

ORGANOMETALLIC DIAZOALKANES

XII *. BIS(DIMETHYLTHALLIUM)DIAZOMETHANE $[\text{Me}_2\text{Tl}]_2\text{CN}_2$, A FIRST EXAMPLE OF THE DIAZOMETHYL ANION $[\text{CN}_2]^{2-}$

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(Received April 26th, 1976)

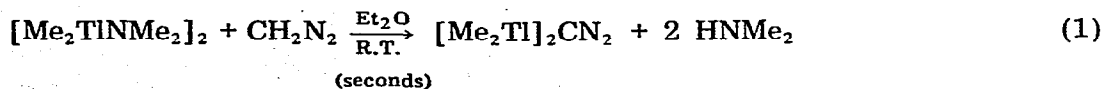
Summary

Reactions of $(\text{Me}_2\text{TlNMe}_2)_2$ or Me_3Tl with diazomethane gave ionic $(\text{Me}_2\text{Tl})_2\text{CN}_2$ in a quantitative yield. Bis(dimethylthallium) diazomethane is the first compound known to contain the linear $[\text{CN}_2]^{2-}$ anion. $[\text{Me}_2\text{Tl}]_2\text{CN}_2$ does not react with $\text{P}(\text{NMe}_2)_3$ in a Staudinger reaction to give phosphazine or undergo the Huisgen reaction with $\text{MeO}_2\text{C}-\text{C}\equiv\text{C}-\text{CO}_2\text{Me}$.

Results and discussion

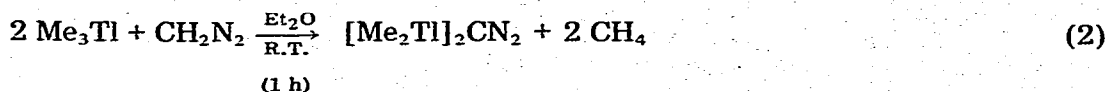
We have previously reported the preparation and the chemical and spectroscopic properties of organometallic diazoalkanes; typical compounds investigated were $\text{L}_n\text{M}(\text{R})\text{CN}_2$, L_nMCHN_2 and $(\text{L}_n\text{M})_2\text{CN}_2$ (where L_nM symbolizes the organometallic moiety), characterized as compounds with covalent bonds between the metal and the diazomethyl ligand.

Thallium derivatives $(\text{Me}_2\text{TlX})_n$ (where X = halide or pseudohalide) are ionic compounds containing the linear $[\text{CH}_3-\text{Tl}-\text{CH}_3]^+$ cation which is easily detected by its metal-to-carbon stretching frequencies in IR/Raman spectra. Analogies were drawn in earlier papers between the isoelectronic, linear three-atom-ions N_3^- and CN_2^{2-} which hold for many organometallic azides and diazomethanes, e.g. mercury compounds [1]. Ionic $\text{Me}_2\text{Tl}^+\text{N}_3^-$ was described [2], and we obtained $(\text{Me}_2\text{Tl})_2\text{CN}_2$ in two ways [3]:



* For part XI see ref. 8.

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Bis(dimethylthallium)diazomethane is a non-volatile, non-explosive pale-yellow to pale-brown coloured solid which shows no melting point, but decomposes at 174°C.

The mass spectra, scanned at 70 eV/200°C show only peaks (m/e) for N_2 (28) and Me_2Tl (233, 235), MeTl (218, 220) and Tl (203, 205) with the isotopic pattern for ^{203}Tl and ^{205}Tl . Peaks of minor intensities were found in the high mass region and assigned to $(\text{Me}_2\text{Tl})_2^+$ (470 m/e) and $(\text{MeTl})_2^+$ (440 m/e).

^1H NMR-spectra were difficult to obtain due to the insolubility of $(\text{Me}_2\text{Tl})_2\text{CN}_2$ in common aprotic organic solvents, e.g. Et_2O , C_6D_6 , CDCl_3 etc. Only strongly solvating and coordinating solvents like $\text{DMSO}-d_6$, $\text{pyridine}-d_5$, $\text{DMF}-d_7$ and D_2O were useful, the latter decomposing $(\text{Me}_2\text{Tl})_2\text{CN}_2$ to $[\text{Me}_2\text{Tl}]_{\text{aqu}}^+$ and CH_2N_2 . ^1H NMR spectra consisted of a doublet for the methyl-thallium protons, split again into a doublet for different coupling $J(^{203}\text{TlCH}_3)$ and $J(^{205}\text{TlCH}_3)$ with a gyromagnetic ratio of $^{203}\text{Tl}/^{205}\text{Tl} = 0.187/0.192$ at constant field. Chemical shifts $\delta(\text{TlCH}_3)$ of the center of these doublets were measured against TMS as external standard:

	DMSO- d_6	Pyridine- d_5	DMF- d_7	D $_2$ O
$\delta(\text{Tl}-\text{CH}_3)$	0.83 ppm	1.1 ppm	0.80 ppm	1.07 ppm
$J(^{203}\text{Tl}-\text{CH}_3)$	420 Hz	490 Hz	414 Hz	396 Hz
$J(^{205}\text{Tl}-\text{CH}_3)$	426 Hz	405 Hz	420 Hz	402 Hz

$^{13}\text{C}\{^1\text{H}\}$ PFT spectra of $(\text{Me}_2\text{Tl})_2\text{CN}_2$ could not be obtained even at high concentrations in these solvents; decomposition occurs after 50 000 scans (with pulse lengths of 0.8 sec.); no distinct signal was produced.

TABLE 1

IR FREQUENCIES IN THE RANGE 4000–250 cm^{-1} , $(\text{Me}_2\text{Tl})_2\text{CN}_2$ IN DIFFERENT SOLVENTS

Mode	Nujol	CsI	KCl	Compare $\text{Me}_2\text{Tl}^+\text{N}_3^-$ [2]
$\nu_{\text{as}}(\text{C}-\text{H})$	—	3000 vw	3000 vw	3020 s
$\nu_{\text{s}}(\text{C}-\text{H})$	—	2920 m	2920 m	2923 m
$\nu_{\text{as}}(\text{CN}_2)$	2105 s(br) 1970 vs(br)	2120 vs 1970 vs(br)	2150 s 2100(sh) 1975 vs	
$2 \times \rho(\text{CH}_3)$	1525–1530 m(br) = (2 × 785)	1600 m(br) (2 × 800)	1600 m(br) (2 × 785)	
$\delta_{\text{as}}(\text{C}-\text{H})$	—	1425 m(br) 1350 m(br)	1450 m(br) 1380 m(br)	1400 s(br)
$\delta_{\text{s}}(\text{C}-\text{H})$	1170 }w 1150 } 1100 w 1040 w	1180 w(br) 1100 vw	1170 w(br) 1120 w(br) 1040 w(br)	1185 vs
$\rho(\text{CH}_3)$	785 s	800 vs	785 vs	810 s
$\nu_{\text{as}}(\text{C}-\text{Tl}-\text{C})^a$	535 m	540 m-s	542 m-s	489 vs

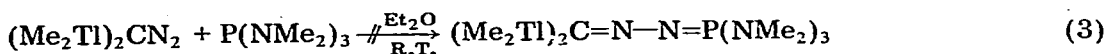
^a $\nu_{\text{s}}(\text{C}-\text{Tl}-\text{C})$ was the only band observed in the Raman spectrum at 485 cm^{-1} . vs, very strong; s, strong; m, medium; w, weak; vw, very weak; (br) broad; (sh) shoulder.

$(\text{Me}_2\text{Tl})_2\text{CN}_2$ decomposed also in the laser beam of the Raman spectrometer; IR absorptions (Nujol mull/CsJ discs) were assigned to the modes shown in Table 1.

The vibrations of the methyl-thallium group are consistent with a linear $[\text{CH}_3\text{—Tl—CH}_3]^+$ cation, and carbon-thallium stretching frequencies $\nu_{\text{as}}(\text{C—Tl—C})$ and $\nu_{\text{s}}(\text{C—Tl—C})$ have been observed in the IR or Raman, respectively, leading us to the conclusion, that $(\text{Me}_2\text{Tl})_2\text{CN}_2$ predominantly consists of Me_2Tl^+ cations and CN_2^{2-} anions.

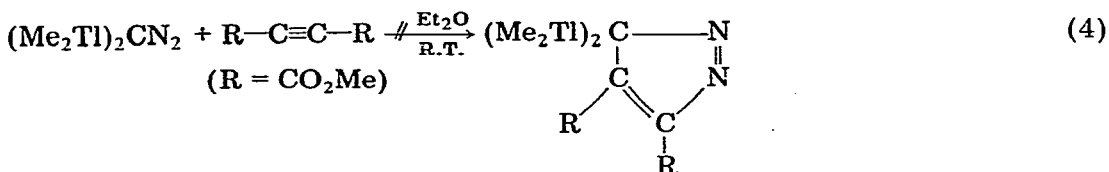
We have tested the chemical reactivity of bis(dimethylthallium) diazomethane in two ways:

(a) Staudinger reaction \rightarrow organometallic phosphazine



The wide scope of these reactions has been noted recently [4].

(b) Huisgen reaction \rightarrow organometallic cycloaddition product



Both reactions 3 and 4 failed, demonstrating again the ionic character of $(\text{Me}_2\text{Tl})_2\text{CN}_2$.

Experimental

The spectroscopic equipment used in these experiments was described previously [5]. Analyses were carried out by A. Bernhardt, Analytical Laboratories, Elbach über Engelskirchen (B.R.D.). Starting materials $(\text{Me}_2\text{TlNMe}_2)_2$ [6] and Me_3Tl [7] were prepared by standard procedures; diazomethane in Et_2O was obtained from *N*-nitrosomethylurea by treatment with 40% aqueous KOH at 0°C; drying of the ethereal solution over KOH-pellets for 48 h at -20°C and condensing $\text{CH}_2\text{N}_2/\text{Et}_2\text{O}$ in vacuo yielded high concentrations of CH_2N_2 in ethereal solution.

A. $(\text{Me}_2\text{TlNMe}_2)_2$ and CH_2N_2 . To 1.39 g (5 mmol) freshly sublimed $(\text{Me}_2\text{TlNMe}_2)_2$ a large excess of $\text{CH}_2\text{N}_2/\text{Et}_2\text{O}$ was condensed at -190°C ; warming to 0°C afforded spontaneous precipitation of $(\text{Me}_2\text{Tl})_2\text{CN}_2$ as a pale-brown powder. Volatiles were removed in vacuo and the residue dried for several hours at -10°C . Isolated yield: 1.2 g; 95% theory. The compound is not explosive on mechanical treatment (hammer) but explodes in a flame. M.p. 174°C (dec.) Found: C, 11.88; H, 2.36; N, 5.50. $\text{C}_5\text{H}_{12}\text{N}_2\text{Tl}$ [508.9] calcd.: C, 11.79; H, 2.36; N, 5.5; Tl, 80.35%.

B. Me_3Tl and CH_2N_2 . To 2.1 g (8.4 mmol) freshly sublimed Me_3Tl an excess of $\text{CH}_2\text{N}_2/\text{Et}_2\text{O}$ was condensed in vacuo at -190°C ; warming to room temperature and stirring of the clear, deep-yellow solution did not lead to a spontaneous

reaction, although gas was evolved continuously. After about 90 minutes precipitation began slowly, and was only completed after stirring at ambient temperature over night. Removing of volatiles and drying in vacuo for several hours yielded a light-brown powder. Isolated yield: 2.0 g; 94% theory. Physical data are analogous to procedure A. Found: C, 11.72; H, 2.42; N, 5.44. $C_5H_{12}N_2Ti_2$ [508.9] calcd.: C, 11.79; H, 2.36; N, 5.50; Ti, 80.35%.

C. $(Me_2Ti)_2CN_2$ and $P(NMe_2)_3$. 2.17 g (4.3 mmol) $(Me_2Ti)_2CN_2$ were suspended in 25 ml dry Et_2O under nitrogen atmosphere and 10 ml (8.95 g, 55 mmol) $P(NMe_2)_3$ were added dropwise. After stirring for 3 h at room temperature, Et_2O was removed in vacuo and $(Me_2Ti)_2CN_2$ was treated with pure, liquid $P(NMe_2)_3$. Reaction was continued for another 24 h and the excess of $P(NMe_2)_3$ was then removed in vacuo; $(Me_2Ti)_2CN_2$ was recovered in quantitative yield.

D. $(Me_2Ti)_2CN_2$ and $MeO_2C-C\equiv C-CO_2Me$. 2.47 g (4.9 mmol) $(Me_2Ti)_2$ suspended in 10 ml dry Et_2O , were treated with 5 g (35.2 mmol) of $MeO_2C-C\equiv C-CO_2Me$ for 24 h. No reaction occurred and the reagents were quantitatively recovered.

Acknowledgment

Experiments were financed by the Fachbereich Chemie, Philipps-Universität Marburg. Our work was supported by "VCI, Fonds der Chemischen Industrie e.V." (for J.L.) and by the "Deutsche Forschungsgemeinschaft" (for P.K.), whose generosity is gratefully acknowledged.

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