Table I

Radical source[a]	Radical trapped	Hyperfine coupling of nitroxide[b] A_N	A_β^H
Phenylazotriphenylmethane	$C_6H_5\cdot$	13.84	2.09
		13.72[c]	2.08[c]
		13.73[d]	2.06[d]
Dibenzylmercury	$C_6H_5CH_2\cdot$	13.88	2.44
Trifluoromethyl iodide	$CF_3\cdot$	13.30	1.54[e]
Dimethylmercury	$CH_3\cdot$	14.20	3.45
		14.15[c]	3.41[c]
		14.19[d]	3.44[d]
Diethylmercury	$C_2H_5\cdot$	14.00	3.19
		13.93[c]	3.21[c]
Di-*n*-butyllead diacetate	$C_4H_9\cdot$	13.95	3.10
		13.94[c]	3.10[c]
		14.04[d]	3.04[d]
Lead tetraacetate	$CH_3COO\cdot$	12.84	1.73
Benzoyl peroxide	$C_6H_5COO\cdot$	12.76	1.40

[a] See text for other sources. [b] A Varian 4502 epr spectrometer was used. Coupling constants were calculated using the Fieldial calibrations with an error of 0.05 gauss maximum deviation from the average of three or more determinations. A low-pressure mercury lamp and quartz cell were used. [c] Nitroxide produced by addition of the appropriate organolithium to PBN followed by reaction with oxygen. [d] Nitroxide produced by *p*-nitroperbenzoic acid oxidation of the appropriate secondary amine. [e] A_γ^F = 1.54 gauss.

In all experiments the concentration of PBN was approximately 0.03 *M* in benzene. In a 0.003 *M* PAT solution the nitroxide concentration was approximately 5.6×10^{-5} *M* after 40 min at room temperature. This accounts for approximately 80% of the phenyl radicals produced.[6] Phenyl radicals produced from PAT are also trapped in other solvents such as toluene, xylene, nitrobenzene, benzonitrile, acetonitrile, aqueous acetonitrile, dimethyl sulfoxide, methylene chloride, carbon tetrachloride, and dioxane. However, in solvents reactive toward phenyl radicals, *e.g.*, dioxane or carbon tetrachloride,[7] the triphenylmethyl radical spectrum is diminished and other radicals (presumably derived from solvent) are trapped by PBN in addition to phenyl. This indicates that PBN competes favorably with triphenylmethyl for reactive radicals (at least at concentrations where $[PBN] \cong 10^2\text{–}10^3[(C_6H_5)_3C\cdot])$.

This method provides a means of readily obtaining answers for a number of interesting questions in free-radical chemistry, two of which are illustrated. (1) It can be concluded from the results of photolyses of a large number of phenyl- and alkylorganometallic acetates and chlorides (Pb, Sn, Hg) that bond cleavage preferentially follows the sequence $C_6H_5 > n\text{-Bu} > CH_3COO > Cl$ if approximately equal trapping efficiency of PBN is assumed. (2) Since at this time we have no reason not to expect the adduct of $Pb(OAc)_3$[8] and the nitrone to be stable, we can conclude that the lifetime of lead triacetate radical is shorter than the lifetime of the acetoxy radical. In fact, no evidence for the presence of other trivalent lead radicals has been obtained. However, in the photolysis of organotin compounds sometimes more than one type of radical was trapped. The identification of the structures of these radicals is being attempted.

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Edward G. Janzen, Barry J. Blackburn
Department of Chemistry, The University of Georgia
Athens, Georgia 30601

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(7) R. F. Bridger and G. A. Russell, *ibid.*, **85**, 3754 (1963).

(8) (a) E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *ibid.*, **90**, 1082 2706 (1968); (b) J. K. Kochi, *ibid.*, **87**, 3609 (1965), and references therein.

Tricyclopropylaluminum Dimer

Sir:

Several recent studies have shown that electron-deficient, three-centered bridge bonds in group III organometallic compounds are stabilized by the presence of π orbitals on the hydrocarbon moiety. It has been suggested[1] that in trivinylgallium dimer the bridge bonds are stabilized due to an interaction between the nonbonding molecular orbital of the three-centered bridging system with the π orbitals of the vinyl group. Evidence for this type of interaction has also been obtained from the crystal structure of triphenylaluminum[2] and from the nmr studies on dimethyl(phenylethynyl)aluminum and dimethyl(*p*-tolyl)aluminum.[3] These studies have further demonstrated that this enhanced stability slows the exchange rate between the bridge and terminal positions in the dimeric species; but even then, at room temperature exchange is rapid on the nmr time scale for all but the phenylethynyl derivative.

We now wish to report that tricyclopropylaluminum dimer appears to have the most stable hydrocarbon bridges so far reported in group III derivatives. This implies that the cyclopropylaluminum system possesses unique bonding characteristics wherein additional π-type interactions explain the unusual stability of the compound.

Tricyclopropylaluminum was prepared by the exchange reaction

$$3Hg(C_3H_5)_2 + Al_2(CH_3)_6 \rightleftharpoons Al_2(C_3H_5)_6 + 3Hg(CH_3)_2$$

It was driven to completion by heating with excess dicyclopropylmercury[4] and removal of the more volatile products *in vacuo*. The remaining white solid was zone refined to give the product, mp 58–61°, in 70% yield. Hydrolysis of a 0.224-g sample gave 4.23 mmoles of cyclopropane and 1.37 mg-atoms of Al (calculated 4.5 mmoles of cyclopropane and 1.5 mg-atoms of Al). The molecular weight determined cryoscopically in cyclohexane was 310 ± 15 (calcd for $Al_2(C_3H_5)_6$, 300).

In Figure 1 the 100-MHz nmr spectrum of tricyclopropylaluminum at room temperature is shown. The spectrum may be interpreted as representing two kinds of cyclopropyl groups in an integrated ratio of 2:1 which correspond to the cyclopropyl groups in the terminal and bridging positions, respectively. The assignments of the regions labeled B_1, B_2, B_3, and T_1, T_2, T_3 are based on the magnitudes of the various coupling constants (Table I) and a comparison of these values with those obtained from the analyses of the nmr spectra of other cyclopropylmetal compounds.[5] One observes from

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(1) H. D. Visser and J. P. Oliver, *J. Am. Chem. Soc.*, **90**, 3579 (1968).

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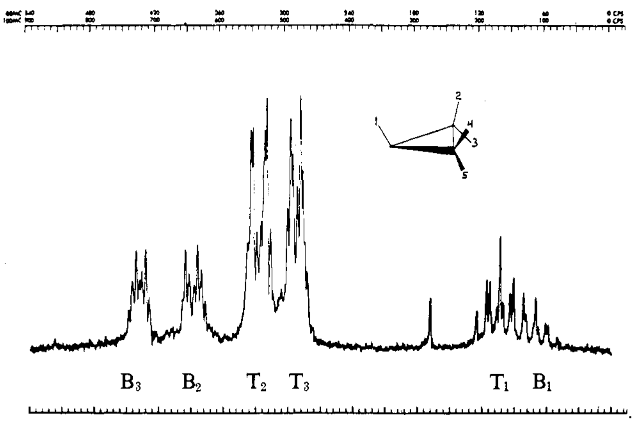

Figure 1. The 100-MHz nmr spectrum at room temperature of tricyclopropylaluminum dimer in benzene. Protons of the cyclopropyl group are labeled as shown. Regions are labeled B for bridging, T for terminal; subscript 1 corresponds to proton 1, subscript 2 to protons 2 and 4, subscript 3 to protons 3 and 5.

the assignments in Figure 1 that in the bridging cyclopropyl groups protons 3 and 5 are deshielded more than 2 and 4, while proton 1 is shielded more than any other proton in the molecule. The gross differences in chemical shift may be explained by the inductive effect which the electrophilic molecular orbitals of the bridging system exert on the cyclopropyl group and by the magnetic effects associated with other cyclopropyl groups in the molecule. The unusual upfield shift of the B_1 protons may be interpreted as resulting from shielding effects associated with the close proximity of the nucleus to (1) the relatively electron-rich bridge bond and (2) the second bridging cyclopropyl group.

Table I. Approximate Chemical Shifts and Coupling Constants for Bridge and Terminal Cyclopropyl Groups in Tricyclopropylaluminum

	δ, ppm[b]			J, cps	
Proton[a]	Bridge	Terminal		Bridge	Terminal
1	3.70	3.44	$J_{1,2}$	9.3	10.3
			$J_{1,3}$	7.5	7.7
			$J_{1,4}$	9.3	10.3
2	1.05	1.60	$J_{1,5}$	7.5	7.7
			$J_{2,3}$	−2.6	−3.0
3	0.65	1.89	$J_{2,4}$	8.5	8.0
			$J_{2,5}$	5.8	4.4
4	1.05	1.60	$J_{3,4}$	5.8	4.4
			$J_{3,5}$	8.3	7.6
5	0.65	1.9	$J_{4,5}$	−2.6	−3.0

[a] Protons are designated as in Figure 1. [b] δ relative to methyl resonance of toluene for a 12% solution in toluene at 35°.

The model proposed to account for these effects is shown in Figure 2, assuming the Walsh[6] model for cyclopropane. The formation of the bridge bond is proposed to be through two types of interaction: (1) the overlap of the sp^2 orbital of the cyclopropyl group with the sp^3 orbitals from the aluminum atoms to give a σ-type three-center bonding molecular orbital somewhat analogous to that proposed for diborane and trimethylaluminum dimer;[7] and (2) the interaction between the p (π-type) orbital of the cyclopropyl group and the three-centered nonbonding molecular orbital.

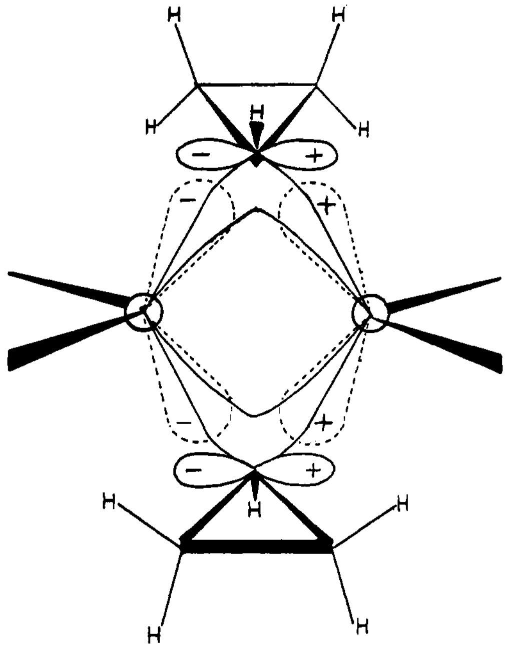

Figure 2. Proposed model for the structure and bonding in tricyclopropylaluminum dimer. The nonbonding MO (dotted line) is superimposed on the bonding MO.

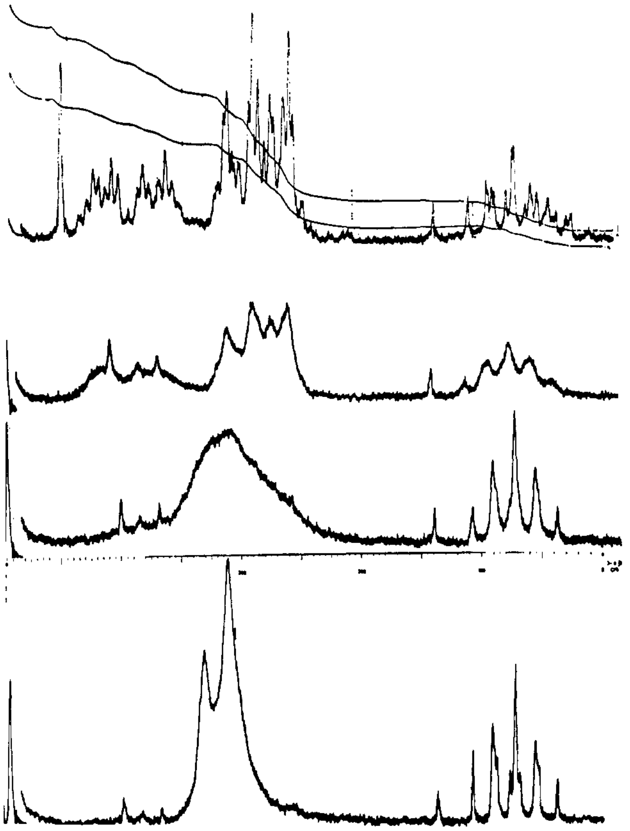

Figure 3. The variable-temperature 60-MHz nmr spectra of tricyclopropylaluminum dimer in toluene. From top to bottom temperatures are 35, 52, 78, and 103°.

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(5) Data in Table I due to Paul A. Scherr from preliminary results in the analysis of the nmr spectrum. Exact analyses of other cyclopropylmetal compounds soon to be published.

(6) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949); W. A. Bernett, *J. Chem. Educ.*, **44**, 17 (1967).

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The enhanced stability of this compound,[8] probably due to the additional π-type interaction, is clearly demonstrated by the temperature dependence of the 60-MHz nmr spectra shown in Figure 3. Rapid exchange on the nmr time scale does not occur until a temperature of $\sim 70°$ is reached, which implies that the exchange process in this system proceeds with a higher activation energy than that observed for any other system studied so far.

Further study of this system should lead to a better understanding of cyclopropyl π-type interactions and the nature of the electron-deficient bridge bond. To this end the exact analysis of the nmr spectrum is continuing and the crystal structure and optical spectra are currently under investigation.

Acknowledgment. We gratefully acknowledge the support of this research by National Science Foundation Grants GP-3908, GP-6762, and GP-8323.

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David A. Sanders, John P. Oliver
Department of Chemistry, Wayne State University
Detroit, Michigan 48202
Received June 12, 1968

Comment on the Thermal Decomposition of Triphenylthallium

Sir:

In a recent interesting publication[1] concerned with thallium in organic synthesis is the statement: "Contrary to the suggestion of Gilman and Jones, we have shown that triphenylthallium does *not* disproportionate to biphenyl and thallium."[2] In the earlier experiments described by us[3] we obtained biphenyl when triphenylthallium dissolved in xylene was refluxed under nitrogen. Also, in two check experiments, a solution of triphenylthallium in xylene was refluxed while a slow stream of dry carbon dioxide was admitted over the surface of the boiling solution. Subsequent to cooling and hydrolysis, there was obtained biphenyl and benzoic acid. It may be relevant to remark that Birch[4] stated after heating what was presumably only a small quantity of solid triphenylthallium: "When heated it decomposes suddenly to give metallic thallium and a vapor possessing an odor of biphenyl."

We now confirm that biphenyl is indeed formed by thermal decomposition of triphenylthallium under our reported conditions which are more vigorous than those employed in ref 1. Thus, biphenyl is formed by thermal decomposition in xylene of freshly prepared triphenylthallium. These experiments were carried out with newly prepared materials. As in our earlier work the identity of the biphenyl was confirmed by the method of mixture melting points with an authentic specimen, and in the present work also by comparison of infrared spectra.

The following item may have some significance. An interesting and important aspect of the coupling reactions[1] is that they take place in the presence of excess TlBr (see footnote 4 of ref 1). In the reference to our experiment in which some biphenyl was obtained when phenyllithium was added to thallous chloride at $-15°$ (see ref 3) it is of interest that the TlCl was present in excess because the phenyllithium was added to it slowly. Ordinarily, in the preparation of organothallium compounds, the thallous chloride or bromide is added slowly to the RMgX or RLi compound so that thallous halide is not present in excess. This suggests that a key step in the coupling reaction may be expressed in eq 2 of ref 1.

$$\mathrm{RTl} + 2\mathrm{TlBr} \longrightarrow \mathrm{RTlBr_2} + 2\mathrm{Tl}$$

There would then be little opportunity for this reaction to take place when TlBr is added to excess RMgX or RLi.

H. Gilman, I. Haiduc
Department of Chemistry, Iowa State University
Ames, Iowa 50010
Received June 19, 1968

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[1] A. McKillop, L. F. Elsom, and E. C. Taylor, *J. Am. Chem. Soc.*, **90**, 2423 (1968).

[2] The authors[1] have informed us that this observation was made under the conditions of their coupling reaction, *i.e.*, in refluxing tetrahydrofuran–benzene (1:1), thus indicating that triphenylthallium was not an intermediate in the coupling.

[3] H. Gilman and R. G. Jones, *J. Am. Chem. Soc.*, **62**, 2357 (1940).

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Synthesis of Novel Substituted (3)-1,7-Dicarbaundecaborate(12) Ions from 1,8-Dicarba-*closo*-undecaborane(11) and Carbanions

Sir:

Recently, the Lewis acid behavior of 1,8-dicarba-*closo*-undecaborane(11)[1-3] and the properties of some of its Lewis base adducts[4] have been reported. We now report the synthesis of a group of analogous ions, including two novel two-cage systems.

The previously described 1,8-$B_9C_2H_{11}$ carborane reacts with 1 mole of methyllithium in diethyl ether–hexane to produce a new $B_9C_2H_{11}CH_3^-$ ion I, which is isolated as its tetramethylammonium salt in 62% yield. Recrystallization from pure acetone yields white air-sensitive crystals. The infrared spectrum of a Nujol mull of I exhibits absorptions at 4.01 (s), 7.73 (w), 9.10 (m), 9.89 (w), 10.24 (m), 10.62 (s), 12.12 (w), and 13.79 μ (s). *Anal.* Calcd for $[(CH_3)_4N][B_9C_2H_{11}CH_3]$: C, 34.40; H, 12.51; B, 46.41; N, 6.63; equiv wt, 209.8. Found: C, 35.02; H, 11.29; B, 46.78; N, 6.57; mol wt (osmometric in acetonitrile), 207.

The 60-Mc/sec ^1H nmr spectrum of the tetramethylammonium salt of I in deuterioacetone exhibited a sharp singlet of intensity 12 at τ 6.64, a broad singlet of intensity 2 at τ 8.55, and a broad singlet of intensity 3 at τ 9.65. The intensity 12 resonance was assigned to the cation methyl protons, and the intensity 2 and 3 resonances were assigned to the carborane protons and to the cage methyl protons, respectively. The 32.1-Mc/sec ^{11}B nmr spectrum of I is complex, with a high-field doublet of intensity 2, a set of overlapping doublets of intensity 3, a singlet of intensity 1, and a low-field set of overlapping doublets of intensity 3. This spectrum, except for the aforementioned singlet, bears a striking resemblance to the spectrum of the previously reported (3)-1,7-$B_9C_2H_{12}^-$ ion,[5] which can now be obtained in

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