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Synthesis of Dialkyltriazanium Chlorides through Chloramination Reactions of Dialkylamines[†]

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The chloramination of some alkyl- and dialkylamines was carried out, and the products were analyzed by infrared spectroscopy, mass spectroscopy, and nuclear magnetic resonance spectroscopy. The results show that (1) chloramine reacts with isopropylamine to give, among other products, isopropyltriazane trihydrochloride, (2) chloramine reacts with diisopropylamine to give 2,2-diisopropyltriazanium chloride, and (3) chloramine reacts with dibenzylamine to give 2,2-dibenzyltriazanium chloride.

Introduction

Compositions of matter that contain high percentages of nitrogen have been found to be extremely useful in formulating energetic materials such as solid propellants, explosives, and the like. A high nitrogen content usually indicates the presence of N–N bonds. Representative of materials that possess high nitrogen content are the hydrazines, aminoguanidines, aminotetrazoles, and their salts. These materials, in addition to triazanium salts,[1-6] have been the subject of numerous investigations. Sisler et al.,[7-13] in a series of papers have reported the preparation and characterization of some 2,2-dialkyltriazanium chlorides.

The reaction of diisopropylamine with chloramine has been studied in a series of experiments,[14] but no diisopropyltriazanium chloride has been obtained from these experiments. Dibenzyltriazanium chloride also has not been prepared; the low basicity of dibenzylamine as well as the steric hindrance around the nitrogen atom would cause the formation and stability of such a triazanium salt to be in question. It was, therefore, an objective of this study to attempt to prepare and characterize these triazanium salts. Isopropylamine is one of the most basic monosubstituted amines; thus, it was considered a logical amine for an attempt to prepare monosubstituted triazanium salts.

Experimental Section

Materials. Diisopropylamine was supplied by Aldrich Chemical Co.; dibenzylamine and isopropylamine were supplied by Eastman Kodak Co. All were distilled under nitrogen prior to use. Distillation was carried out over potassium hydroxide pellets to remove moisture.

Chloramine was prepared by using a Sisler–Mattair type apparatus;[15] the gaseous effluent from the chloramine generator was used in these reactions.

Analytical reagent grade solvents were either distilled or dried over sodium metal or 3-Å molecular sieves prior to using and were then stored in airtight containers with polyethylene closure liners. All transfers were performed under nitrogen.

Equipment. All storing, transferring, and experimental purification work was carried out under a dry nitrogen atmosphere by using a KSE Model 2C 405R controlled-atmosphere box.

Distillations were carried out in a Mini-lab ₸ 14/20 apparatus. All filtrations were performed under nitrogen with a low-temperature filtration apparatus.

Melting points were obtained by using sealed capillary tubes in a Thomas-Hoover capillary melting point apparatus and are reported uncorrected. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, TN.

Infrared spectra were recorded on a Perkin-Elmer 283B infrared spectrophotometer. Samples of the salts were examined in KBr pellets. Samples of the amines were examined neat on sodium chloride plates. Table I lists the infrared spectral data for the amines and triazanium chlorides.

Proton nuclear magnetic resonance spectra were recorded on a Varian EM 360L NMR spectrometer or a Nicolet NT 300 spectrometer operating at a field of 7 T (Table II). Carbon-13 as well as nitrogen-15 measurements were recorded on an FT 300-MHz multinuclear spectrophotometer (Table III). Chloroform-*d* ($CDCl_3$) and dimethyl-d_6 sulfoxide [$(CD_3)_2SO$] were used as solvents, and TMS was used as the internal reference standard.

Electron-impact mass spectra were obtained on an AEI MS-30 mass spectrometer operating at 70 eV and equipped with a DS-30 data system.

Reactions of the Chloramine–Ammonia Mixture with Diisopropylamine. The gaseous effluent from the chloramine generator was passed for about 2 h over glass wool soaked with 0.1 mol of diisopropylamine. The product on the glass wool was then extracted with 30 mL of hot absolute ethanol. Acetone (90 mL) was added to the ethanol extract, and the solution was chilled. Crystals of NH_4Cl formed. To the supernatant liquid was added 80 mL of absolute diethyl ether. The solution was cooled overnight. Long thick crystals of $[(CH_3)_2CH]_2N(NH_2)_2{}^+Cl^-$ formed, decomposing at 146 °C [3.1 g (0.019 mol)]. Anal. Calcd: C, 42.97; H, 10.82; N, 25.07; Cl, 21.14. Found: C, 43.01; H, 10.80; N, 24.97; Cl, 21.28.

The gaseous effluent from the chloramine generator was passed into 0.15 mol of diisopropylamine dissolved in 100 mL of toluene at 0 °C for 150 min. A white precipitate formed, which was filtered out and extracted with 30 mL of hot absolute ethanol, and 90 mL of hot acetone was added. When the solution was cooled, a precipitate of NH_4Cl formed; to the supernatant liquid was added 50 mL of absolute diethyl ether, and white, flaky crystals formed. These proved to be $[(CH_3)_2CH]_2N(NH_2)_2{}^+Cl^-$. Anal. Calcd: C, 42.97; H, 10.82; N, 25.07; Cl, 21.14. Found: C, 42.71; H, 11.24; N, 24.81; Cl, 21.60. Satisfactory NMR, carbon-13, nitrogen-15, and infrared spectra were obtained[16] (Tables I–III).

The mass spectrum[16] shows the major fractions of the molecule, *m/e* at 86, 58, 44, and 36, which correspond to $(CH_3)_2CN_3H_2{}^+$, $(CH_3)_2CH-NH^+$, $H_2N_3{}^+$, and HCl^+, respectively.

Reactions of Chloramine–Ammonia with Dibenzylamine. The gaseous effluent from the chloramine generator was passed into 50 mL of dibenzylamine dissolved in 50 mL of benzene at 0 °C for approximately 1 h. As the NH_2Cl-NH_3 gas mixture was passed into the solution, a white solid precipitated. After the reaction mixture was allowed to stand overnight, it was filtered, and the solid was washed three times with benzene and dried under vacuum. The white solid was treated with a 1:1 mixture of hot ethanol–acetone (60 mL). To the supernatant liquid was added 30 mL of absolute diethyl ether, and a white precipitate formed and was found to be $(C_6H_5CH_2)_2NH_2{}^+Cl^-$ (mp 260–262 °C). To the supernatant liquid were added over a period of 2 days five portions of 30 mL of diethyl ether. The crystals that formed were filtered out, washed with absolute diethyl ether, and dried. The weight of the dry crystals was 4.80 g or 0.2 mol of $(C_6H_5CH_2)_2N(NH_2)_2{}^+Cl^-$, or about 70% of theory on the basis of NH_2Cl used. This compound decomposed at 168–169 °C

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(1) Gosl, R. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 405.
(2) Schmitz, E.; Schramm, S.; Siomon, H. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 578.
(3) Utvary, K. *Monatsh. Chem.* **1968**, *99*, 1473.
(4) Utvary, K. *Monatsh. Chem.* **1968**, *99*, 2321.
(5) Giordano, T.; Palenik, G.; Sisler, H. H. *Inorg. Chem.* **1976**, *15*, 751.
(6) Utvary, K. *Monatsh. Chem.* **1968**, *99*, 1483.
(7) Utvary, K.; Sisler, H. H. *Inorg. Chem.* **1968**, *7*, 698.
(8) Giordano, T. J.; Sisler, H. H. *Inorg. Chem.* **1977**, *16*, 2043.
(9) Sisler, H. H.; Highsmith, R. E. *Inorg. Chem.* **1968**, *7*, 1740.
(10) Utvary, K.; Sisler, H. H. *Inorg. Chem.* **1966**, *15*, 1835.
(11) Mathur, M. A.; Sisler, H. H.; Morgenthaler, N. *Inorg. Chem.* **1979**, *18*, 2350.
(12) Utvary, K.; Sisler, H. H.; Kitzmantel, P. *Monatsh. Chem.* **1969**, *100*, 401.
(13) Highsmith, R.; Sisler, H. H. *Inorg. Chem.* **1969**, *8*, 1029.
(14) Sisler, H. H.; Mathur, M. A. *J. Inorg. Nucl. Chem.* **1981**, *43*, 3389.
(15) Sisler, H. H.; Mattair, R. *J. Am. Chem. Soc.* **1951**, *73*, 1619.
(16) Khatib, A. A. Studies on Chloramine Reactions in the Synthesis of Substituted Hydrazine and Triazanium Salts. Order No. DA89523847; University Microfilm International: Ann Arbor, MI, 1985.

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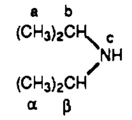
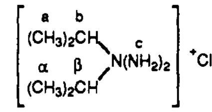
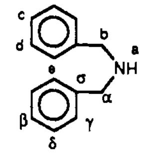
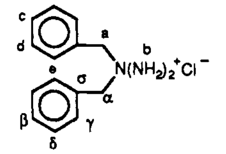
Table I. Infrared Spectral Data (cm^{-1})[20,21,a]

$[(CH_3)_2CH]_2NH$	$[(CH_3)_2CH]_2N(NH_2)_2{}^+Cl^-$	$(C_6H_5CH_2)_2NH$	$(C_6H_5CH_2)_2N(NH_2)_2{}^+Cl^-$	assgnt
		3315 (br)		ν(NH)
	3295 (s)			$\nu(NH_2)$
	3225 (m) 3130 (s)		3230–3100 (br)	$\nu_{as}(NH_2)$
2930 (s) 2870 (sh)	3020–2900 (br)	3045–2810 (br)	3050 (br)	ν_s(CH),[22] ν_{as}(CH)
	1600 (vs)		1640 (s) 1620 (sh)	$\delta(NH_2)$
1465 (s) 1375 (s) 1365 (sh)	1475 (vs) 1400 (w) 1390 (w) 1370 (w)	1495 (vs) 1450 (br)	1490 (s) 1460 (s)	$\delta(CH_3)$
1330 (m)	1325 (m)			δ(CH)
		1198 (m)	1220 (s)	$C_6H_5CH_2$ vib
1170 (s)	1185 (sh) 1170 (sh)	1152 (w)	1170 (vs)	ν(C–N)
	1110 (m)		1100 (s)	ν(N–N–N)[23] speculative
1010 (m)	1040 (vs) 965 (m)	1025 (s) 985 (w)	1080 (s) 995 (s)	δ(CH), $\delta(CH_3)$
	900 (vs)		905 (s)	$\nu_s(CN^+C)$

[a] Abbreviations: br, broad; d, doublet; m, medium; s, strong; sh, shoulder; v, very; w, weak.

Table II. 300-MHz ^1H NMR Data[a]

compd	δ, ppm	assgnt	*J*, Hz	rel area
 I	0.980 (d)	a + c	$J_{H_aH_b} = 6.39$	13
	2.830 (b)	b	$J_{H_bH_a} = 6.22$	2
 II	1.330 (d)	a	$J_{H_aH_b} = 6.40$	12
	3.910 (b)	b	$J_{H_bH_a} = 6.41$	2
	5.659 (s)	c		4
 III	2.480 (s)	a		1
	3.688 (s)	b		4
	7.185 (t,t)	c	$J_{H_cH_e} = 6.87$, $J_{H_cH_d} = 1.60$	2
	7.275 (t,d)	d	$J_{H_dH_e} = 5.14$, $J_{H_dH_c} = 1.62$	4
	7.350 (d,d)	e	$J_{H_eH_c} = 3.18$, $J_{H_eH_d} = 1.45$	4
 IV	4.950 (s)	a		4
	6.067 (s)	b		4
	7.470	c + d	$J_{H_dH_c} = 7.50$	6
	7.710	e	$J_{H_eH_c} = 5.94$, $J_{H_eH_d} = 1.80$	4

[a] Abbreviations: s, singlet, d, doublet; t, triplet; b, broad.

with gas evolution, leaving a solid that melts at 260–262 °C. Anal. Calcd for $(C_6H_5CH_2)_2N(NH_2)_2{}^+Cl^-$: C, 63.75; H, 6.88; N, 15.98. Found: C, 63.94; H, 7.01; N, 16.16. Satisfactory hydrogen, carbon-13, and nitrogen-15 NMR and IR spectra were obtained[16] (Tables I–III).

The mass spectrum[16] shows the major fractions of the molecule, *m/e* at 36, 51, 65, 77, 91, 105, 119, 210, 211, and 212, which are assigned to the molecular ions HCl^+, NH_2Cl^+, NNH_2Cl^+, $C_6H_5{}^+$, $C_6H_5CH_2{}^+$, $C_6H_5CH_2N^+$, $C_6H_5CH_2NN^+$, $(C_6H_5CH_2)_2NN^+$, $(C_6H_5CH_2)_2NNH^+$, and $(C_6H_5CH_2)_2NNH_2{}^+$, respectively.

Reaction of the Chloramine–Ammonia Mixture with Isopropylamine. The gaseous effluent from the chloramine generator was passed into 100 mL of a solution of toluene containing 6 mL of isopropylamine at 0 °C for 2 h. A small amount of solid formed, it was filtered out, washed with toluene and then diethyl ether, and dried under vacuum; 0.2 g of $(CH_3)_2CHNH_3{}^+Cl^-$ (mp 152 °C) was collected. The filtrate was kept in the refrigerator for about 2 months. A small amount of solid had formed; the solid was filtered out, washed three times with diethyl ether, and then dried under vacuum. The solid liberated free iodine from acidified KI solution. This solid was extracted with chloroform. The nonsoluble material (mp 142 °C) liberated free iodine from acidified KI solution. Anal. Calcd for $[(CH_3)_2CHNH(NH_3)_2]^{3+}(Cl^-)_3$: C, 18.16; H, 7.06; N, 21.18; Cl, 53.60. Found: C, 20.22; H, 9.12; N, 19.93; Cl, 50.55. The rather poor elemental analysis can be attributed to some loss of HCl plus some decomposition of the triazanium moiety yielding nitrogen molecules. The proton NMR spectrum of the product[16] shows three sets of protons, a doublet at $\delta = 1.3$ ppm, a heptet at $\delta = 3.2$ ppm, and a singlet at $\delta = 7.8$ ppm with a ratio close to 6:1:7, which may be assigned to CH_3, CH, and NH plus NH_3, respectively. The NH and NH_3 protons are indistinguishable because of rapid exchange. The nitrogen-15 spectrum of the product shows two kinds of ^{15}N peaks: a broad singlet centered at $\delta = -327.725$ ppm and a triplet centered at -262.808 ppm. Though not as we expected (a doublet for NH and a quartet for NH_3), the spectrum does not contradict the proposed structure if protons exchange rapidly enough to give a singlet and a triplet. However, the assigned structure must be considered as tentative only.

Discussion

Chloramine reacts with diisopropylamine to form both diisopropylhydrazinium chloride and diisopropyltriazanium chloride. The reaction to form $[(CH_3)_2CH]_2N(NH_2)_2{}^+Cl^-$ can take place with diisopropylamine adsorbed onto glass wool or with diisopropylamine dissolved in toluene. The formation of triazanium salts from amines is proposed to proceed in three steps. The thin films of diisopropylamine formed on the glass wool strands may have facilitated the formation of the two products:

$$(i\text{-}C_3H_7)_2NH + NH_2Cl \rightarrow (i\text{-}C_3H_7)_2NNH_3{}^+Cl^-$$

$$(i\text{-}C_3H_7)_2NNH_3{}^+Cl^- + NH_3 \rightarrow (i\text{-}C_3H_7)_2NNH_2 + NH_4{}^+Cl^-$$

$$(i\text{-}C_3H_7)_2NNH_2 + NH_2Cl \rightarrow (i\text{-}C_3H_7)_2N(NH_2)_2{}^+Cl^-$$

As shown in the proton NMR spectrum of diisopropyltriazanium chloride, the quaternization of the central nitrogen increases its electronegativity, thus causing a downshift, compared to the case of diisopropylamine, of the peaks associated with the groups attached to it. The closer the groups, the larger the effect; CH_3 proton resonances are shifted from 0.980 to 1.330 ppm, whereas CH proton resonances are shifted from 2.830 to 3.910 ppm. The coupling constant is not affected; it remains at 6.4 Hz.

The carbon-13 spectra show the expected quartet for CH_3 at 16.034 ppm ($^1J = 138.94$ Hz, $^2J = 2.18$ Hz, $^3J = 1.15$ Hz) and a doublet for CH at 68.116 ppm ($^1J = 146.71$ Hz, $^2J = 3.11$ Hz, $^3J = 2.21$ Hz). The parent amine spectra show the α-carbon

Table III. Carbon-13 and Nitrogen-15 Spectral Data[a]

compd	δ, ppm	assgnt	J, Hz	δ, ppm	assgnt	J, Hz
I	23.036 (q)	α	$^1J_{CH} = 127.56$, $^2J_{CH} = 3.30$, $^3J_{CH} = 1.70$	−304.774	NH	
	44.382 (d)	β	$^1J_{CH} = 134.68$, $^2J_{CH} = 4.01$, $^3J_{CH} = 3.13$			
II	16.034 (q)	α	$^1J_{CH} = 138.94$, $^2J_{CH} = 2.18$, $^3J_{CH} = 1.15$	−256.050 (s)	N^+	
	68.116 (d)	β	$^1J_{CH} = 146.71$, $^2J_{CH} = 3.11$, $^3J_{CH} = 2.21$	−275.459 (t)	NH_2	$J_{NH} = -68.42$
III	52.376 (t)	α	$^1J_{CH} = 136.96$, $^3J_{CH} = 4.08$	−340.105	NH	
	126.389 (t)	β	$^1J_{CH} = 7.30$, $^2J_{CH} = 4.40$, $^3J_{CH} = 3.70$			
	127.833 (d)	γ	$^1J_{CH} = 7.30$, $^2J_{CH} = 4.40$, $^3J_{CH} = 3.70$			
	127.964 (d)	δ	$^1J_{CH} = 7.30$, $^2J_{CH} = 4.40$, $^3J_{CH} = 3.70$			
	140.750 (t)	σ	$^2J_{CH} = 6.30$, $^3J_{CH} = 4.70$, $^4J_{CH} = 1.80$			
IV	73.378 (t)	α	$^1J_{CH} = 59.85$, $^3J_{CH} = 1.70$	−326.417 (s)	N^+	
	127.396 (d)	β	$^1J_{CH} = 32.60$, $^2J_{CH} = 6.32$, $^3J_{CH} = 4.70$	−260.146 (t)	NH_2	$J_{NH} = -69.05$
	128.122 (t)	σ	$^1J_{CH} = 3.50$, $^2J_{CH} = 2.41$			
	130.973 (t)	δ	$^1J_{CH} = 32.60$, $^2J_{CH} = 6.30$, $^3J_{CH} = 4.70$			
	134.484 (t)	δ	$^1J_{CH} = 37.60$, $^2J_{CH} = 6.30$, $^3J_{CH} = 4.70$			

[a] Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; h, heptet.

quartet at 23.036 ppm, or contrary to what was expected, the signal is shifted upfield upon quaternization. The β-carbon doublet at 44.382 has been, as expected, shifted downfield. The coupling constant is higher for the diisopropyltriazanium chloride than for the parent amine.

The nitrogen-15 spectrum shows a singlet at −256.050 ppm assigned to R_2N and a triplet centered at −275.459 ppm (J = −68.42 Hz) assigned to NH_2. The decoupled spectrum of the parent amine shows a singlet centered at −304.774 ppm for NH. These data illustrate two points: (1) quaternization causes the nitrogen signal to shift downfield (less negative), i.e. from −304.774 to −256.050 ppm, and (2) the quaternized nitrogen signal (−256.050 ppm) is shifted to a lower field than that of NH_2 (−275.459 ppm).

Chloramine reacts with dibenzylamine, in spite of steric hindrance and low basicity, to form dibenzyltriazanium chloride in appreciable amounts. Dibenzyltriazanium chloride decomposes with gas evolution at 168–169 °C, yielding a solid that melts at 260–262 °C. This decomposition point is higher than that of any other known triazanium chloride. This can be explained by the presence of two phenyl groups, which makes the quaternized nitrogen even more electronegative and results in stronger C–N bonds as well as stronger hydrogen bonding in the lattice of the salt. Decomposition of nitrogen base compounds with N–N single bonds has been postulated to start with the formation of N–N and then $N_2(g)$.[17] The second melting point results from the formation of dibenzylammonium chloride (lit. mp 260–262 °C) by the decomposition of the triazanium chloride:

$$(C_6H_5CH_2)_2N(NH_2)_2{}^+Cl^- \rightarrow N_2 + (C_6H_5CH_2)_2NH_2{}^+Cl^- + \text{other products}$$

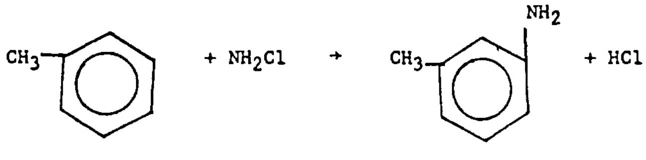
The proton NMR spectrum of dibenzyltriazanium chloride shows four sets of protons: a singlet at 4.950 ppm that is assigned to CH_2 protons, a singlet at 6.067 ppm assigned to NH_2 protons, a multiplet at 7.470 ppm (J = 7.50 Hz) assigned to meta and para protons on the phenyl groups, and a multiplet at 7.710 ppm (^1J = 5.94 Hz, ^2J = 1.80 Hz) that is assigned to the ortho protons on the phenyl groups. The proton NMR spectrum of the parent amine shows that the splitting of the phenyl protons is not as large as that for the dibenzyltriazanium chloride (0.15 ppm compared to 0.4 ppm). The signals for the dibenzyltriazanium chloride are, as expected, shifted to a lower field than those of the parent amine.

The carbon-13 NMR spectrum of dibenzyltriazanium chloride shows five kinds of carbons: a triplet (^1J = 59.85 Hz, ^3J = 1.70 Hz) at 73.378 ppm is assigned to a α-carbon and the other carbons are those of the phenyl groups as shown in Table III. These carbons appear as a triplet with coupling constants of ^1J = 32.60 Hz, ^2J = 6.32, and ^3J = 4.70. The parent amine carbon-13 NMR spectra show five kinds of carbons: a triplet (^1J = 136.96 Hz) at 52.376 ppm may be assigned to α-carbons, and the other carbons are those of the phenyl groups. Two points can be emphasized again here: (1) quaternization causes a downshift in the carbon-13 signal (52.376–73.378 Hz), and (2) the coupling constant is higher for the amine (59.85–136.96 Hz).

The nitrogen-15 spectrum shows a singlet at −326.417 ppm and a triplet (J = 69.05 Hz) centered at −260.146 ppm. These were assigned to R_2N^+ and NH_2, respectively, which is opposite to what we observed in the diisopropyltriazanium chloride case (the less negative peak was assigned to the R_2N^+). The steric hindrance and the presence of the phenyl group may have some effect in producing such an anomaly. The spectrum of the parent amine shows one signal for NH at −340.105 ppm, which is, contrary to what we expected, closer to the R_2N^+ than the NH_2 signal of the dibenzyltriazanium chloride.

Isopropylamine, almost as basic as dimethylamine (K_b is 3.28 for $(CH_3)_2CHNH_2$ and 3.29 for $(CH_3)_2NH$), reacts with chloramine in toluene to form a compound that melts at 142 °C, gives three distinctive proton NMR signals for CH_3, CH, and NH_3 with the ratio 6:1:7, respectively, and liberates iodine from acidified KI solution. The elemental analyses as well as the nitrogen-15 spectrum indicate strongly that the compound is the isopropyltriazane trihydrochloride $[(CH_3)_2CHNH(NH_3)_2]^{3+}(Cl^-)_3$.

This compound should only form in acidic media, just as the hydrazine dihydrochloride $N_2H_6{}^{2+}(Cl^-)_2$ requires an acidic medium for its formation from N_2H_5Cl. A possible source of the acidic medium might be the reaction between toluene and chloramine. Kovacic et al., in a series of papers,[18,19] reported the formation of *m*-toluidine, *N*-methyltoluidine, and *N*,*N*-dimethyltoluidine from the reaction of toluene in the presence of $AlCl_3$ with trichloramine, methylchloramine, and dimethylchloramine, respectively. Thus, the acidic medium could have arisen over a long period of time (more than 60 days) from the reaction of chloramine with toluene to give *m*-toluidine and hydrogen chloride:



The stability of isopropyltriazane trihydrochloride is comparable to that of hydrazine dihydrochloride (a white crystalline solid that melts at 198 °C). The inductive effect of the isopropyl group would increase the stability of the isopropyltriazane cation.

Finally, the IR spectra[20-23] of $[(CH_3)_2CH]_2N(NH_2)_2{}^+Cl^-$ and $[(C_6H_5CH_2)_2N(NH_2)_2]^+Cl^-$ along with those of $[(CH_3)_2CH]_2NH$

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[17] Overberger, C. G.; Anselme, J. P.; Lombardino, J. G. *Organic Compounds with Nitrogen-Nitrogen Bonds*; Ronald Press: New York, 1966; Chapter 1.

[18] Kovacic, P.; Goralski, C. T.; Hiller, J. J.; Levisky, J. A.; Lange, R. M. *J. Am. Chem. Soc.* **1965**, *87*, 1262.

[19] Heasley, V. L.; Kovacic, P.; Lange, R. M. *J. Org. Chem.* **1966**, *31*, 3050.

[20] Dollish, F. R. *Characteristic Raman Frequencies of Organic Compounds*; John Wiley & Sons: New York, 1973.

[21] Bellamy, L. J. *Advances in Infrared Group Frequencies*; Chapman and Hill: London, 1968.

[22] Arshad, M.; Beg, A. *Can. J. Chem.* **1965**, *43*, 608.

[23] Dellepiane, G.; Zerbi, G. *J. Chem. Phys.* **1968**, *48*, 3573.

and $(C_6H_5CH_2)_2NH$ are summarized in Table I. These spectra show the distinctive differences between a dialkyltriazanium salt and its parent amine. The bands in the range 3300–3100 cm^{-1} are indicative of NH_2 stretching, that at 1600 cm^{-1} is indicative of NH_2 bending, and that at 900 cm^{-1} is indicative of CNC stretching. The band between 1110 and 1100 cm^{-1} does not show in the amines but is fairly strong in the triazanium salts. One might tentatively assign this band to N–N–N stretching.

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Polymeric Ruthenium(I) and Binuclear Ruthenium(I) and Osmium(I) Carboxylate-Bridged Complexes Containing Diphosphine, Diarsine, Arsinophosphine, Diphosphine Chalcogenide, and Dithioether Ligands: The Structure of $[Ru_2(CO)_4(\mu\text{-}O_2CMe)_2(MeSCH_2SMe)]_2\cdot THF$

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The addition of 1 molar equiv of the bidentate ligands $L^\frown L$, $R'_2P(CH_2)_nPR'_2$, $R'_2As(CH_2)_nAsR'_2$, $Ph_2P(CH_2)_2AsPh_2$, $Ph_2PCH_2P(S)Ph_2$, $Ph_2P(S)CH_2P(S)Ph_2$, and $R'SCH_2SR'$ (R' = Me, Ph; n = 1–4), to THF/acetone solutions of either the polymer $[Ru_2(CO)_4(\mu\text{-}O_2CMe)_2]_n$ or the dimers $[Ru_2(CO)_4(\mu\text{-}O_2CR)_2(NCMe)_2]$ (R = Me, Et) affords a new class of polymeric species, $[Ru_2(CO)_4(\mu\text{-}O_2CR')_2(L^\frown L)]_n$, in which the carboxylate-bridged dimeric units are linked by the bidentate $L^\frown L$ ligands. The use of 2 molar equiv of either $Ph_2PCH_2PPh_2$ (dppm) or $Ph_2PCH_2P(S)Ph_2$ (dppmS) in the reaction with the acetate-bridged dimer yields complexes of the type $[Ru_2(CO)_4(\mu\text{-}O_2CMe)_2(\eta^1\text{-}Ph_2PCH_2P(X)Ph_2)_2]$ (X = S, electron pair). The osmium analogues $[Os_2(CO)_4(\mu\text{-}O_2CMe)_2(\eta^1\text{-}Ph_2PCH_2P(X)Ph_2)_2]$ can be obtained by heating $[Os_2(CO)_6(\mu\text{-}O_2CMe)_2]$ with 2 equiv of dppm or dppmS in $CHCl_3$. The pendant PPh_2 moieties of $[Os_2(CO)_4(\mu\text{-}O_2CMe)_2(\eta^1\text{-dppm})_2]$ can be oxidized to $P(O)Ph_2$ groups by treatment with 2 molar equiv of H_2O_2. The structure of the dithioether species $[Ru_2(CO)_4(\mu\text{-}O_2CMe)_2(MeSCH_2SMe)]_2\cdot THF$ has been determined by an X-ray diffraction study and has been shown to consist of a polymeric chain of $[Ru_2(CO)_4(\mu\text{-}O_2CMe)_2]$ units linked by $MeSCH_2SMe$ ligands. Each dimer unit has a sawhorse-like arrangement in which the four carbonyls are opposite the bridging acetate groups. The independent Ru–Ru bonds are 2.682 (1) and 2.684 (1) Å. This compound crystallizes in the space group $P\bar{1}$ with a = 15.838 (2) Å, b = 17.562 (2) Å, c = 8.238 (2) Å, α = 102.55 (1)°, β = 101.87 (1)°, γ = 68.17 (1)°, V = 2056.3 Å^3, and Z = 2. The asymmetric unit contains two $[Ru_2(CO)_4(\mu\text{-}O_2CMe)_2(MeSCH_2SMe)]$ moieties. On the basis of 3533 unique observations and 435 parameters varied, the structure was refined to R = 0.046 and R_w = 0.055.

Introduction

In previous papers[1,2] we reported the use of the acetate-bridged species $[Ru_2(CO)_4(\mu\text{-}O_2CR)_2]_n$ and $[Ru_2(CO)_4(\mu\text{-}O_2CR)_2(NCMe)_2]$ as convenient synthons for the preparation of an unusual series of binuclear Ru(I) complexes, either through replacement of the carboxylate groups by other bridging anionic ligands[1] or by substitution of the labile groups opposite the Ru–Ru bond by bidentate diphosphine and dithioether ligands.[2] In this paper we describe in detail some of the diphosphine and dithioether chemistry that was outlined in the preliminary communication[2] and also extend this work to include the use of a broader range of diphosphine, arsinophosphine, diarsine, and diphosphine chalcogenide ligands, $Ph_2P(Y)CH_2P(X)Ph_2$ (X = S, electron pair; Y = O, S, Se), and to include some related chemistry of Os(I).

Experimental Section

General Considerations. All compounds described in this paper were prepared under an atmosphere of dinitrogen by using Schlenk techniques and solvents that were appropriately dried and distilled under dinitrogen immediately before use. The ligands $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PCH_2CH_2PPh_2$ (dppe), $Ph_2PCH_2CH_2CH_2PPh_2$ (dppp), $Ph_2PCH_2CH_2CH_2CH_2PPh_2$ (dppb), $Ph_2AsCH_2AsPh_2$ (dpam), $Ph_2AsCH_2CH_2AsPh_2$ (dpae), $Ph_2P(CH_2)_2AsPh_2$ (arphos), $PhSCH_2SPh$, and $MeSCH_2SMe$ were purchased from Aldrich Chemicals; $Me_2PCH_2PMe_2$ (dmpm) was obtained from Strem Chemicals. The compounds $Ph_2PCH_2P(S)Ph_2$ (dppmS)[3] and $Ph_2PCH_2P(Se)Ph_2$ (dppmSe)[4] and complexes $[Ru_2(CO)_4(\mu\text{-}O_2CR)_2]_n$ (R = Me, Et),[5] $[Ru_2(CO)_4(\mu\text{-}O_2CR)_2(NCMe)_2]$ (R = Me, Et),[5] $[Os_2(CO)_6(\mu\text{-}O_2CMe)_2]$,[6] and $[Os_2(CO)_4(\mu\text{-}O_2CMe)_2(NCMe)_2]$[6] were prepared by literature methods. Infrared spectra were recorded on either a Nicolet 7199 or Mattson Polaris FT IR spectrometer as Nujol mulls on KBr plates or as solutions in 0.1 mm thick sodium chloride cells. The $^{31}P\{^1H\}$ NMR spectra were recorded on either a Bruker WH-200 (operating at 81.0 MHz), WH-400 (at 161.4 MHz), or AM-300 (at 121.5 MHz) FT spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained at 300.1 and 75.5 MHz, respectively, on a Bruker AM-300 instrument. Second-order $^{31}P\{^1H\}$ NMR spectra were analyzed by computer simulation using the PANIC program supplied by Bruker. Chemical shifts are reported relative to external H_3PO_4 (^{31}P) and external $SiMe_4$ (^1H and ^{13}C). Either C_6D_6 or $CDCl_3$ was used as the NMR solvent, and in each case, the deuterium resonance served as the lock for the spectrometers. For all nuclei, positive chemical shifts lie downfield from the standard. Elemental analyses were performed by the microanalytical departments at the University of Alberta and CSIR.

Preparation of the Metal Complexes. (1) $[Ru_2(CO)_4(\mu\text{-}O_2CR)_2(L^\frown L)]_n$ (1–10). For these complexes, R = Me for **1**, **2**, and **5–10**, R = Et for **3** and **4**, and $L^\frown L$ = $Me_2PCH_2PMe_2$ (**1**, **3**), $Ph_2PCH_2PPh_2$ (**2**, **4**), $Ph_2PCH_2CH_2PPh_2$ (**5**), $Ph_2PCH_2CH_2CH_2PPh_2$ (**6**), $Ph_2PCH_2CH_2CH_2CH_2PPh_2$ (**7**), $Ph_2AsCH_2AsPh_2$ (**8**), $Ph_2AsCH_2CH_2AsPh_2$ (**9**), and $Ph_2P(CH_2)_2AsPh_2$ (**10**).

Method A. Typically, a suspension of the acetate-bridged polymer $[Ru_2(CO)_4(\mu\text{-}O_2CMe)_2]_n$ and 1 molar equiv (per dimer unit) of the appropriate diphosphine, diarsine, or arsinophosphine were heated under reflux in 20 mL of THF for 4–6 h. Gradually, the starting polymer disappeared and a clear yellow solution formed. Upon cooling, a yellow

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(1) Cowie, M.; Sherlock, S. J.; Singleton, E.; Steyn, M. M. d. V. *J. Organomet. Chem.* **1989**, *361*, 353.

(2) Cowie, M.; Sherlock, S. J.; Singleton, E.; Steyn, M. M. d. V. *Organometallics* **1988**, *7*, 1663.

(3) Grim, S. O.; Mitchell, J. D. *Inorg. Synth.* **1976**, *16*, 195.

(4) Grim, S. O.; Walton, E. D. *Inorg. Chem.* **1980**, *19*, 1982.

(5) Crooks, G. R.; Gamlen, G.; Johnson, B. F. G.; Lewis, J.; Williams, I. G. *J. Chem. Soc. A* **1969**, 2761.

(6) Deeming, A. J.; Hursthouse, M. B.; Randle, N. P.; Short, R. L. *J. Chem. Soc., Dalton Trans.* **1987**, 2473.

0020-1669/90/1329-3161$02.50/0