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Metal–Nitrogen Bonding. Covalent Complexes of 1,3-Dimethyltriazene with Elements of Groups I, II, III, IV, and V[1]

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A series of 1,3-dimethyltriazeno–metal derivatives (Cu(I), Zn, B, Al, Si, Sn, Ti, Zr, and P) have been synthesized and their properties were examined. One particularly useful route involves treatment of the reactive nitrogen "Grignard" intermediate which results directly from reaction between an organic azide (RN_3; R = aryl or alkyl) and a Grignard reagent ($R'MgX$; R′ = aryl or alkyl; X = Cl, Br, or I) with appropriate metallic or organometallic halides under inert conditions. Preliminary examination of proton n.m.r. spectra indicates involvement of the $CH_3N—N{=}N—CH_3$ ligand in several modes of bonding, the modes being dependent on the central atom.

Introduction

The bidentate character of the 1,3-diphenyltriazeno ligand (dpt) was recognized early by Dwyer,[3] who proposed intramolecular coordination to metals resulting in four-membered cyclic complexes. Later work of Harris, *et al.*,[4] employing refined molecular weight determinations and magnetic susceptibility measurements, indicated that binuclear bridged bonding is more likely with the transition metal compounds reported. Their postulated structures for the copper(I) and copper(II) diphenyltriazene complexes have been recently supported by an X-ray study[5] on the dimeric copper(I) diphenyltriazene which indicates a planar symmetric eight-membered heterocyclic structure with almost linear N–Cu–N bonding. In addition, a number of polymeric derivatives of group I and II metals were reported by the workers mentioned above. Our initial work[6] revealed preferred monomeric behavior for the complexes of 1,3-diphenyltriazene with metals of groups III and IV as well as Fe(III). Thus, the question of the influence of metal and 1,3-triazene substituents on the nature of bonding in the complex suggested additional studies.

The purpose of the present paper is to describe the preparation and the characteristic properties of a series of 1,3-dimethyltriazeno–metal compounds along with structural considerations based on proton n.m.r. studies. While the synthetic routes cited here are clearly amenable to a wider range of organic substituents on the –N—N=N– function, the symmetric 1,3-dimethyltriazeno (dmt) ligand was examined in greater detail. The metal derivatives of 1,3-dimethyltriazene would be expected to be more soluble and more volatile than analogous aryl complexes; moreover, the role of the nitrogen atom σ-bonded to the metal could be compared with the fate of the terminal imino nitrogen by proton n.m.r. spectroscopy of the respective groups.

Experimental

General.—Because of the well-known explosive hazards associated with catenated N compounds and, indeed, with certain preparative phases of the work herein, the authors have undertaken to describe the experimental part in greater detail. In general, with the specific triazeno–metal compounds cited or with their related intermediate addition complexes, heating above 110° is to be carefully avoided unless otherwise specified. In all instances, the preparations have been repeated at least several times and optimum conditions are reported. Characterization properties of the new compounds are collected in Table I.

The yields cited in the tables and in the detailed descriptions are based on the amount of metal or metalloid halide used. Melting points are uncorrected and as determined in capillary tubes under nitrogen. Molecular weights were determined cryoscopically (Bender–Hobein automatic apparatus) in benzene under nitrogen. Sample concentrations ranged from 0.02 to 0.09 *m*, affording convenient ΔT values of $\sim$0.1 to 0.4° for the compounds cited in Table I with the exception of $Zn(dmt)_2$ (0.0948 *m*, $\Delta T = 0.031°$).

The extreme air- and moisture-sensitivity of the new compounds required all additional manipulations to be performed under inert conditions employing an efficient drybox or conventional glass high-vacuum apparatus; reactions were conducted in glass under dry nitrogen. Microanalyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., and this laboratory.[7]

Proton n.m.r. spectra (Table II) are those of pure liquid compounds or benzene solutions recorded on a modified Varian Model DP-60 array providing readout (and integration) comparable to A-60 instrumentation. Infrared spectra were measured on a Beckman Model IR-5A (NaCl) spectrophotometer using neat liquids or Nujol mulls. All spectra obtained are complex, but display characteristic absorptions in the regions 550–650 and 700–800 cm.$^{-1}$ (strong, sharp), 900–1050 cm.$^{-1}$ (strong, sharp), 1340–1500 cm.$^{-1}$ (medium strong, doublets), and 2800–3000 cm.$^{-1}$ (strong C–H structure). Generally the bands observed for the metalloid triazenes (B, Si, and P) are sharper and better defined than those of the metallic derivatives.

Special Preparations. 1,3-Dimethyltriazenocopper(I).—This compound was prepared either *via* the method described in the literature[8] (yield 15 to 20%) or a method using the corresponding triazenoaluminum compound as starting material (this gives a much better yield and higher purity). Tris(1,3-dimethyltriazeno)aluminum (2.43 g., 10 mmoles) dissolved in 100 ml. of diethyl ether was added to a stirred solution of 9.9 g. (100 mmoles of copper(I) chloride in 30 ml. of 25% aqueous ammonia covered with 50 ml. of diethyl ether. The yellow ethereal layer was separated and dried over sodium sulfate; the solvent was removed by distillation to give bright yellow needles. The distillate was

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[3] F. P. Dwyer, *J. Am. Chem. Soc.*, **63**, 78 (1941).

[4] C. M. Harris, B. F. Hoskins, and R. L. Martin, *J. Chem. Soc.*, 3728 (1959).

[5] I. D. Brown and J. D. Dunitz, *Acta Cryst.*, **14**, 480 (1961).

[6] F. E. Brinckman and H. S. Haiss, *Chem. Ind.* (London), 1124 (1963).

[7] P. P. Wheeler and A. C. Richardson, *Mikrochim. Acta*, 609 (1964).

TABLE I

1,3-DIMETHYLTRIAZENO–METAL COMPLEXES

				Yield,	Analysis, %[a]					Mol.
MX_n	Compound	M.p. [b.p.], °C.	Color	%	C	H	N	M	X	wt.
$CuCl$	Cu(dmt)	185–186	Yellow	20[b]	17.71	4.46	30.98			136
					18.00	4.54	30.91			539
$ZnCl_2$	$(Zn(dmt)_2)_x$	100	Colorless	100	22.93	5.77	40.10	31.20		210
					23.21	5.80	39.79	31.55		3288
BF_3	$B(dmt)_3$	108–110	Colorless	22	31.74	7.99	55.51	4.76		227
					31.87	8.08	55.45	4.89		214
$AlCl_3$	$Al(dmt)_3$	125–127	Colorless	71–72	29.63	7.46	51.82	11.09		243
					29.83	7.65	51.70	11.48		239
$(CH_3)_2SiCl_2$	$(CH_3)_2Si(dmt)_2$	[38 (0.2 mm.)]	Colorless	85	35.62	8.97	41.53	13.88		202
					35.74	9.07	41.40	13.69		190
$(CH_3)_3SiCl$	$(CH_3)_3Si(dmt)$	[57 (50 mm.)]	Colorless	92	41.34	10.41	28.92	19.33		145
					41.52	10.54	29.21	19.73		141
	$(CH_3)_2Sn(dmt)_2$	[50–52 (0.2 mm.)]	Colorless	26	24.60	6.19	28.69	40.52		293
					24.79	6.09	28.40	40.16		278
$(CH_3)_2SnCl_2$	$(CH_3)_2Sn(dmt)Br$	[38 (0.2 mm.)]	Colorless	45	15.98	4.02	13.97	39.46	26.57	301
					15.75	4.23	14.21	39.43	26.76	305
	$(CH_3)_2Sn(dmt)I$	[50 (0.2 mm.)]	Pale yellow	85	13.82	3.48	12.08	34.13	36.49	348
					13.97	3.54	11.37	34.25	36.46	333
$TiCl_4$	$Ti(dmt)_4$	130	Dark red	46	28.58	7.19	49.99	14.24		336
					28.44	7.39	49.77	14.03		312
$ZrCl_4$	$Zr(dmt)_4$	120	Orange	75	25.32	6.37	44.28	24.03		380
					25.33	6.43	44.30	24.36		379
PCl_3	$P(dmt)_3$	[91–92 (0.2 mm.)]	Colorless	52	29.15	7.34	50.99	12.53		247
					28.89	7.10	51.29	12.26		241
$C_6H_5PCl_2$	$C_6H_5P(dmt)_2$	[109 (0.2 mm.)]	Colorless	40	47.61	6.79	33.32	12.28		252
					47.90	6.75	33.53	12.12		243

[a] Top figure denotes calculated value and bottom figure denotes found. [b] Prepared according to Dimroth's method.

TABLE II[a]

CHEMICAL SHIFTS AND SPIN COUPLING CONSTANTS IN 1,3-DIMETHYLTRIAZENE–METAL COMPLEXES

Compound[b]	$N-CH_3$ chemical shift, p.p.m.[c,d]	$M-CH_3$ chemical shift, p.p.m.[c,d]	J_{M-C-H}, c.p.s.	$J_{M-N-C-H}$, c.p.s.
Cu(dmt)	3.82	...	...	...
$B(dmt)_3$	3.92[e]	...	...	...
$Al(dmt)_3$	4.03	...	...	...
$Ti(dmt)_4$	3.88	...	...	...
$Zr(dmt)_4$	3.97	...	...	...
$(CH_3)_2Sn(dmt)Br$	4.08 (1)	6.50 (1)	73.0[f]	16.4[g]
			75.6	
$(CH_3)_2Sn(dmt)I$	4.05 (1)	6.27 (1)	68.6[f]	15.0[g]
			71.7	
$(CH_3)_2Sn(dmt)_2$	3.92 (2)	6.51 (1)	65.0[f]	10.8[g]
			67.6	
$(CH_3)_3Si(dmt)$	3.75, 4.41 (1:1)	7.01 (3)	6.7	...
$(CH_3)_2Si(dmt)_2$	3.80, 4.39 (1:1)	6.72 (1)	7.1	...
$C_6H_5P(dmt)_2$	3.78, 4.17[h] (2:1:1)	...	...	4.6
$P(dmt)_3$	3.80, 4.25[h] (2:1:1)	...	...	4.7

[a] Spectra obtained at 60 Mc.; resonances measured by audiofrequency side-band technique, or from calibrated (A-60) charts. [b] Samples run in benzene solution at 25°. Substantially identical values were obtained for Si and Sn compounds also run as neat liquids. All samples were sealed in tubes under N_2 or vacuum. [c] Relative (upfield) to benzene taken as 0.00 p.p.m. [d] Relative peak intensities are indicated in parentheses. [e] Minor peaks centered at 3.60 p.p.m. (two) and 4.33 p.p.m. (three) are probably impurity. [f] Upper value refers to Sn^{117}; lower to Sn^{119}. [g] Value taken from unresolved multiplet centers. [h] Value taken for P^{31}–N–C–H doublet center.

again treated with copper chloride–ammonia to give a second fraction of 1,3-dimethyltriazenocopper. Both fractions were combined and recrystallized from *n*-hexane, yield 2.86 g. (70%). Since no molecular weight of the copper compound was previously known and only the analysis for copper had been carried out by Dimroth,[8] we determined these data (see Table I). The recrystallized substance showed a molecular weight of 502 (calculated for the tetramer, 543) while the molecular weight increased to 539 for a sample sublimed at 150° (0.1 mm.).

Bis(1,3-dimethyltriazeno)zinc.—1,3-Dimethyltriazene (7.3 g., 100 mmoles) dissolved in 50 ml. of *n*-pentane was combined with a solution of 6.17 g. (50 mmoles) of diethylzinc in 50 ml. of *n*-pentane. After 1 hr., during which ethane was evolved, the solvent was evaporated *in vacuo*—first at room temperature and then at 50° to give an amorphous solid, softening point 100°; yield 100%. **Tris(1,3-dimethyltriazeno)aluminum** was prepared in similar fashion by combining equivalent amounts of 1,3-dimethyltriazene and triethyl- or trimethylaluminum in ethyl ether at room temperature. Following evaporation of solvent, the residue was sublimed at 70° (0.1 mm.).; yield 85–90%.

Preparation of 1,3-Dimethyltriazeno Compounds *via* the Grignard Intermediate. 1,3-Dimethyltriazenomagnesium Iodide.—

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(8) O. Dimroth, *Ber.*, **39**, 3906 (1906).

About 100 mmoles of methyl azide prepared according to the literature[8] was condensed in a flask which was maintained below −20° and contained a filtered ethereal solution (50 ml.) of 100 mmoles of methylmagnesium iodide. After the cooling system was removed, the mixture warmed and was allowed to reflux for 20 min., resulting in a brown-yellow air-sensitive solution. The bromide and chloride analogs were prepared in the same way by initial reaction of methylazide and the appropriate Grignard reagent in 200 ml. of ethyl ether at −40°. The solutions were then kept at 0° (bromide) or −10° (chloride) for 30 min. prior to use at room temperature.

Tris(1,3-dimethyltriazeno)aluminum.—Aluminum trichloride (3.34 g., 25 mmoles) dissolved in 50 ml. of diethyl ether was added slowly to a stirred solution of dimethyltriazenomagnesium iodide. At once two layers were formed; the orange lower layer contained mainly inorganic magnesium salts. This separation was completed by adding 100 ml. of *n*-pentane to the continuously stirred solution. After 10 min., the solvent of the upper layer was removed *in vacuo* and gave a white waxy residue which was further separated into fraction F_1—easily soluble in *n*-pentane (extraction with 50 ml.)—and fraction F_2—soluble only in benzene. F_1 sublimed at 70° (0.1 mm.) to give 3.34 g. (13.75 mmoles) of tris(1,3-dimethyltriazeno)aluminum; m.p. 125–127°, yield 55% (P_1).

A second fraction of sublimed material was obtained by heating F_2 to 110–130°. This compound was found to be identical (infrared, melting point, analysis) with the tris(1,3-dimethyltriazeno)aluminum isolated from F_1; yield 10% (P_2).

The reaction between aluminum chloride and dimethyltriazenomagnesium chloride was carried out under the same conditions with the yields being lower. This result is compared and summarized with yields *vs.* reactant ratios for the iodide case in Table III.

TABLE III

REACTION CONDITIONS *vs.* YIELDS FOR ALUMINUM CHLORIDE AND DIMETHYLTRIAZENOMAGNESIUM HALIDES

Ratio, mmoles	Reaction time, min.	P_1, %[c] (pentane)	P_2, %[c] (benzene)	Σ, %
$AlCl_3:CH_3MgI$				
50:150	5	62	0	62
50:200[a]	5[a]	55	10	65
30:200	5	5	48	53
15:200	5	4.6	38.4	43
50:150	120	60	0	60
50:200[a]	120[a]	66	5.4	71.4
30:200	120	1–2	28	29
$AlCl_3:CH_3MgCl$[b]				
30:200	5	3.3	40.3	43.6

[a] Optimum reaction conditions. [b] Run at −10°. [c] P_1 and P_2 are actual product yields recovered from fractions F_1 and F_2, respectively.

Partial analysis of F_2 was accomplished by dissolving the material in benzene and fractionally precipitating with additions of *n*-pentane. Fractions thus obtained gave on elemental analyses a wide range of values for C, H, N, Al, Mg, and halogen. Molecular weights varied with starting Grignard reagent (530–605 for chloride and 680–760 for iodide). None of the fractions isolated showed an infrared frequency characteristic for pure $Al(dmt)_3$ (1000 cm.$^{-1}$), although a proton n.m.r. spectrum for one sample displayed a broadened singlet only slightly displaced from that observed for $Al(dmt)_3$.

Tris(1,3-dimethyltriazeno)borane.—Boron trifluoride etherate (4.25 g., 30 mmoles) in 50 ml. of diethyl ether was added dropwise to a stirred ethereal solution of dimethyltriazenomagnesium iodide which had been diluted to 250 ml. and maintained at −30°. After continuing the stirring for an additional 20 min., 100 ml. of *n*-pentane was added; the solvent of the upper layer was removed by pumping. The residue obtained (F_1 and F_2) was separated by extracting it with 200 ml. of *n*-pentane: F_1, soluble in *n*-pentane and sublimable at 80° (0.2 mm.), and F_2, partially soluble in benzene. The sublimate from F_1 (a white fluffy material containing traces of colorless, oily residue) was purified by washing it with several 10-ml. portions of *n*-pentane. F_2, upon attempts to sublime it at higher temperature (120°), yielded no additional tris(1,3-dimethyltriazeno)borane as with the aluminum analog.

Dimethylbis(1,3-dimethyltriazeno)silane.—Dimethyldichlorosilane (5.16 g., 40 mmoles) dissolved in 50 ml. of diethyl ether was added dropwise to a stirred ethereal solution (cooled to 0°) of dimethyltriazenomagnesium iodide. After continuing stirring for an additional 10 min., 100 ml. of *n*-pentane was added; the upper layer separated and its solvent evaporated *in vacuo* [75° (20 mm.)]. On addition of 50 ml. of *n*-pentane to this yellow liquid residue a white amorphous fraction precipitated (discard). The filtrate was fractionated *in vacuo* after removal of solvent to give a colorless liquid. The same conditions afforded **trimethyl(1,3-dimethyltriazeno)silane** from trimethylchlorosilane (80 mmoles) and dimethyltriazenomagnesium iodide.

Dimethylbis(1,3-dimethyltriazeno)tin.—Powdered dimethyltin dichloride (8.79 g., 40 mmoles) was added to a stirred ethereal solution (room temperature) of dimethyltriazenomagnesium chloride. After continuing the stirring for another 20 min. the precipitated magnesium salts were filtered off and 100 ml. of *n*-pentane was added to the filtrate in order to obtain two layers. The upper, yellowish layer (F_1 and F_2) was separated; its solvent was removed *in vacuo*. When another 50 ml. of *n*-pentane was added, additional magnesium salts precipitated. After filtration and evaporation of the solvent, the whole procedure was repeated with 20 ml. of *n*-pentane. The final residue (F_1) was fractionated to give a colorless liquid. The preparation and isolation of **dimethyl(1,3-dimethyltriazeno)tin bromide** or **iodide** follows this procedure employing 80 mmoles of organotin halide treated with the appropriate triazeno Grignard.

Tetrakis(1,3-dimethyltriazeno)titanium.—The ethereal solution of dimethyltriazenomagnesium iodide was allowed to react at room temperature with a stirred solution of 20 mmoles (3.8 g.) of titanium tetrachloride in 50 ml. of ethyl ether. The reaction mixture was worked up as described with dimethylbis(1,3-dimethyltriazeno)tin; that is, the residue of the upper layer (F_1 and F_2) was treated several times with decreasing amounts of *n*-pentane in order to separate a brownish yellow solid fraction (F_2) containing partially-substituted titanium salts and explosive magnesium–titanium–triazeno halide complexes. The final residue, soluble in about 20 ml. of *n*-pentane (F_1), was a dark red wax which could be sublimed at 70° (0.1 mm.) to give a crystalline compound.

Tetrakis(1,3-dimethyltriazeno)zirconium.—The preparation and isolation of this derivative was conducted in the same way as described for the titanium compound. Instead of an ethereal solution of the metal halide, a suspension of insoluble zirconium tetrachloride etherate (20 mmoles, 4.67 g. of zirconium tetrachloride plus 50 ml. of ethyl ether) was employed. The sublimation of the orange waxy residue (F_1) at 70° (0.1 mm.) yielded the zirconium compound.

Tris(1,3-dimethyltriazeno)phosphine and Phenylbis(1,3-dimethyltriazeno)phosphine.—Phosphorus trichloride (25 mmoles) or phenyldichlorophosphine (40 mmoles) dissolved in 50 ml. of diethyl ether was added dropwise to a stirred ethereal solution of dimethyltriazenomagnesium iodide maintained at −30°. Stirring was continued for 10 min. at the same temperature. Then 100 ml. of *n*-pentane was added, and the upper layer of the reaction mixture was separated and worked up as described with dimethylbis(1,3-dimethyltriazeno)tin. The final residue, a viscous, yellow oil, was vacuum distilled. *NOTE:* In order to avoid explosions the oil bath temperature must be kept below 120° during the distillation.

Exchange Reactions. Preparation of 1,3-Dimethyltriazene.—Generally, the free aliphatic triazene can be best obtained by treating the metal- or metalloid–triazene compound with a slight excess of aromatic triazene.[9] The preparation using dimethyltriazenoaluminum is representative. 1,3-Diphenyltriazene (12.8 g., 65 mmoles) was thoroughly pulverized and added (drybox) in portions to 4.86 g. (20 mmoles) of powdered dimethyltriazenoaluminum. The red tar initially formed converted into an orange solid after adding the stochiometric amount of aromatic triazene. Then the mixture was slowly (1 hr.) heated up to 100° at 0.1 mm. and the volatile 1,3-dimethyltriazene collected in a cold trap (below −40°). The slightly yellow product was further purified by high vacuum trap-to-trap distillation to give a colorless liquid; b.p. 40° (25 mm.); yield 4.03 g. (92% of the theoretical amount). The triazene is monomeric in benzene (mol. wt. calcd. 73.1, found 72.9).

Reaction between Dimethyl(1,3-dimethyltriazeno)tin Iodide and 1,3-Diphenyltriazenosilver.—Dissolved in 50 ml. of diethyl ether, 10.43 g. (30 mmoles) of dimethyl(1,3-dimethyltriazeno)tin iodide was combined with a suspension of 1,3-diphenyltriazenosilver (9.12 g., 30 mmoles) in 100 ml. of ether in a Schlenk tube. After shaking 3 hr. the silver iodide formed was removed by filtration and the ether evaporated *in vacuo* (0.2 mm.) at room temperature. The residue, a mixture of orange crystals and orange-red oil, was treated with 30 ml. of *n*-pentane, cooled to 0°; the undissolved crystals were collected in a filter funnel; yield 7.46 g. (13.8 mmoles). Then the volume of the filtrate was reduced to 10 ml. by evaporating *n*-pentane; a second fraction of dimethyl(1,3-diphenyltriazeno)tin (m.p. 164°)[6] was isolated (0.32 g., 0.6 mmole). The over-all yield of aromatic tin compound was 96% of the theoretical amount. The solvent of the filtrate was evaporated *in vacuo;* the remaining oil was fractionated to give colorless dimethyl(1,3-dimethyltriazeno)tin at 52° (0.2 mm.) in a yield of 61%.

Reaction between Dimethyl(1,3-dimethyltriazeno)tin Iodide and Dimethylaminolithium.—Finely divided dimethylaminolithium (3.57 g., 70 mmoles) was slowly added to 20.9 g. (60 mmoles) of the triazenotin iodide dissolved in 50 ml. of *n*-hexane. The mixture was heated to reflux for 3 hr. while being stirred. Then the solid precipitate was filtered off; the solvent of the filtrate was removed *in vacuo* [25° (20 mm.)]. The residue, a slightly yellow liquid, was fractionated at 56° (0.2 mm.) to give 5.97 g. (20.4 mmoles) of dimethyl(1,3-dimethyltriazeno)tin; yield 68%. The solid distillation residue could be washed with *n*-hexane to give white crystals melting at 110°. The analysis of this compound suggests an addition complex: dimethyl(1,3-dimethyltriazeno)(dimethylamino)tin lithium iodide (yield 8%). *Anal.* Calcd. for $C_6H_{18}N_4SnLiI$: C, 18.07; H, 4.55; N, 14.05; I, 31.82; Sn, 29.76. Found: C, 18.19; H, 4.66; N, 14.28; I, 31.14, 32.54; Sn, 28.15. No dimethylbis(dimethylamino)tin[10] was found. The first solid, however, also contained C, H, N, I, Sn, and Li, but no definite compound could be isolated by fractionation here since this material was insoluble in petroleum ether and benzene.

Results and Discussion

General Properties of the Dimethyltriazeno Complexes.—The only previously known metal compounds, 1,3-dimethyltriazenocopper and 1,3-dimethyltriazenosilver, were first isolated by Dimroth *via* the free triazene which in turn was prepared by hydrolysis of the Grignard intermediate. The free triazene was extracted with ether, and the ethereal solution was treated with ammoniacal copper(I) chloride to give the copper compound in a 20% yield. Actually this yield can seldom be achieved under these conditions, but the yield of the Grignard intermediate increases to at least 80% if the mixture of Grignard and methyl azide is allowed to warm up and reflux until the exothermic reaction is completed.

The resulting clear amber solution of triazeno-Grignard may be allowed to react directly with a variety of metal and metalloid halides.

$$n(\mathrm{CH_3N_3CH_3})\mathrm{MgX} + \mathrm{MX}_n \longrightarrow (\mathrm{CH_3N_3CH_3})_n\mathrm{M} + n\mathrm{MgX_2} \qquad (\mathrm{X} = \mathrm{Cl, Br, or\ I}) \tag{1}$$

Using another synthetic route, the free triazene may be allowed to react with some metal alkyls to give the desired metal triazenes.[11]

$$n(\mathrm{CH_3N_3CH_3})\mathrm{H} + \mathrm{MR}_n \longrightarrow (\mathrm{CH_3N_3CH_3})_n\mathrm{M} + n\mathrm{RH} \qquad (\mathrm{M} = \mathrm{Al, Zn};\ \mathrm{R} = \mathrm{CH_3, C_2H_5}) \tag{2}$$

As further studies showed, reaction 1 is rather complex. Systematic investigation of the preparation of tris(1,3-dimethyltriazeno)aluminum revealed two main competitive reactions take place: primarily the replacement of halogen by 1,3-dimethyltriazeno groups, and, secondly, the formation of addition complexes of the triazeno–metal compound (fully or partially substituted) with unreacted Grignard intermediate. This leads to a product mixture which can be separated into two fractions: F_1, easily sublimed to yield pure $Al(dmt)_3$ (P_1), and F_2, which decomposes on heating to yield smaller amounts (P_2) of product. The ratio P_1/P_2 varies (Table III) with the amount of metal halide used and with the reaction time, in that any excess of Grignard intermediate causes at once a decrease of P_1 as well as of the over-all yield; this decrease is the more obvious the longer Grignard intermediate and metal halide are allowed to react. Similar results were obtained using the chloro-Grignard instead of the iodo-Grignard.

Characterization of the F_2 complexes using ordinary methods is not conclusive; however, present evidence suggests that these be formulated as $[\mathrm{Al(dmt)_3}]_x \cdot [\mathrm{Mg(dmt)hal}]_y \cdot [\mathrm{Mg(dmt)_2}]_z$, whose composition is strongly dependent on reaction conditions.

Similar formation of addition complexes can be observed for titanium and zirconium. These products, however, could not be characterized since continuous decomposition in benzene occurs with precipitation of intractable material. In addition, the mentioned reaction mixtures showed explosive character at higher temperature (≃120°) without any evidence of sublimation at lower temperature.

Further studies with group IV-A elements showed that both silicon and tin chlorides react in a different way when employed in reaction 1, that is, little or no addition complexes are formed in competition with simple triazeno derivatives under a wide range of reactant ratios and reaction times. While anticipated dimethyltriazeno substitution on halosilanes proceeds with good yields, this is definitely not the case for tin. For example, in contrast to the facile preparation of trimethyl(1,3-dimethyltriazeno)silane no comparable

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(9) The pure 1,3-dimethyltriazene cannot easily be prepared by hydrolysis of a metal compound and following fractionation of the ethereal extract because of its volatility with ether. See H. C. Ramsperger and J. A. Leermakers, *J. Am. Chem. Soc.*, **53**, 2061 (1931).

(10) K. Jones and M. F. Lappert, *Proc. Chem. Soc.*, 358 (1962).

(11) G. E. Coates and R. N. Mukherjee, *J. Chem. Soc.*, 1295 (1964), have recently reported the reaction between $(CH_3)_3Ga$ and 1,3-diphenyltriazene which, interestingly enough, affords not $(dpt)_3Ga$ but nearly monomeric (benzene) $(CH_3)_2Ga(dpt)$.

tin analog was isolated in several attempts upon treatment of trimethyltin bromide with dimethyltriazenomagnesium iodide.

Using the rather unstable chloro-Grignard intermediate in reaction 1, dimethylbis(1,3-dimethyltriazeno)tin is obtained in rather low yields. Starting with the more stable bromo- or iodo-Grignard intermediate, the reacted dimethyltin dichloride can be regained only as dimethyl(1,3-dimethyltriazeno)tin bromide or iodide, respectively. Regardless of the ratio of metal halide to Grignard, and of the reaction time, no bis-substituted compound was isolated. This means the exclusive isolation of these triazeno metal halides is representative of some peculiar chemical features, which is certainly in contrast to the behavior of the silicon and group IV-B derivatives. The proton n.m.r. spectra which will be discussed later indeed show significant structural differences between these compounds.

Starting with dimethyl(1,3-dimethyltriazeno)tin iodide the bis(1,3-dimethyltriazeno)tin compound could be prepared in good yields by reaction of the triazenotin halide with 1,3-diphenyltriazenosilver or lithium dimethylamide.

$$2(CH_3)_2Sn(dmt)I + 2Ag(dpt) \longrightarrow (CH_3)_2Sn(dpt)_2 + (CH_3)_2Sn(dmt)_2 + 2AgI \quad (3)$$

$$2(CH_3)_2Sn(dmt)I + 2(CH_3)_2NLi \longrightarrow (CH_3)_2Sn(dmt)_2 + \text{solid residue} \quad (4)$$

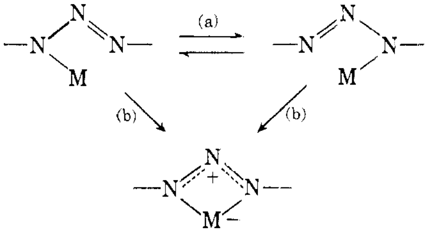
Both disproportionation reactions show the instability of the expected mixed derivatives, $(CH_3)_2Sn(dmt)(dpt)$ and $(CH_3)_2Sn(dmt)N(CH_3)_2$. Only a minor amount of the dimethylaminotriazine compound could be isolated (reaction 4) as the lithium iodide addition complex. No volatile bis(dimethylamino)dimethyltin was found; most probably it is contained in the insoluble residue in a complexed form.

It is interesting to note, however, the facility with which apparent metathesis occurs in disproportionation of mixed triazeno groups or triazenoamino groups in these compounds. This tendency for displacement without decomposition of those catenated groups bonded to metals is further demonstrated by the convenient preparation of the copper(I) derivative (5) or the free triazene (6).

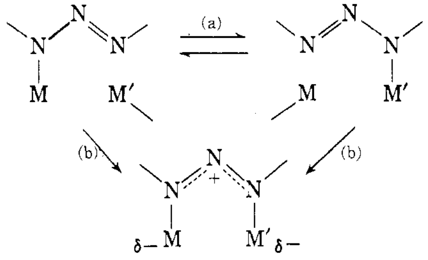
$$Al(dmt)_3 + 3CuCl \longrightarrow AlCl_3 + 3Cu(dmt) \quad (5)$$

$$\left.\begin{aligned} Cu(dmt) + (dpt)H &\longrightarrow Cu(dpt) + (dmt)H \\ Al(dmt)_3 + 3(dpt)H &\longrightarrow Al(dpt)_3 + 3(dmt)H \end{aligned}\right\} \quad (6)$$

Interpretation of Proton N.m.r. Spectra.—It is clear from molecular weight data (Table I) that the dimethyltriazeno ligand may be involved in both intramolecular as well as intermolecular coordination.[12] In applying the spectral information gained from n.m.r. measurements to elucidation of such bonding, a consideration of how apparent symmetricization of the two dissimilar CH_3–N groupings in the triazeno moiety arises is necessary. This might occur by several mechanisms, including (a) time-averaging of nonequivalent chemical sites in rapid intramolecular (process I) or intermolecular (process II) exchange processes, or (b) by comparatively stable configurations involving significant resonance delocalization of the lone-pair and π-bond electrons of the nitrogen available in the dimethyltriazeno function with suitable spd-hybrid orbitals of the metal atom(s).



I



II

In either of these pathways, however, it can be seen that the effective coordination number of the metal atom(s) involved necessarily increases.

Comparing the tabulated n.m.r. data (Table II) with selected spectra (Figure 1) reveals that dimethyltriazene participates in several possible modes of bonding. In the free parent compound, 1,3-dimethyltriazene (Figure 1A), the downfield imino-methyl (3.90 p.p.m.) and upfield amino-methyl protons (4.40 p.p.m.) are clearly distinguished as peaks of equal intensity.[13] Thus rapid tautomerism by a prototropic mechanism (*i.e.*, H bonding) is not involved in the neat liquid or in benzene solutions.[14] In contrast to this, certain of the dimethyltriazeno compounds giving rise to single sharp peaks of intermediate chemical shift (*i.e.*, boron, aluminum, titanium,

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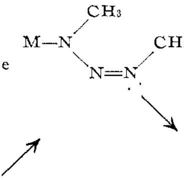
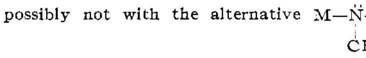
(12) Steric effects are significant in the degree of association ($\bar{n}$) of alkyl amino derivatives of a number of metals. For example, J. K. Ruff, *J. Am. Chem. Soc.*, **83**, 2836 (1961), finds $\bar{n}$ = 2.22 (benzene) for $[(CH_3)_2N]_3Al$, whereas $\{[(CH_3)_2CH]N\}_3Al$ is monomeric ($\bar{n}$ = 1.06). Similarly, D. C. Bradley and I. M. Thomas, *J. Chem. Soc.*, 3857 (1960), observed association in $(CH_3)_2N$ derivatives of Ti and Zr but not with their higher alkyl homologs. In the present instance it appears unlikely that the important steric inhibition to dative bonding should exist in the



case and possibly not with the alternative



$M\text{—}\ddot{\underset{\displaystyle CH_3}{N}}\text{—}N{=}N\text{—}CH_3$

case. Consequently, it can be reasonably argued that the absence of association observed for $Al(dmt)_3$, $Zr(dmt)_4$, etc., can very likely stem from strong intramolecular coordination. Also see ref. 11.

(13) This does not, however, preclude *syn–anti* isomerization. The shoulder observed in Figure 1A about 3 c.p.s. upfield from the main peak at 4.40 p.p.m. may well stem from local steric constraint to N–N rotation in the *syn* isomer. The effect is almost invariant in benzene solutions of varying concentrations or pure liquid, as is the lack of broadening for the iminomethyl peak.

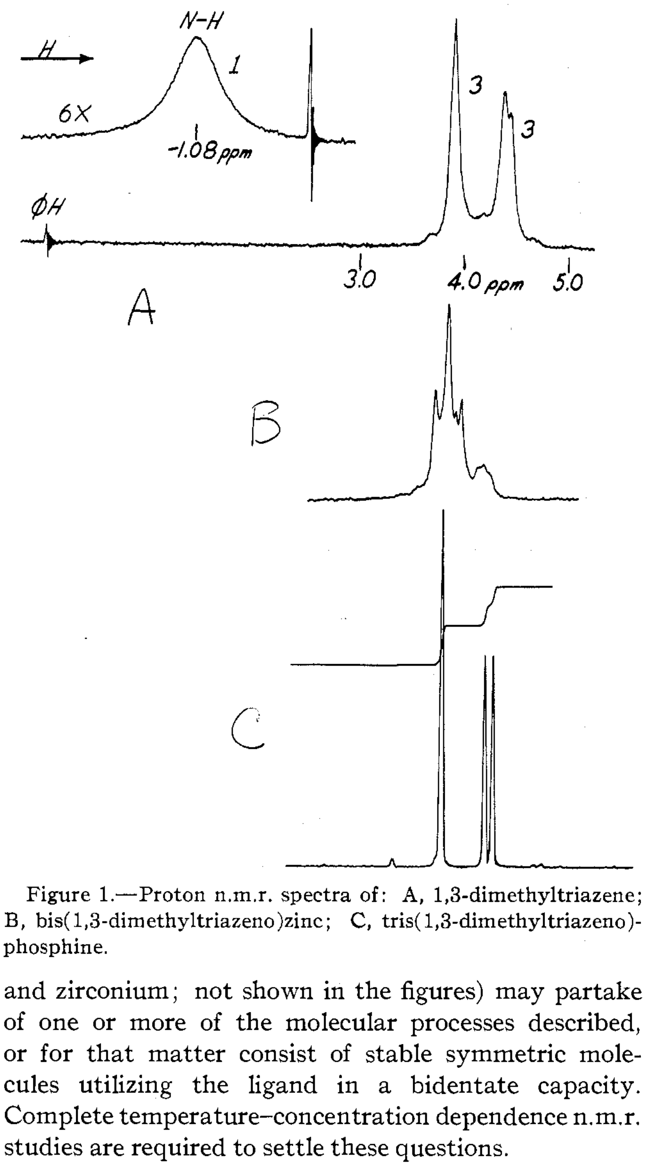
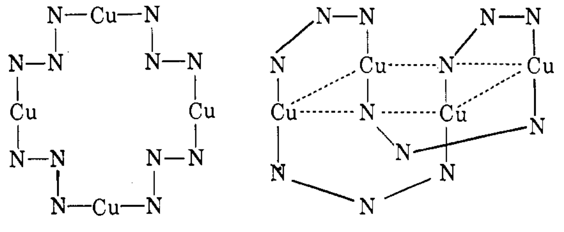


Figure 1.—Proton n.m.r. spectra of: A, 1,3-dimethyltriazene; B, bis(1,3-dimethyltriazeno)zinc; C, tris(1,3-dimethyltriazeno)phosphine.

and zirconium; not shown in the figures) may partake of one or more of the molecular processes described, or for that matter consist of stable symmetric molecules utilizing the ligand in a bidentate capacity. Complete temperature–concentration dependence n.m.r. studies are required to settle these questions.

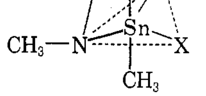
The single, sharp resonance observed in the tetrameric dimethyltriazenocopper spectrum may well represent still another circumstance, *i.e.*, comparatively long-lived bonding (in benzene) which results in an array of N–CH_3 groups possessing high symmetry. This view is suggested by the unusually good thermal and oxidative stability of this volatile crystalline compound, but more strongly required by n.m.r. spectra since a linear arrangement would necessitate[15] at least two kinds of dimethyltriazeno groups with respect to Cu–N bonding, *viz.*, binuclear bridge bonding and possible four-center chain termination. Such a structure would not be expected to give a single proton resonance even under fast exchange conditions while yet maintaining oligomer integrity. Indeed, it can be seen by comparing the complex spectrum obtained for polymeric dimethyltriazenozinc (Figure 1B) that under some circumstances several modes of coordination may be obtained for a given metal atom. Moreover, if each copper atom achieves linear N–Cu–N coordination, as is anticipated from experience with dimeric diphenyltriazenocopper,[4,5] then several cyclic structural models (III) are available which better fit present data, although we cannot at this point differentiate between them.[16]



III

Inspection of the proton n.m.r. spectrum of tris-(1,3-dimethyltriazeno)phosphine (Figure 1C) reveals interesting but not unexpected contrasts to the foregoing, *i.e.*, (a) the dimethyltriazeno moiety is not involved with the phosphorus atom(s) in processes or structures permitting symmetricization since both the =N—CH_3 and P—N—CH_3 protons are distinguished; and (b) the P^{31} nucleus is spin-coupled only with methyl protons of the σ-bonded N atom to give a doublet. This verifies our first surmise that no rapid bond breaking or forming of the σ-P—N linkage occurs nor does the terminal =N—CH_3 grouping become importantly involved with phosphorus.

In turning to the group IV-A derivatives, comparison of the spectra shown in Figure 2 vividly points to an important difference in the manner of bonding for dimethyltriazene with silicon or tin. Fortunately the case with monomeric $(CH_3)_2Sn(dmt)X$ compounds is clear by virtue of singular proton resonances afforded by N–CH_3 and Sn–CH_3 (equal areas) with associated spin-coupling satellites, $J_{Sn^{117}-H}$ and $J_{Sn^{119}-H}$, for both the methyl groups attached to tin as well as nitrogen. In the latter instance long-range coupling appears operative and is similar to that observed for $R_nSn[N(C_2H_5)_2]_{4-n}$ compounds.[17] We conclude from these facts that molecular processes washing out such fine structure are not involved,[18] and the results are satisfactorily described by a stable molecule whose central tin atom is symmetrically bonded to two methyl groups and the triazeno ligand in relation to the Sn–X bond (IV). Consequently, it appears that the liquid compounds dimethyl(1,3-dimethyltriazeno)tin bromide



IV

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[14] Use of unsymmetrically substituted aryltriazenes labeled with N^{15} has recently been described where, by an infrared comparison of N–H bands, tautomer ratios are determined. See T. Mitsuhashi and O. Simamura, *Chem. Ind.* (London), 578 (1964).

[15] Recently, F. A. Cotton and R. C. Elder, *J. Am. Chem. Soc.*, **86**, 2294 (1964), have studied one of several known cases involving polymeric equilibria in noncoordinating solvents. These workers find for tetrameric bis(acetylacetonato)cobalt(II) a linear centrosymmetric molecule involving three distinct forms of the bidentate ligand.

[16] Dr. E. R. Corey, University of Cincinnati, has recently begun a study of the crystal structure of dimethyltriazenocopper.

[17] M. Kula, C. G. Kreiter, and J. Lorberth, *Ber.*, **97**, 1294 (1964).

[18] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, Chapter 10.

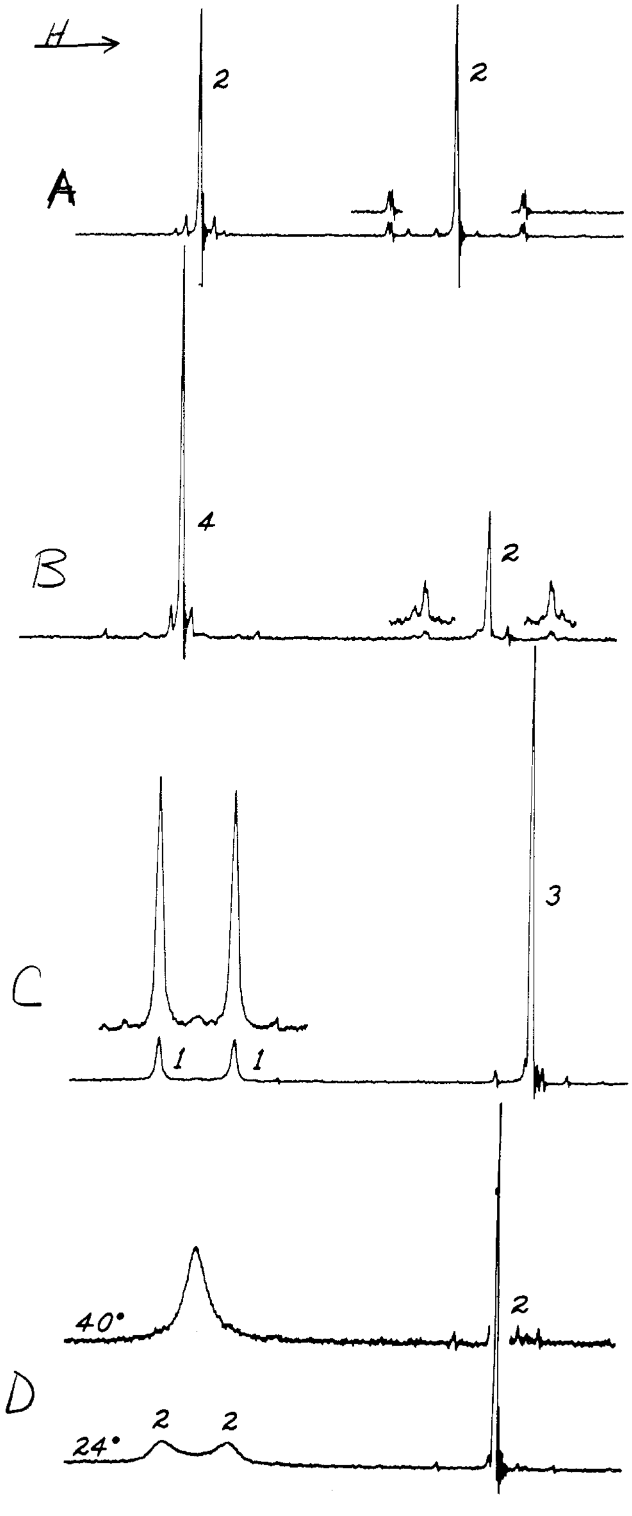

Figure 2.—Proton n.m.r. spectra of: A, dimethyl(1,3-dimethyltriazeno)tin iodide; B, dimethylbis(1,3-dimethyltriazeno)tin; C, trimethyl(1,3-dimethyltriazeno)silane; D, dimethylbis(1,3-dimethyltriazeno)silane at 24 and 40°.

and dimethyl(1,3-dimethyltriazeno)tin iodide involve tin in a pentacoordinate complex arising from four-membered metal–triazene bonding. This is of particular interest in view of recent evidence presented for five-coordinate tin in several unsaturated nitrogenous complexes.[19] A further point of significance is raised upon examination of the spectrum for dimethylbis(1,3-dimethyltriazeno)tin (Figure 2B), which reveals features interpretable in light of the preceding case. Here, of course, $N-CH_3$ and $Sn-CH_3$ protons are observed in an appropriate ratio (2:1) with associated Sn–H spin multiplets as before, but now tin is involved in a hexacoordinate complex.

For the mono- and bisdimethyltriazenosilanes, a striking difference from tin derivatives is observed. Both of these monomeric compounds show (Figures 2C and D) two kinds of $N-CH_3$ groups, *i.e.*, the upfield resonance for methyl on nitrogen attached to silicon and the downfield resonance for the terminal iminomethyl. The dimethyltriazeno ligand in these compounds and under these conditions (24°) obviously is not symmetric with respect to the central atom.

In the case of dimethylbis(1,3-dimethyltriazeno)silane, however, the $N-CH_3$ protons appear rather broadened at 24°, suggesting an exchange process may be thermally accessible and, as Figure 1D demonstrates, a temperature increase causes collapse to an averaged resonance line. Thus over a range of roughly 30° we have found n.m.r. spectra for this compound to display a classic exchange process[18] by which protons of $N-CH_3$ groups in nonequivalent sites at the lower temperature achieve equivalency *via* a molecular rate process whose mechanism is strongly temperature dependent. Initial experiments with trimethyl(1,3-dimethyltriazeno)silane yield entirely similar results, but over an increased temperature range (15–60°). This could reflect energetic differences in the pathway (*i.e.*, a hexacoordinate intermediate complex for dimethylbis(1,3-dimethyltriazeno)silane exchange and pentacoordination[20] with trimethyl(1,3-dimethyltriazeno)silane) rather than steric effects, but in any event is compatible with the idea[21] that acceptor strength for methylsilanes increases as the methyl group is replaced by electronegative groups (here, methyl by dimethyltriazene). Further speculation on these and other questions must await quantitative temperature-dependence studies, but the thermal behavior of analogous dimethyl(1,3-dimethyltriazeno)tin iodide shows, in sharp contrast to silicon, that the structure of this compound is altered very little over a significant temperature range (5–57°), with long-range spin coupling seen to coalesce only a little below the upper temperature.

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(19) In which nonvolatile compounds trigonal planar $(CH_3)_3Sn$ configuration is involved, *viz.*, $(CH_3)_3SnCl$(pyridine), I. R. Beattie, G. P. McQuillan, and R. Hulme, *Chem. Ind.* (London), 1429 (1962); N-trimethylstannylimidazole, J. G. A. Luijten, M. J. Janssen, and G. J. M. van der Kerk, *Rec. trav. chim.*, **81**, 202 (1962).

(20) J. Y. Corey and R. West, *J. Am. Chem. Soc.*, **85**, 4034 (1963).

(21) See several examples cited by I. R. Beattie, *Quart. Rev.* (London), **17**, 382 (1963).