyrromethene derivative **7**, where the bridging olefinic carbon resonates at 72.6 ppm. This carbon is in the same structural environment as the meso positions in the porphyrins, yet it resonates some 20 ppm downfield from them. This is consistent with a significantly reduced resonance interaction between the two pyrrole rings by the bridging carbon in **7** relative to that expected in a porphyrin.

Inspection of the spectra of **3** (Figure 1) and **4** reveals that the acetyl and propionyl groups, respectively, have removed the degeneracy[12] of the C-1,3 and C-5,8 methyl resonances encountered in the spectra of the other derivatives studied. In the case of **3**, separate resonances are observed for *all* methyl resonances, whereas in **4** some broadening of the methyl resonances was noted. A similar, but smaller, effect has been noted in studies of the pmr of these compounds[4d] and it has been proposed[13] that such side-chain groups exist in a preferred geometry with the methyl groups at C-1,3 trans to the carbonyl oxygen. Such a geometry would place the methyl groups in nonequivalent steric environments and could be responsible for the observed shift differences. However, a subtle electronic effect would be difficult to rule out.[12]

Although intermolecular ring current effects can be dismissed as being the cause of the pronounced upfield shift of the meso positions, and it is apparent that the shift can be considered as a consequent of inner ring resonance, it is difficult to decide what the effect of the resultant large ring current has on the resonance position of these nuclei located directly on the periphery of this ring. At first glance one would guess that no conventional ring current effect would be observable because one is crossing from a shielding to a deshielding region. However, conventional ring current shift equations[14] are based on the premise that one can factor the wave function of the group causing the shift from that being shifted.[15] Clearly this is impossible for *any* position on the porphyrin ring and further theoretical work needs to be done in this area.[16]

The chemical shifts reported in this study will be useful in ^{13}C investigations of diamagnetic heme proteins and other porphyrin derivatives. It is envisaged that the meso positions will be important in such studies because they fall in a region of the spectrum relatively free from overlap with other carbons.

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(12) It should be noted that in all the porphyrin derivatives studied, the C-1,3 and C-5,8 methyls are structurally nonequivalent but appear to give rise to only two resonance lines, except in 3 and 4 where four separate resonances are encountered.

(13) W. S. Caughey, to be published.

(14) J. D. Memory, "Quantum Theory of Magnetic Resonance Parameters," McGraw-Hill, New York, N. Y., 1968, p 111.

(15) A similar approximation is used in the derivation of equations describing the screening from a group of atoms possessing anisotropy in their magnetic susceptibility: H. M. McConnell, *J. Chem. Phys.*, 27, 226 (1957).

(16) Grant and coworkers have also briefly discussed this problem: A. Jones, T. D. Alger, D. M. Grant, and W. M. Litchman, *J. Amer. Chem. Soc.*, **92**, 2386 (1970).

(17) Contribution No. 2028.

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Transition Metal Bicyclo[2.2.1]hept-1-yls

Sir:

Neutral compounds in which transition metals are attached only to saturated hydrocarbon ligands undergo thermal decomposition if processes such as α or β elimination of metal hydride, homolysis, or coupling of ligands at the transition metal atom occur.[1-4] Bridged or fused alicyclic ring systems of appropriate geometry are rather inert to β elimination, homolysis, or nucleophilic displacement of substituents bonded to bridgehead carbons.[5-7] These characteristics enable

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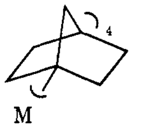
Table I. Bicyclo[2.2.1]hept-1-yl Transition-Metal Compounds

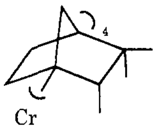
					Mol wt, g/mol		—Thermolysis—		Decomposition at room temperature[f]	
Formula	Starting material	Product color	Yield,[b] %	μ_{eff}	Cryoscopic	Theor	Half-life	Temp, °C[e,f]	0.1 M H_2SO_4 in dioxane	Air in isooctane
Nor_4Ti	$TiCl_4 \cdot 2THF$	Yellow	90	0 BM[c]	384	429	29 hr	100	20%/day	Stable
Nor_4V	VCl_4	Purple	14	1.82[d]			10.2 hr	100	70%/day	70%/day
Nor_4Cr	$CrCl_3 \cdot 3THF$	Red-brown	71	2.84[c]	441	432	7.6 hr	250	Stable	Stable
Nor_4Mn	$MnBr_2$	Green	62	3.78[c]	477	435	13.7 min	100	On contact	50%/day
Nor_4Fe	$FeCl_3 \cdot OEt_2$	Purple	50	0[c]	418	436	30 hr	23	50%/day	60%/day
Nor_4Co	$CoCl_2 \cdot 1.5THF$	Brown	47	2.00[c]	416	439	8.7 min	100	On contact	7%/day
Nor_4Zr[a]	$ZrCl_4 \cdot 2OEt_2$	Lt pink	88	0.46[d]			>1 wk	23	On contact	On contact
Nor_4Hf[a]	$HfCl_4 \cdot 3OEt_2$	Lt pink	86	0.46[d]			>1 wk	23	On contact	On contact
$(1\text{-Cam})_4Cr$	$CrCl_3 \cdot 3THF$	Red-brown	51	2.96[d]			39 min	115	Stable	Stable
$(4\text{-Cam})_3Cr$	$CrCl_3 \cdot 3THF$	Green	61	3.52[d]			>1 wk	23	On contact	On contact

[a] Preparations contain a purple, paramagnetic impurity. [b] Based on alkyllithium. [c] Nmr method (J. L. Deutsch and S. M. Poling, *J. Chem. Educ.*, **46**, 167 (1969)). [d] Gouy balance. [e] In oxygen-free decalin solution; half-lives the average of two determinations; first-order kinetics assumed. [f] Followed spectrophotometrically.

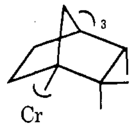
the preparation of exceptionally stable transition metal alkyls.[8] We now report the synthesis and characterization of R_4M and R_3M compounds in which R is a bicyclo[2.2.1]hept-1-yl and M is a first-, second-, or third-row transition metal. Some well-characterized examples are tetrakis(1-norbornyl)hafnium, -zirconium, -titanium, -vanadium, -chromium, -manganese, -iron, and -cobalt compounds (denoted Nor_4M), as well as tetrakis(2,3,3-trimethylbicyclo[2.2.1]hept-1-yl)chromium ($(1\text{-Cam})_4Cr$) and tris(2,2,3-trimethylbicyclo[2.2.1]hept-1-yl)chromium ($(4\text{-Cam})_3Cr$).



Nor_4M, M = Hf, Zr, Ti, V, Cr, Mn, Fe, Co



$(1\text{-Cam})_4Cr$



$(4\text{-Cam})_3Cr$

Reaction of alkyllithiums with transition-metal halides on tumbling with glass beads in pentane, filtration (except in the cases of Nor_4Zr, Nor_4Hf, and $(4\text{-Cam})_3Cr$) of pentane solutions of products through a column of alumina, followed by recrystallization from pentane, gave the crystalline compounds listed in Table I.

Elemental analyses for lithium, halide, transition metal, carbon, and hydrogen were consistent with the formulas assigned. Mass spectra of Nor_4Cr, Nor_4Mn, and $(1\text{-Cam})_4Cr$ contained peaks at m/e values corresponding to tetraalkyls, while peaks at highest m/e in the mass spectra of Nor_4Ti and Nor_4Zr corresponded to the loss of one ligand. Photolyses of the norbornyl metals in pentane (or hydrolyses in the cases of Nor_4Zr and Nor_4Hf) were shown to give quantitative yields of norbornyl as norbornane or 1,1′-binorbornane by gas chromatographic and mass spectroscopic analysis of the degradation products.

During the reactions of di- or trivalent Cr, Mn, Fe, and Co halides with 1-norbornyllithium, negatively charged complexes probably form and undergo oxidation by other transition-metal species present. The high ligand field strength of a tertiary carbanion ligand and the inability of pentane solvent to serve as a ligand may be factors leading to disproportionation. This hypothesis is reminiscent of the findings of Owen and Hawthorne[9] that a biscarboranyldilithium and $CoCl_2$ in diethyl ether gave an anionic Co^{II} complex which could be oxidized by $CuCl_2$ in methylene chloride to a Co^{III} compound. A Cr^{III} product results in the case of 4-camphyllithium because the two β-methyl substituents give ligand interrepulsions which do not allow four 4-camphyls simultaneously to be close enough to form strong bonds to Cr^{IV}. Analogously, the reaction of lithium diethylamide with chromium trichloride is reported to give tetrakis(diethylamido)chromium, while the bulkier lithium diisopropylamide and chromium trichloride give the corresponding trisamidochromium.[10,11]

The tetranorbornyls of Hf, Zr, Ti, and V are expected to be tetrahedral complexes by analogy to the tetrachlorides of these metals. Preliminary X-ray crystal-structure data and epr spectra indicate tetrahedrally arranged norbornyls in Nor_4Cr. Ligand interrepulsions would favor a tetrahedral, as opposed to tetragonal, ligand arrangement in the cases of Mn, Fe, and Co tetranorbornyls as well. Magnetic data indicate that no d electrons are spin paired in the d^2 and d^3 complexes Nor_4Cr and Nor_4Mn, whereas four of the d electrons of Nor_4Fe and Nor_4Co are paired.

An indication of the stabilities of some bridgehead bicycloheptyl transition metal compounds under three sets of experimental conditions is given by the data of Table I. The question of whether attack of a reagent occurs on the metal–carbon bond or on thermolytic intermediates has not been resolved by experiment. However, molecular models suggest that small reagents cannot penetrate the coordination spheres of tetranorbornyls of first-row transition elements. The visible

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spectra of Nor$_4$Ti through Nor$_4$Co were negligibly changed on substituting pyridine for isooctane as solvent, indicating that at least pyridine is too bulky to fit in among four norbornyls. A greater transition metal ionic radius, as in the cases of Nor$_4$Zr and Nor$_4$Hf compared to fourth period tetravalent compounds, or three bicycloheptyl ligands instead of four, as in the case of (4-Cam)$_3$Cr compared to (1-Cam)$_4$Cr or Nor$_4$Cr, would give a sterically more open coordination sphere and tend to favor attack of sufficiently small reagents on the metal-carbon bonds.

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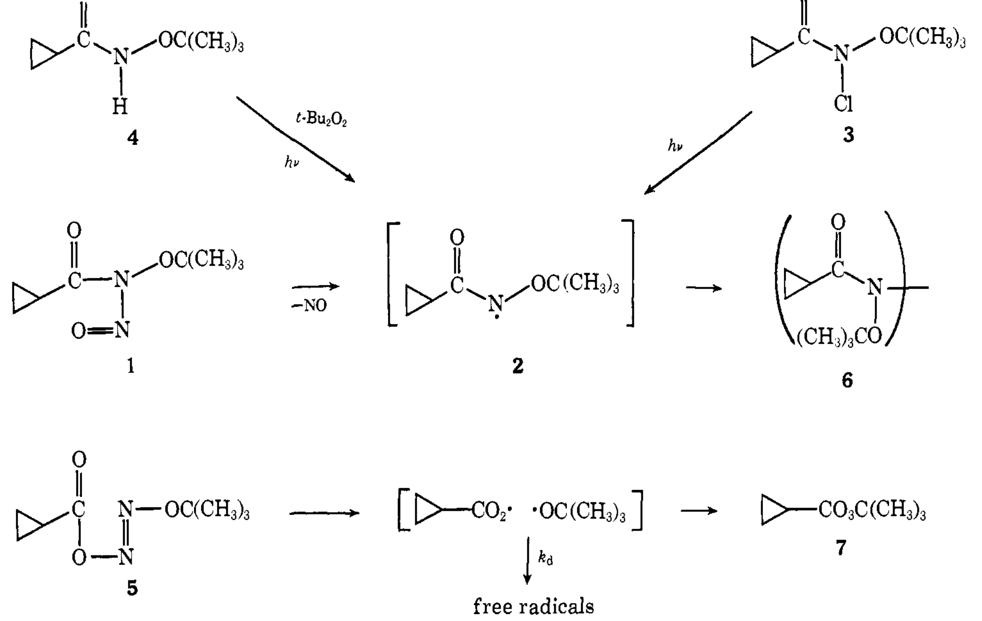
Thermal Decomposition of *N*-Nitrosohydroxylamines. V. Denitrosation and *N-tert*-Butoxyamido Radicals

Sir:

We wish to report the direct observation of the esr spectra of several *N-tert*-butoxyamido radicals. The *N*-cyclopropanecarbonyl member of this series, **2**, has been observed by warming the corresponding *N*-nitrosohydroxamate (**1**), by direct photolysis of the corresponding *N*-chloro compound **3**, and by photolysis of di-*tert*-butyl peroxide in the presence of the hydroxamate (**4**) itself.



In the foremost case, the denitrosation is in competition with rearrangement to the corresponding *O*-acyl *O'-tert*-butyl hyponitrite[1] (**5**) which is the major (78%) reaction pathway. The products, isolated from the overall decomposition of **1** after 1.5 hr at 32° in carbon tetrachloride solution (0.2 *M*), include a 14% yield (0.07 mol/mol of **1**) of the dimeric hydrazine[2] **6** and a 15% yield of the perester **7**. When this product mixture is allowed to stand at room temperature overnight, the dimer **6** is partially converted to *tert*-butyl cyclopropanecarboxylate.[3] When 1 *M* styrene is added initially, the yield of dimer is 22% (by nmr) after 1.5 hr and subsequent decomposition is slow. The perester yield for the present case is greater (18%) than that previously found for the benzoyl analog (13%)[1] when the 22% side reaction is taken into account. This result indicates that factors such as the rate constants for the combination process are more important than the radius of the diffusing species in determining the diffusion-combination ratio.

Direct confirmation of the presence of the *N-tert*-butoxyamido radical **2** was obtained when the reaction was carried out in the cavity of a Varian E-3 spectrometer. Warming cold solutions of the nitroso compound **1** in the cavity immediately gave a three-line (1:1:1) spectrum which grew in intensity as the temperature increased. Essentially identical spectra were obtained when the corresponding *N*-chloro compound **3** was photolyzed directly or when solutions containing di-*tert*-butyl peroxide and the parent hydroxamate **4** were irradiated with a focused 100-W high-pressure mercury light source using quartz or thin-wall Pyrex sample tubes. The latter method was used to obtain spectra of a series of such amido radicals. The results are summarized in Table I.

The observed *g* values are slightly larger than those recently reported[4] for *N*-alkoxyamino radicals (2.006 *vs.* 2.005). The a_N values are somewhat smaller ($\sim$10 *vs.* $\sim$14 G). The magnitude of the reduction compares with changes observed when an acyl group replaces an alkyl group in nitroxides.[5] Both variations are in the direction expected for a π-amido radical

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(3) If the 1.5-hr product solution is washed with dilute aqueous hydroxide and dried, the dimer no longer disappears so rapidly. Cooley[2] has already reported on the synthesis and acid-catalyzed reactions of this class of substituted hydrazines. We have found that **6** is formed in essentially quantitative yield through treatment of the *N*-chloro compound **3** with an ether solution of the sodium salt of **4**. The *N*-chloro compound **3** is readily obtained from **4** and *tert*-butyl hypochlorite over solid potassium carbonate.

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