MERCURY—NITROGEN COMPOUNDS

II*. N-(METHYLMERCURY)TRIS(DIMETHYLAMINO)PHOSPHINE IMIDE, MeHgNP(NMe2)3

JÖRG LORBERTH

Fachbereich Chemie der Philipps-Universität, D-3550 Marburg/Lahn, Lahnberge (West Germany)

(Received November 12th, 1973)

Summary

Several routes for the synthesis of N-(organomercury)phosphine imides have been investigated; only transamination reactions are satisfactory for preparation of the title compounds in good yields. Spectroscopic data, Raman/IR, ^{1}H NMR, ^{31}P NMR and mass spectra, support a monomeric structure for this covalent mercury—nitrogen compound.

Introduction

The chemistry of mercury—nitrogen compounds has recently been reviewed[1], and many interesting structural features have been revealed; among oligomeric species only a few monomeric derivatives are obtained, e.g. $Hg(NR'_2)_2$ ($R' = CF_3$ [2], $SiMe_3$ [3]), $RHgNR'_2$ ($R = Me$, Et, $R' = SiMe_3$ [4]; R = Me, SCF_3, $R' = CF_3$ [5]) and $RHgN_3$ [4, 6] (R = alkyl, aryl). The well-known affinity of mercury for bonding to nitrogen should also lead to formation of dimeric species with a four membered ring system $(-Hg-N\lessgtr)_2$; suitable choice of substituents at nitrogen and mercury should lead to control of the oligomerisation process.

In some cases simple phosphine imides are dimeric, e.g. $(Cl_3PNMe)_2$ [7, 8] $(PhF_2PNMe)_2$ [9], $(PhCl_2PNMe)_2$, $(Ph_2ClPNMe)_2$ [10], and X-ray analysis of these compounds has confirmed an almost planar configuration of equally spaced nitrogen and phosphorus atoms, with trigonal-bipyramidal coordination at phosphorus and an overall symmetry of C_{2h} for the molecule [7]. Organometallic phosphine imides [11], obtained in reactions (A)—(D) of the scheme, are monomeric in solution; only for Group IIB elements have ex-

---

* For Part I, see ref. 4.

ceptions been reported: viz. $(RMNPR'_3)_4$, with R = Me; M = Zn, Cd; R' = Me, Et [12].

SCHEME

(A)　$R_nMN_3 + PR'_3 \rightarrow R_nM-N=PR'_3 + N_2$
　　　"Staudinger reaction" mainly for IVB elements

(B)　$R_nM + H-N=PR'_3 \rightarrow R_nM-N=PR'_3 + RH$
　　　Restricted to highly reactive metal alkyls

(C)　$R_nMNR''_2 + H-N=PR'_3 \rightarrow R_nM-N=PR'_3 + HNR''_2$
　　　Restricted to available amino derivatives of the metal

(D)　$R_nM-Hal + LiN=PR'_3 \rightarrow R_nM-N=PR'_3 + Li-Hal.$
　　　Restricted to available stable N-lithium salts.

Derivatives of zinc and cadmium are tetrameric in solution (and possibly also in the vapour phase) with a suggested cubane structure; we undertook experiments to investigate the coordination chemistry of mercury in its hitherto unknown phosphine imide complexes.
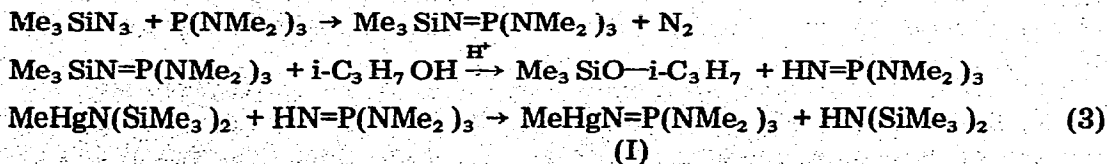
Results and discussion

Of the reactions shown in the scheme, we have tried (A) without success; reactions of $RHgN_3$ in molten PPh_3 or pure, liquid $P(NMe_2)_3$ in evacuated sealed Carius tubes at elevated temperatures for several hours led to complete decomposition of the mercurials [13]:

$$RHgN_3 \xrightarrow[\text{T/Vac.}]{R_3P} \text{Hg-metal + Dec. products} \qquad (1)$$
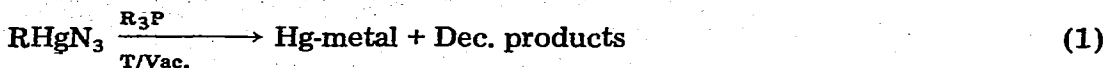
Reaction (B), which occurs only with strong acids for R_2Hg (cleavage of an aryl—mercury bond being easier than that of an alkyl—mercury bond) also failed:

$$R_2Hg + H-N=P(NMe_2)_3 \xrightarrow{T} \text{No reaction} \qquad (2)$$

Transaminations of organometallic amides with phosphine imides according to reaction (C), have been used for the synthesis of (organotin)phosphine imides [14]; the following reaction sequence (3) led to successful preparation of the first organomercury phosphine imide.

$$Me_3SiN_3 + P(NMe_2)_3 \rightarrow Me_3SiN=P(NMe_2)_3 + N_2$$

$$Me_3SiN=P(NMe_2)_3 + i\text{-}C_3H_7OH \xrightarrow{H^+} Me_3SiO-i\text{-}C_3H_7 + HN=P(NMe_2)_3$$

$$MeHgN(SiMe_3)_2 + HN=P(NMe_2)_3 \rightarrow \underset{(I)}{MeHgN=P(NMe_2)_3} + HN(SiMe_3)_2 \qquad (3)$$

Compound (I) was distilled as a colourless liquid, b.p. 68—70°/0.01 mm in a 90% yield; the compound crystallizes at about 30—35°, and is sensitive to hydrolysis. The molecular weight in benzene solution corresponds with the monomer. Compound (I) is readily soluble in a variety of organic solvents, but with chlorinated hydrocarbons reaction occurs. The stoichiometry was established by elemental analyses and by spectroscopic methods.
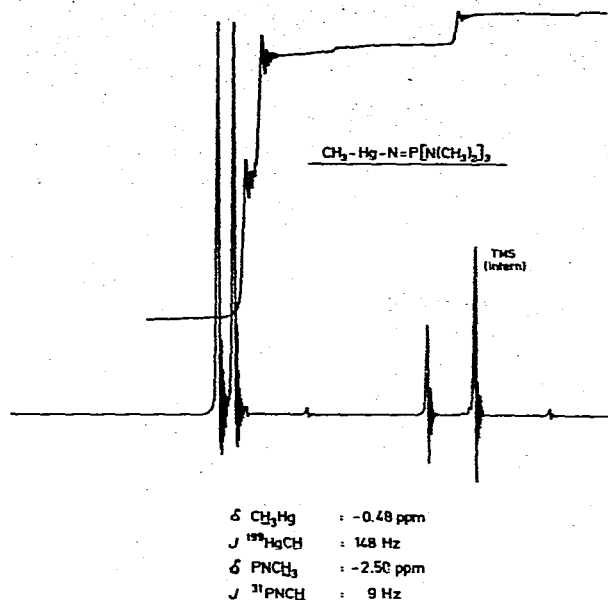
$CH_3-Hg-N=P[N(CH_3)_2]_3$

TMS
(intern)

δ CH_3Hg	: -0.48 ppm
J $^{199}HgCH$	: 148 Hz
δ $PNCH_3$	: -2.50 ppm
J $^{31}PNCH$	: 9 Hz

Fig. 1. ^{1}H NMR spectrum of MeHgN=P(NMe$_2$)$_3$ (I).

(a). ^{1}H NMR spectrum

The ^{1}H NMR spectrum in benzene solution, with the correct integration (1/6) is shown in Fig. 1. Spin-coupling of N-methyl protons with ^{31}P gives rise to a doublet, which is shifted 0.07 ppm downfield compared to P(NMe$_2$)$_3$ with δ -2.43 ppm. Spin coupling of metal-methyl protons with ^{199}Hg produces satellite signals with $J(^{199}$Hg—CH) 140 Hz; this agrees closely with corresponding values for other covalent Hg—N-compounds [4]. No indication is found for the dimeric structure $(R_3P=N-R')_2$ in solution: In this case evidence for an $X_n AA'X'_n$ -spin system should be provided by the ^{1}H NMR spectrum, as shown by Schmidbaur et al. [16] for compounds of the type (Me$_3$P=NAR$_2$)$_2$.

The ^{31}P NMR chemical shift of -33.5 ppm (H$_3$PO$_4$ external standard) is in the range reported for four-coordinated phosphorus compounds P(N)$_4$ [17, 18].

(b). Mass spectrum

In the mass spectrum of (I) shown in Fig. 2, the formation of almost all fragments can be explained in terms of the metastable transitions listed in Table 1. With maximum amplification, peaks are observed in the high mass region from m/e 400 to 780, but there is considerable doubt whether these fragments arise from dimeric (or oligomeric) species of from decomposition products.

(c). IR and Raman spectra

IR and Raman spectra (including a polarized spectrum) of the neat liquid are shown in Fig. 3, and tentative assignments are made in Table 2.
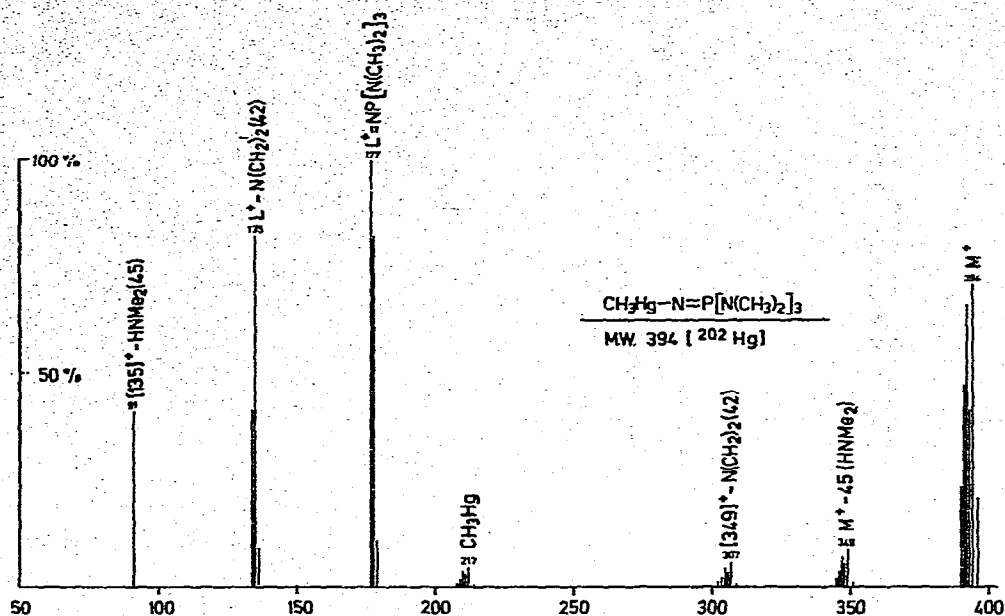
Fig. 2. Mass spectrum of (I) at 70 eV.

Experimental

The spectroscopic equipment used has been described elsewhere [4]. Elemental analysis was performed by A. Bernhardt, Analytical Laboratory, 5251 Elbach über Engelskirchen, GFR. Me_3SiN_3, $P(NMe_2)_3$ and $MeHgN(SiMe_3)_2$ were prepared by published procedures.

(a). $Me_3SiN=P(NMe_2)_3$

Me_3SiN_3 (30.8 g, 0.31 mole) was added dropwise to ca. 60 ml (excess) $P(NMe_2)_3$ in a 100 ml flask equipped with magnetic stirrer and condenser; the colourless precipitate initially formed gradually dissolved with evolution of nitrogen. After addition of the azide, stirring was continued for 3 h, and the mixture checked for azide-absorptions by IR. $P(NMe_2)_3$ was removed in vacuo and the oily residue distilled, yielding a colourless, moisture-sensitive liquid, b.p. 95—97°/0.1 mm. Yield 55 g (82%). The product was identified by analysis, IR, ^{1}H NMR, and mass spectroscopy.

TABLE 1

METASTABLE TRANSITIONS IN THE MASS SPECTRUM OF MeHgN=P(NMe$_2$)$_3$ (I)

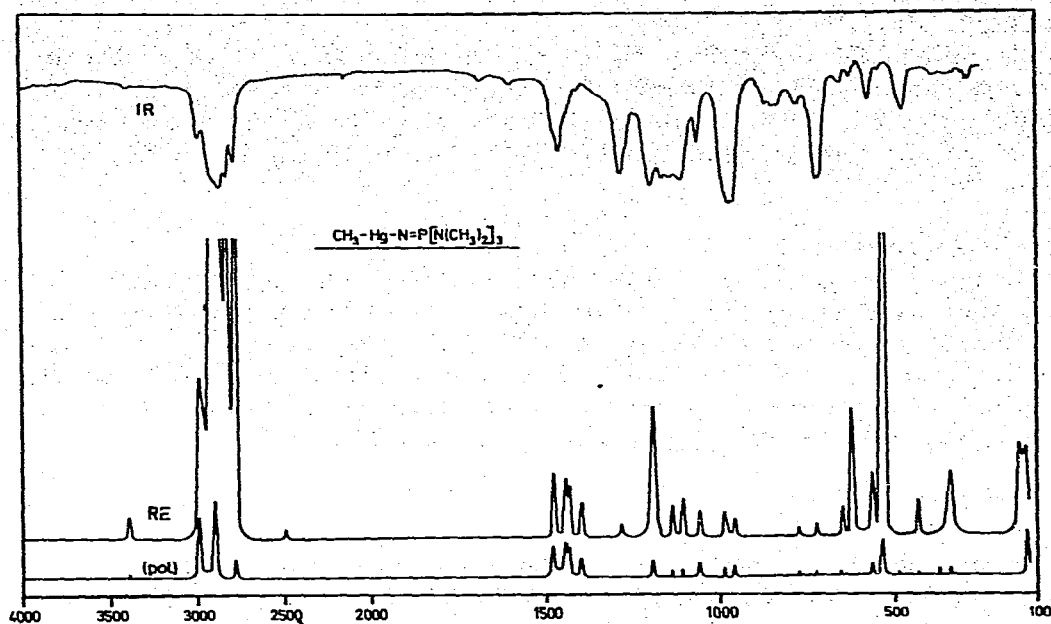| $m^*.(m/e)$	Transition (m/e)
80.5	379 → 177
102.5	177 → 135
250	379 → 307
312	394 → 349
369	394 → 379 [a]

[a] Only very weakly observed.

Fig. 3. IR and Raman spectra of (I).

TABLE 2

IR AND RAMAN SPECTRA OF $MeHgN=P(NMe_2)_3$ (cm^{-1})

Raman	IR	Assignment
3400 w		
3000 m	2990 s	
2930 vs		
2890 vs	2870 s	$\nu_{as}, \nu_s(C\!-\!H)$
2840 vs	2838 s	
2800 m	2790 s	
1480 w	1480 m—w	
1450 w	1460 m (br, sh)	
1440 w		$\delta_{as}(CH_3)$
1410 vw	1415 vw	
1290 vw	1285 m—s	$\nu(P=N)$
	1200 m—s	
	1165 m	
	1145 m	$\delta_s(CH_3)$
	1112 m	
1110 m	1060 w	
960 vw	975 s 960 s }	$\rho(CH_3)$
	870 vw	
	840 vw	
820 vw	825 vw	$\rho(CH_3)$
	775 w	
720 vw	720 s	$\nu_{as}(P\!-\!N_3)$
	650 vw	$\nu_s(P\!-\!N_3)$
630 s	625 vw	$\nu(Hg\!-\!C)$
	570 m—w	$\nu(Hg\!-\!N)$
490 vw	475 m	
350 w		

(b). HN=P(NMe₂)₃

Me₃SiN=P(NMe₂)₃ (6.75 g, 27 mmole), added to 30 ml i-C₃H₇OH with 2—5 drops conc. H₂SO₄, was distilled at atmospheric pressure with continuous addition during 2 h of another 50 ml alcohol; removal of solvent and distillation yielded a colourless liquid, b.p. 60—62°/0.1 mm. Yield 4.1 g (85%), identified as in (*a*).

(c). MeHgN=P(NMe₂)₃

MeHgN(SiMe₃)₂ (6.1 g, 16.2 mmole) and 2.9 g (16.2 mmole) HN=P(NMe₂)₃ were heated from 60—90° for 3 h; evaporation of volatile compounds and distillation yielded a colourless liquid, b.p. 68—70°/0.01 mm, which crystallized at room temperature. Yield 5.8 g (92%). (Found: C, 21.43; H, 5.87; N, 14.06; Hg, 50.68. Mol. wt. (cryoscopically in benzene solution), 334 and 356. Calcd.: C, 21.41; H, 5.35; N, 14.20; Hg, 51.00%. Mol. wt., 392.)

Acknowledgement

References

1 D. Breitinger and K. Brodersen, Angew. Chem., 82 (1970) 379.
2 J.A. Young, S.N. Tsoukalas and R.D. Dresdner, J. Amer. Chem. Soc., 80 (1958) 3604.
3 H. Bürger, W. Sawodny and U. Wannagat, J. Organometal. Chem., 3 (1965) 113.
4 J. Lorberth and F. Weller, J. Organometal. Chem., 32 (1971) 145.
5 R.C. Dobbie and H.J. Emeleus, J. Chem. Soc. A, (1966) 367.
6 K. Dehnicke and D. Seybold, J. Organometal. Chem., 11 (1968) 227.
7 H. Hess and D. Forst, Z. Anorg. Allg. Chem., 342 (1966) 240.
8 L.G. Hoard and R.A. Jacobson, J. Chem. Soc. A, (1966) 1203.
9 J.W. Cox and E.R. Corey, Chem. Commun., (1967) 123.
10 P.B. Hormuth and H.P. Latscha, Z. Anorg. Allg. Chem., 365 (1969) 26.
11 H. Schmidbaur, Advan. Organometal. Chem., 9 (1970) 259.
12 H. Schmidbaur and G. Jonas, Chem. Ber., 101 (1968) 1271.
13 J. Lorberth, unpublished results.
14 J. Lorberth, H. Krapf and H. Nöth, Chem. Ber., 100 (1967) 3511.
15 R.K. Harris, Can. J. Chem., 42 (1964) 2275.
16 H. Schmidbaur, W. Wolfsberger and K. Schwirten, Chem. Ber., 102 (1969) 556.
17 A. Schmidpeter, C. Weingand and E. Hafner-Roll, Z. Naturforsch. B, 24 (1969) 799.
18 A. Schmidpeter and K. Schumann, Z. Naturforsch. B, 25 (1970) 1364.