Substitution Reactions of *N*-Phenylmercuriocycloazaheptathiane and Related Compounds

By **Robert J. Ramsay** and **Henry G. Heal,*** Department of Chemistry, Queen's University of Belfast Belfast, BT9 5AG
Henri Garcia-Fernandez, Faculté des Sciences, Université de Besançon, France

The behaviour of *N*-phenylmercuriocycloazaheptathiane, $(PhHgN)S_7$ (I), with hydrogen chloride and with various covalent halides of the elements of periodic Groups 3—6 is described. In some cases reaction occurs with formation of (NS_7) derivatives of the halides. With iodine, (I) gives mainly nitrides of the series $(S_7N)_2S_x$. The general pattern of reactivity of (I) has been established and its usefulness for the preparation of (NS_7) derivatives assessed. Thermodynamic and mechanistic factors responsible for reaction or non-reaction of (I) in particular cases are discussed. A few observations are also reported on the corresponding reactions of mercury derivatives of cyclo-1,4-diazahexathiane. The following new compounds are described: $SO(NS_7)_2$; $[Ph_2P(S)N]S_6$; 1,4-$[Ph_2P(S)N]_2S_6$; and $(CONS_7)_2$.

IN the previous paper[1] we described the preparation and properties of some new mercury and organomercury derivatives of cycloazathianes. We indicated in a note[2] that these mercury compounds react with covalent and organic halides of various elements M as in equation (1), (X = Cl or Br), providing a new route to derivatives of cycloazathianes.

$$>\!N\text{-HgR} + \text{-M-X} \xrightarrow[0-20\ ^\circ\mathrm{C}]{CS_2} \text{HgRX}\downarrow + >\!N\text{-M-} \quad (1)$$

There is strong current interest in inorganic heterocyclics, the preparation of which has been gradually systematized over the last few years. A natural next step in this field would be to investigate systematically the synthesis of more complicated structures such as fused rings, cages, and polymers, made up of atoms of the second-row non-metals and nitrogen, some examples of which are, of course, already known. Cycloazathianes are attractive building blocks for such a study, and the recent synthesis of the fused-ring nitride $S_{11}N_2$[3] illustrates what might be done with them. The work now reported was an exploration of one possible non-destructive way of forming links between the NH nitrogen atoms and other elements such as sulphur, boron, silicon, and phosphorus. It was made mainly with $(PhHgN)S_7$, (I), chosen as a model compound because of its structural simplicity, stability, and ease of preparation.

---

[1] R. J. Ramsay, H. G. Heal, and H. Garcia-Fernandez, *J.C.S. Dalton*, 1975, preceding paper.

[2] H. G. Heal and R. J. Ramsay, *J. Inorg. Nuclear Chem.*, 1974, **36**, 950.

[3] H. G. Heal, M. S. Shahid, and H. Garcia-Fernandez, *J. Chem. Soc.* (*A*), 1971, 3846.

RESULTS AND DISCUSSION

Substitution Reactions of (I).—The results are summarized in Table 1, and will first be reviewed factually by periodic Groups. All results refer to tests made in carbon disulphide solution at room temperature or slightly below.

TABLE 1

Behaviour of $(PhHgN)S_7$, (I), with covalent halides in CS_2 at 0—20 °C

Periodic Group	Compounds and results
Hydrogen	HCl [a,b]
3	BCl_3,[a] BBr_3,[a,b] BI_3 [a]
	$AlCl_3$,[c] $AlBr_3$ [c]
4	CCl_4,[c] $MeCl$,[c] MeI [c]
	Me_3CCl,[c] Ph_3CCl [c]
	$MeCOCl$,[c] $MeCOBr$,[a,b] $PhCOCl$ [c]
	$PhCOBr$,[c] $EtOCOCl$,[c] $(CH_2COCl)_2$ [c]
	$(COCl)_2$ [a,b]
	$SiCl_4$,[a] $SiMe_3Cl$,[c] $SiPh_3Cl$ [c]
	$GeCl_4$,[a] $GeBrPh_3$ [c]
	$SnCl_4$,[a] $SnMe_3Cl$,[a,b] $SnBu^i{}_3Cl$ [c]
	$SnPh_3Cl$ [c]
	$PbMe_3Cl$,[a,b] $PbEt_3Cl$ [a,b]
5	PCl_3,[c] PBr_3,[c] $PPhCl_2$,[b,c] PPh_2Cl [a]
	$Ph_2P(S)Cl$ [c]
	$AsCl_3$ [c]
6	SCl_2,[a] S_2Cl_2,[a,b] Cl_3CSCl [c]
	$SOCl_2$,[c] $SOBr_2$ [a,b]
	SO_2Cl_2,[c] 3-$MePhSO_2Cl$ [c]
7	I_2 [a,b]

[a] Reaction observed. [b] Reaction examined in detail. [c] No reaction.

Hydrogen chloride reacted quantitatively with (I) according to equation (2). In Group 3 there was no reaction with anhydrous aluminium(III) chloride or bromide. Boron tri-iodide immediately gave much iodine, presumably because the NS_7 ring was destroyed;[4] this reaction was not further examined. With boron trichloride and tribromide complicated reactions took place, of which only some main features were elucidated. Phenylmercury(II) halide was immediately precipitated and the i.r. spectra of the solutions showed that chlorine or bromine was being substituted by NS_7.[4] Addition of 1 mol of (I) to boron tribromide caused near disappearance of the BBr_3 doublet[4] at 810 and 845 cm^{-1}, and the appearance of the known doublets[4] of $(Br_2BN)S_7$ at 869 and 899 and 1 190 and 1 220 cm^{-1}. The 1 220 cm^{-1} component appeared relatively too intense; this effect was traced by means of a control experiment to a known reaction[5] between BBr_3 and the precipitated MgBrPh, yielding BBr_2Ph which also has a strong band at 1 220 cm^{-1}. More (I), up to a total of 3 mol, caused the bands of $(Br_2BN)S_7$ to disappear, and ultimately produced a strong, broad, structured absorption centred at 1 200 cm^{-1}, together with various weaker bands between 700 and 1 100 cm^{-1}. Apart from $(Br_2BN)S_7$, at least three compounds were involved, some of them perhaps NS_7 substitution products of BBr_2Ph. In a second experiment designed to minimize the formation of BBr_2Ph, BBr_3 was added slowly to 4 mol of (I), so that very little unchanged BBr_3 was ever present. The i.r. spectrum of the resulting solution was simpler; apart from bands due to unchanged excess of (I) and unidentified fairly weak bands at 1 220 and 1 285 cm^{-1}, it showed only a strong doublet at 1 200 and 1 250 cm^{-1} (intensity ratio *ca.* 4 : 1) which should probably be assigned to ν_3 (E') for the B–N stretch of planar $B(NS_7)_3$. In support of this view, addition of pyridine to this solution, or to a solution prepared similarly from BCl_3, yielded a crystalline precipitate giving a satisfactory sulphur analysis for $C_5H_5N{\cdot}B(NS_7)_3$ (Table 2). [A saturated CS_2 solution of (I) or of HgBrPh gave no precipitate with py.] Trisubstitution of halogen by NS_7 groups seems the best explanation of these results; we accordingly correct our earlier statement,[2] made before taking account of the side reactions, that BBr_3 could not be fully substituted.

$$(PhHgN)S_7 + HCl \longrightarrow (HN)S_7 + HgPhCl \quad (2)$$

In Group 4, methyl iodide did not react with (I). Neither carbon tetrachloride nor any of the alkyl or acyl chlorides tested reacted, except oxalyl chloride, which gave the new derivative $[(CON)S_7]_2$ in 87% yield; it forms colourless crystals, melting with decomposition at 174 °C, and sparingly soluble in CS_2. Our earlier statement[2] that acetyl and benzoyl chloride reacted with (I) was found to be erroneous when carefully purified samples were tested. Acetyl bromide reacted with (I), but no $(MeCON)S_7$ was found in the products, showing that the reaction was not a simple substitution. The tetrachlorides of silicon, germanium, and tin all reacted; investigation of the products was deferred because of the likelihood of multiple substitution. The chloro-trimethyl and -triphenyl derivatives of these elements did not react, except for $SnMe_3Cl$, which afforded $(Me_3SnN)S_7$ in 50% yield. This compound[2] forms orange crystals which decompose at 50 °C. The analogous $(Me_3SiN)S_7$ was recently reported[6] from the reaction of NS_7^- with $SiMe_3Cl$. The compounds $PbMe_3Cl$ and $PbEt_3Cl$ reacted with (I), giving respectively a yellow oil and a waxy orange solid; neither could be crystallized, but they analysed satisfactorily for $(Me_3PbN)S_7$ and $(Et_3PbN)S_7$ (Table 2).

In Group 5, PCl_3, PBr_3, and $AsCl_3$ did not react with (I), nor did $PPhCl_2$. Chlorodiphenylphosphine, however, reacted readily, giving not $(Ph_2PN)S_7$ but the new phosphorus(V) compound $[Ph_2P(S)N]S_7$, a colourless crystalline solid melting at 123 °C with decomposition. The addition of the sulphur atom to phosphorus must have occurred after replacement of chlorine by NS_7, and not before, since $Ph_2P(S)Cl$ did not react with (I). This sulphur can only have come from attack on NS_7 rings, a reaction to be expected from a substituted phosphine. Accordingly some polymer was also formed (*M* 750) and only 72% of the NS_7 introduced as (1) appeared as such in the product $[Ph_2P(S)N]S_7$.

---

[4] H. G. Heal, *J. Chem. Soc.*, 1962, 4442.

[5] W. Gerrard, M. Howarth, E. F. Mooney, and D. E. Pratt, *J. Chem. Soc.*, 1963, 1582.

[6] M. H. Mendelsohn and W. L. Jolly, *J. Inorg. Nuclear Chem.*, 1973, **35**, 95.

In Group 6, SCl_2 and S_2Cl_2 both reacted with (I) by simple substitution, giving the known[7] compounds $S_{15}N_2$ and $S_{16}N_2$ in over 90% yield. In contrast, the sulphenyl chloride CCl_3SCl, thionyl chloride, sulphonyl chloride, and toluene-*p*-sulphonyl chloride all failed to react. Thionyl bromide with (I) gave the new compound $SO(NS_7)_2$ in 50% yield as colourless crystals melting at 125 °C. The same compound was also obtained in 49% yield from reaction (3).

$$2(HN)S_7 + SOCl_2 \xrightarrow[CS_2]{py} SO(NS_7)_2 + [Hpy]Cl \quad (3)$$

In Group 7, iodine reacted rapidly with 2 mol of (I) giving a precipitate of HgPhI and a mixture of CS_2-soluble products. About 81% of this consisted of compounds with an average analysis and molecular weight corresponding to $(S_7N)_2S_6$, and with an i.r. spectrum appropriate for a mixture of compounds of the known series $(S_7N)_2S_x$.[7] There were small quantities of S_8, S_4N_4, and S_4N_2. There was no evidence of the still unknown compound $(S_7N)_2$ (compare ref. 8).

TABLE 2

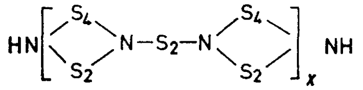
Analytical and i.r. data for the new compounds

Compound	Analyses [a](%) S	N	C	H	Cl	M [a]	Characteristic i.r. bands (cm^{-1}) and tentative assignments
Presumed $C_5H_5N{\cdot}B(BS_7)_3$							[b]
from BBr_3	81.9 (83.6)						
from BCl_3	82.1 (83.6)				0.8 (0)		[b]
$(CONS_7)_2$	83.9 (84.2)	5.2 (5.3)	4.6 (4.5)			500 [c] (532)	C–N 1 095s C=O 1 695s (KBr disc)
$(Me_3SnN)S_7$	55.8 (55.8)	3.3 (3.5)	9.1 (9.0)	2.0 (2.3)			Me bands near 3 000 and 1 200; S–N and Sn–C mixed, 780s, br, 735m, and 870m
$(Me_3PbN)S_7$	46.6 (45.7)	3.4 (2.9)	8.2 (7.3)	1.9 (1.8)			[b]
$(Et_3PbN)S_7$		2.4 (2.6)	14.8 (13.5)	2.8 (2.8)			[b]
$[Ph_2P(S)N]S_7$	56.0 (56.3)	3.2 (3.1)	31.5 (31.6)	2.3 (2.2)		458 [d] (456)	P=S 654m, P–N 1 100s, S–N 780s and 816s (CS_2 solution)
1,4-$[Ph_2P(S)N]_2S_6$	39.0 (39.2)	4.1 (4.3)	43.7 (44.0)	3.0 (3.1)		420 [c] (654)	P=S 652m, P–N 1 100s, S–N 810m and 850m (CS_2 solution)
$SO(NS_7)_2$	91.5 (91.6)	5.4 (5.3)				510 [c] (524)	S=O 1 190s, S–N 695s, 718m, and 836m (CS_2 solution)
Presumed $(S_7N)_2S_6$	95.8 [d] (95.8)	4.2 [e] (4.2)				600—900 [c] (670)	S–N 770s, br, agreeing with ref. 7

[a] Calculated values are given in parentheses. [b] Not examined. [c] Estimated from elution volume in g.p.c. chromatogram. [d] Mechrolab vapour-pressure osmometer, CS_2 solution. [e] After correction for *ca.* 7% of occluded CS_2 which could not be removed from the red gum *in vacuo* but was recognized from carbon analysis of the crude product.

Substitution Reactions of Mercury Derivatives of 1,4-$(HN)S_6$.—The compound 1,4-$(PhHgN)_2S_6$, (II), is described in the preceding paper.[1] It reacted readily with 2 mol of PPh_2Cl in analogous fashion to (I), giving the new compound 1,4-$[Ph_2P(S)N]_2S_6$ as colourless crystals melting at 94 °C. Unlike (I), (II) did not react with $SnMe_3Cl$.

The unstable inorganic mercury derivative[1] of 1,4-$(HN)_2S_6$ reacted with S_2Cl_2 (1 mol per formula weight of 'HgN_2S_6') in CS_2 at −10 °C, precipitating $HgCl_2$ and giving a solution with the i.r. spectrum of the known[9] polymers shown below.



Thermodynamics and Mechanism of the Substitution Reactions.—In the general reaction (4) the contribution

$$>N\text{-}HgPh + \text{-}M\text{-}Cl \xrightarrow[\text{solution}]{CS_2} >N\text{-}M\text{-} + HgPhCl \quad (4)$$

to ΔG from precipitation of HgPhCl is small (*ca.* 3 kJ mol^{-1}) because of the compound's relatively high solubility.[2] For the reaction in solution, ΔS is probably small because the products resemble the reactants in structure, and because all are covalent compounds in a non-polar medium. Hence the main contribution to the overall ΔG is likely to be the ΔH term for the reaction in solution. The enthalpy term, ΔH, is approximately equal to $(E_{HgN} - E_{HgCl}) + (E_{MCl} - E_{MN})$, where the E terms are the appropriate bond energies. The term $(E_{HgN} - E_{HgCl})$ is common to all the reactions; its value is difficult to judge directly because E_{HgN} is not reliably known. Tabulated bond energies[10] give the following approximate values (kJ mol^{-1}) for $(E_{MCl} - E_{MN})$:

M	H	alkyl C	acyl C	Si	P	S
$(E_{MCl} - E_{MN})$	+29	−13	−75	+56	+119	+7

Experimentally, substitution took place even in the most unfavourable case in this table, that of M = phosphorus, showing that the expression is negative and exceeds

---

[7] H. G. Heal, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 375.

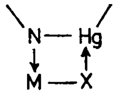
[8] J. P. Buckley and H. G. Heal, *J. Inorg. Nuclear Chem.*, 1963, **25**, 321.

[9] H. G. Heal and J. Kane, *J. Polymer Sci., Part C, Polymer Symposia*, 1968, 3491.

[10] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York, 1972, p. 113.

119 kJ mol^{-1}. The main reason is, of course, the exceptional affinity of Hg^{II} for chlorine; ΔH for the reaction $HgCl_2 \longrightarrow HgCl + Cl$ is 336 kJ mol^{-1}.[11] Similar arguments apply to bromides and iodides. Probably, then, all or nearly all the reactions attempted are thermodynamically allowed; where no reaction was observed, the obstacle is likely to have been mechanistic. Explanations for reaction or non-reaction will therefore be sought in terms of the structure of likely transition states.

When M is a Group 3, 4, or 6 element, with little or no donor power, the transition state may be based on the four-centre configuration shown below. The N→M donor–acceptor bond would form easily when M = boron, hence the easy reaction with boron halides. In dimeric aluminium(III) chloride (and also bromide) vacant aluminium *d* orbitals exist, but access to them by the nitrogen atom of (I) is probably sterically hindered. In Group 4, carbon has no suitable acceptor orbital in the alkyl and acyl compounds tested, so there was no reaction with (I), except in the case of oxalyl chloride where the carbon is unusually electropositive and may pass into a carbonium ion state, $>\overset{+}{C}\text{–}O^-$, with a vacant acceptor orbital. On Si, Ge, Sn, and Pb, vacant *d* orbitals are available, and reaction with (I) occurred except where sterically hindered by substituents; the non-reaction with $SiMe_3Cl$, and reaction with $SnMe_3Cl$ and $PbMe_3Cl$, which have larger central atoms, seem consistent with this explanation. In Group 6, steric hindrance by oxygen atoms will explain why SCl_2 and S_2Cl_2 reacted with (I), while SO_2Cl_2, with its more electropositive sulphur, did not, but we can offer no explanation for the non-reaction of CCl_3SCl and $SOCl_2$; $SOBr_2$, which did react with (I), may have some thermodynamic advantage over $SOCl_2$, but it seems unlikely that this could be decisive.



X = Cl, Br, or I

When M = phosphorus it is striking that replacement of two chlorines of PCl_3 by phenyl groups makes reaction with (I) possible, in spite of the accompanying increase in steric hindrance and reduction of phosphorus acceptor power, and in contrast to the effect of phenyl substitution in $SiCl_4$ and $SnCl_4$. It seems necessary here to postulate a different mechanism. We suggest that the transition state involves a donor–acceptor bond from phosphorus to mercury, the formation of which should be facilitated by phenyl substitution on phosphorus, and which seems likely because of the known stability of phosphine-mercury(II) complexes.

These substitution reactions could alternatively be discussed in terms of the ' hard and soft acids and bases ' viewpoint of Pearson, as elaborated by Saville.[12] This, however, would be merely to reiterate in qualitative language the semiquantitative arguments already put forward, introducing no new insight.

In the reaction with iodine, most of the NS_7 rings initially present ended up in the main product, $(S_7N)_2S_6$. Some, however, broke down to give the central sulphur chain in this product, and the minor products S_4N_4, S_4N_2, and S_8. These results suggest the formation of NS_7 radicals with an appreciable, but short, lifetime.

Value of the Mercury Compounds for Synthesis of Azathiane Derivatives.—Compound (I) is easy to prepare, and can be weighed out conveniently at room temperature as a pure solid, insensitive to moisture. It is more stable and easily handled than the previously known $Hg(NS_7)_2$ and is conveniently soluble in CS_2. It will readily replace halogen by NS_7 in many covalent halides but not those in which the central atom lacks electrophilic character or is sterically protected. In this respect it is less useful than the NS_7^- anion, which although unstable can now be prepared in 100% yield in thf solution[6] and which, unlike (I), will replace halogen in methyl iodide or chlorotrimethylsilane. Compound (I) probably has no important advantage as a substituting reagent over a combination of $(HN)S_7$ and pyridine, which, like (I), replaces chlorine in sulphur chlorides by NS_7, and unlike (I) will do the same with acetyl, benzoyl, and thionyl chlorides. Compound (II), and other phenylmercury derivatives of the diaza- and triaza-thianes, may find some use for building up sulphur–nitrogen cages, fused rings, *etc.* but redistribution reactions[1] would probably interfere with such applications.

EXPERIMENTAL

Materials.—Compounds (I) and (II) were prepared as described in the preceding paper.[1] Carbon disulphide was distilled from phosphorus(V) oxide under dry nitrogen shortly before use. Hydrogen chloride was B.D.H. research grade (99.99%). Thionyl bromide and trimethyltin chloride (Alfa Inorganics) were used without further purification. Sulphur chlorides were purified by published methods.[13] Trimethyl-lead chloride,[13] triethyl-lead chloride,[14] and chlorodiphenylthiophosphorane[15] were prepared by literature methods. Aluminium(III) chloride and bromide, and iodine, were sublimed *in vacuo* before use. Carbon tetrachloride, the alkyl halides, and toluene-*p*-sulphonyl chloride were of reagent or spectroscopic grade. The other halides, which are easily hydrolyzed, were all distilled under dry nitrogen before use, rejecting the first third of the distillate, in order to remove dissolved hydrogen halide.

Procedure.—Usually the covalent halide, in stoicheiometric amount, was added under dry nitrogen to a nearly saturated solution of (I), in dry carbon disulphide, magnetically stirred. Reaction was indicated by formation of a silky precipitate of phenylmercury halide. The temperature was always 0—20 °C. Neither heating nor prolonged standing could be allowed because of decomposition of (I)

---

[11] ' Gmelins Handbuch der Anorganischen Chemie,' 8th edn., ' Quecksilber, Teil B,' Verlag Chemie, Weinheim, 1967, p. 481.

[12] R. G. Pearson, ' Benchmark Papers in Inorganic Chemistry: Hard and Soft Acids and Bases,' Dowden, Hutchinson, and Ross, Stroudsburg, Pennsylvania, 1973.

[13] W. I. Gordon, Ph.D. Thesis, Queen's University of Belfast, 1970 (describes improvements on literature methods).

[14] R. Heap and B. C. Saunders, *J. Chem. Soc.*, 1949, 2983.

[15] N. K. Patel and H. J. Horwood, *J. Org. Chem.*, 1967, **32**, 2999.

in the solution.[1] Precipitated phenylmercury halides were identified by elemental analysis. They were produced in all cases of reaction in over 90% of the theoretical yield.

The carbon disulphide solutions of reaction products were concentrated and separated by gel-permeation chromatography (g.l.c.) in the following cases: reactions of (I) with oxalyl chloride, chlorodiphenylphosphine, sulphur chlorides, thionyl bromide, iodine; reaction of (II) with chlorodiphenylphosphine; and reaction of cycloazaheptathiane with thionyl chloride in the presence of pyridine. Details of the s.p.s. technique are given in the preceding paper.

Evidence for the identity of products is summarized in Table 2.

[5/233 *Received, 4th February*, 1975]