

## Synthesis, Solution Structure, and Halide Addition Compounds of Bis(dicyclohexylphosphinothioite)mercury(II)

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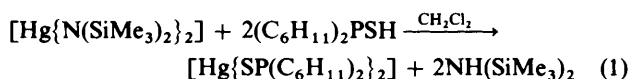
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The compound  $[\text{Hg}\{\text{SP}(\text{C}_6\text{H}_{11})_2\}_2]$  (**1**) was prepared from  $[\text{Hg}\{\text{N}(\text{SiMe}_3)_2\}_2]$  and  $(\text{C}_6\text{H}_{11})_2\text{PSH}$ . According to its  $^{31}\text{P}$  and  $^{199}\text{Hg}$  n.m.r. spectra it exists in solution both as cyclic dimers  $[\text{Hg}_2\{\mu\text{-SP}(\text{C}_6\text{H}_{11})_2\}_2\{\text{SP}(\text{C}_6\text{H}_{11})_2\}_2]$  and as a species containing two equivalent  $\text{SP}(\text{C}_6\text{H}_{11})_2$  ligands bound *via* phosphorus to mercury. Addition of halides to compound (**1**) affords  $[\text{Hg}_2\{\mu\text{-SP}(\text{C}_6\text{H}_{11})_2\}_2\{\text{SP}(\text{C}_6\text{H}_{11})_2\}_2\text{X}_2]^{2-}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{or I}$ ).

Deprotonated secondary phosphine sulphide (phosphinothioite) ligands  $\text{R}_2\text{PS}^-$  may co-ordinate end-on through phosphorus or sulphur, side-on, or may act as a bridge between two metal centres *via* phosphorus and sulphur. All these types of co-ordination have been observed, mainly in transition-metal complexes.<sup>1-10</sup> Since no phosphinothioitomercury complexes were known, we have prepared the compound  $[\text{Hg}\{\text{SP}(\text{C}_6\text{H}_{11})_2\}_2]$  (**1**) and studied some of its properties and reactions.

### Results and Discussion

The compound  $[\text{Hg}\{\text{SP}(\text{C}_6\text{H}_{11})_2\}_2]$  (**1**) has been prepared as colourless crystals by the reaction (1). Phosphorus-31 and



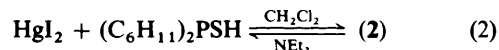
$^{199}\text{Hg}$  n.m.r. spectroscopy revealed that compound (**1**) exists in solution (dichloromethane or benzene) in part as  $[\text{Hg}_2\{\mu\text{-SP}(\text{C}_6\text{H}_{11})_2\}_2\{\text{SP}(\text{C}_6\text{H}_{11})_2\}_2]$ . The bridging ligands form six-membered  $\text{HgPSHgPS}$  rings and the terminal ligands are co-ordinated *via* phosphorus:  $\delta(^{31}\text{P}_\text{A})$  94.7,  $\delta(^{31}\text{P}_\text{B})$  89.9,  $^1J(^{199}\text{Hg}-^{31}\text{P}_\text{A})$  4 854,  $^1J(^{199}\text{Hg}-^{31}\text{P}_\text{B})$  2 701, and  $^2J(^{31}\text{P}_\text{A}-^{31}\text{P}_\text{B})$  202 Hz;  $\delta(^{199}\text{Hg})$  1 787, 0.25 mol dm<sup>-3</sup> in  $\text{CH}_2\text{Cl}_2$  at 300 K. The n.m.r. parameters are considerably medium dependent. Data for benzene are given in the Experimental section. The presence of distinct  $^{31}\text{P}$  n.m.r. signals for both ligand types shows the kinetic stability of the  $\text{Hg-S}$  bonds of the rings on the n.m.r. time-scale.

Besides this species, another species is present in solution which contains mercury co-ordinated by two equivalent  $\text{SP}(\text{C}_6\text{H}_{11})_2$  ligands *via* phosphorus. The mercury-199 resonance at relatively high frequency indicates additional co-ordination, presumably by sulphur:  $\delta(^{31}\text{P})$  90.1,  $^1J(^{199}\text{Hg}-^{31}\text{P})$  3 714 Hz;  $\delta(^{199}\text{Hg})$  1 967. The equivalence of the  $\text{SP}(\text{C}_6\text{H}_{11})_2$  ligands could be due to exchange since the coupling constant of

this species is near the average for the terminal and bridging sites of  $[\text{Hg}_2\{\mu\text{-SP}(\text{C}_6\text{H}_{11})_2\}_2\{\text{SP}(\text{C}_6\text{H}_{11})_2\}_2]$ . A possible explanation of the origin of this species is that the ligating power of the sulphur of the terminal  $\text{SP}(\text{C}_6\text{H}_{11})_2$  ligands of the ring prevents the complete ring formation. The intensity ratio of these two species is around 2:1 and is essentially independent of temperature between 300 and 230 K.

In contrast, the oxygen analogue  $[\text{Hg}(\text{OPBu}^t)_2]$  has only one  $^{31}\text{P}$  resonance with  $^{199}\text{Hg}$  satellite patterns at ambient temperature<sup>11</sup> implying that there are no  $\text{Hg-O}$  interactions kinetically stable on the n.m.r. time-scale. Below 183 K bridging and terminal  $\text{Bu}^t\text{PO}$  ligands are however resolved:  $\delta(^{31}\text{P}_\text{A})$  135.6,  $\delta(^{31}\text{P}_\text{B})$  140.9,  $^1J(^{199}\text{Hg}-^{31}\text{P}_\text{A})$  3 099,  $^1J(^{199}\text{Hg}-^{31}\text{P}_\text{B})$  2 798, and  $^2J(^{31}\text{P}_\text{A}-^{31}\text{P}_\text{B})$  245 Hz, 0.1 mol dm<sup>-3</sup> in  $\text{CH}_2\text{Cl}_2$  at 183 K. Only one (the ring) species is present. This different behaviour is in keeping with the much weaker affinity of oxygen towards mercury compared to that of sulphur.

The addition of iodide to compound (**1**) produces the mercurate (**2**), which was characterized by  $^{31}\text{P}$  and  $^{199}\text{Hg}$  n.m.r. spectroscopy (Table). Both species present in a solution of (**1**) (see above) afford (**2**) in the course of this reaction. The addition compound (**2**) is also formed according to equation (2). The



position of equilibrium lies to the right only at temperatures below 233 K. Compound (**2**) could be isolated as the tetraphenylphosphonium salt. Analogous compounds are formed with bromide and chloride (Table).

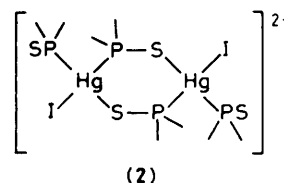


Table. N.m.r. parameters of  $[\text{Hg}_2\{\mu\text{-SP}(\text{C}_6\text{H}_{11})_2\}_2\{\text{SP}(\text{C}_6\text{H}_{11})_2\}_2\text{X}_2]^{2-}$  (0.125 mmol per cm<sup>3</sup> of  $\text{CH}_2\text{Cl}_2$ ) at 233 K;  $J$  values in Hz

Cation	X	$\delta(^{31}\text{P}_\text{A})$	$\delta(^{31}\text{P}_\text{B})$	$\delta(^{199}\text{Hg})$	$^1J(^{199}\text{Hg}-^{31}\text{P}_\text{A})$	$^1J(^{199}\text{Hg}-^{31}\text{P}_\text{B})$	$^2J(^{31}\text{P}_\text{A}-^{31}\text{P}_\text{B})$
$\text{NEt}_3\text{H}^+$	I	81.7	81.6	1 829	4 511	3 511	205
$\text{PPh}_4^+$	I	83.4	83.2	1 813	4 574	3 423	204
$\text{NBu}_4^+$	I	83.6	83.2	1 813	4 631	3 361	206
$\text{NBu}_4^+$	Br	84.9	81.8	1 819	4 712	3 438	217
$\text{NBu}_4^+$	Cl	85.1	82.0	1 833	4 777	3 498	222

### Experimental

N.m.r. spectra were recorded on a multinuclear Bruker WP-80 spectrometer operating in the Fourier-transform mode and processed using the program PANIC on a Bruker Aspect 2000 computer. Chemical shifts are in p.p.m. to high frequency of 85%  $\text{H}_3\text{PO}_4$  or aqueous  $\text{Hg}(\text{ClO}_4)_2$  (2 mmol  $\text{HgO}$  per  $\text{cm}^3$  of 60%  $\text{HClO}_4$ ), and coupling constants are in Hz. Chemical analyses were obtained on a Heraeus EA 415.  $(\text{C}_6\text{H}_{11})_2\text{PSH}^{12}$  and  $[\text{Hg}\{\text{N}(\text{SiMe}_3)_2\}_2]^{13}$  were prepared according to the literature. All operations were carried out in dried solvents under dinitrogen.

*Preparation of Bis(dicyclohexylphosphinothioito)mercury, (1).*— $(\text{C}_6\text{H}_{11})_2\text{PSH}$  (461 mg, 2.00 mmol) was added to a solution of  $[\text{Hg}\{\text{N}(\text{SiMe}_3)_2\}_2]$  (521 mg, 1.00 mmol) in dichloromethane ( $3 \text{ cm}^3$ ) at ambient temperature. The reaction proceeds exothermically and is complete within a few minutes. The product precipitated as large colourless crystals upon cooling the solution to  $-20^\circ\text{C}$  overnight and was separated and washed with a small amount of cold  $\text{CH}_2\text{Cl}_2$ . Yield 625 mg (95%), m.p.  $106^\circ\text{C}$  (Found: C, 43.8; H, 6.5.  $\text{C}_{24}\text{H}_{44}\text{HgP}_2\text{S}_2$  requires C, 43.7; H, 6.7%). N.m.r. (saturated solution in benzene):  $\delta(^{31}\text{P})$  84.1 (s),  $^1J(^{199}\text{Hg}-^{31}\text{P})$  3 736;  $\delta(^{31}\text{P}_A)$  88.9,  $\delta(^{31}\text{P}_B)$  84.5,  $^1J(^{199}\text{Hg}-^{31}\text{P}_A)$  4 935,  $^1J(^{199}\text{Hg}-^{31}\text{P}_B)$  2 392, and  $^2J(^{31}\text{P}_A-^{31}\text{P}_B)$  204 Hz. Molecular weight (cryoscopy in benzene): 1 237.

*Preparation of Bis(tetraphenylphosphonium) [Bis( $\mu$ -dicyclohexylphosphinothioito-P,S)-bis(dicyclohexylphosphinothioito-P)di-iodo]dimercurate(2-), (2).*—This compound was obtained as a colourless crystalline solid in almost quantitative yield upon evaporation of a dichloromethane solution containing stoichiometric quantities of (1) and  $\text{PPh}_4\text{I}$ . The compound decomposes above  $100^\circ\text{C}$  (Found: C, 51.5; H, 6.0.  $\text{C}_{96}\text{H}_{128}\text{Hg}_2\text{I}_2\text{P}_6\text{S}_4$  requires C, 51.2; H, 5.7%).

*Reaction of  $\text{HgI}_2$  with  $(\text{C}_6\text{H}_{11})_2\text{PSH}$  [equation (2)].*—Mercury(II) iodide (114 mg, 0.25 mmol),  $(\text{C}_6\text{H}_{11})_2\text{PSH}$  (116 mg,

0.50 mmol) and  $\text{NEt}_3$  (101 mg, 1.00 mmol) were mixed in dichloromethane ( $1 \text{ cm}^3$ ). Analogous reactions with  $\text{HgBr}_2$  and  $\text{HgCl}_2$  could be carried out. The compounds  $[\text{NBu}_4]_2-[\text{Hg}_2\{\mu\text{-SP}(\text{C}_6\text{H}_{11})_2\}_2\{\text{SP}(\text{C}_6\text{H}_{11})_2\}_2\text{X}_2]$  ( $\text{X} = \text{I}, \text{Cl}, \text{or Br}$ ) could not be crystallized.

### Acknowledgements

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### References

- 1 D. M. Anderson, E. A. V. Ebsorth, T. A. Stephenson, and M. D. Walkinshaw, *Angew. Chem.*, 1981, **93**, 290; *J. Chem. Soc., Dalton Trans.*, 1982, 2343.
- 2 V. Marsala, F. Faracone, and P. Piraino, *J. Organomet. Chem.*, 1977, **133**, 301.
- 3 D. H. M. W. Thewissen, *J. Organomet. Chem.*, 1980, **192**, 115.
- 4 H. P. M. M. Ambrosius, J. H. Noordik, and G. J. A. Ariaans, *J. Chem. Soc., Chem. Commun.*, 1980, 832.
- 5 E. Lindner, F. Bouachir, and S. Hoehne, *Chem. Ber.*, 1983, **116**, 46.
- 6 K. P. Wagner, R. W. Hess, P. M. Treichel, and J. C. Calabrese, *Inorg. Chem.*, 1975, **14**, 1121.
- 7 B. Walther, B. Messbauer, and H. Mayer, *Inorg. Chim. Acta*, 1979, **37**, L525.
- 8 E. Lindner and B. Schilling, *Chem. Ber.*, 1977, **110**, 3889.
- 9 B. Klingert and H. Werner, *J. Organomet. Chem.*, 1983, **252**, C47.
- 10 E. Lindner and H. Dreher, *J. Organomet. Chem.*, 1976, **105**, 85.
- 11 P. Peringer and J. Eichbichler, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2033.
- 12 M. M. Rauhut, H. A. Currier, and N. P. Wystrach, *J. Org. Chem.*, 1961, **26**, 5133.
- 13 H. Buerger, W. Sawodny, and U. Wannagat, *J. Organomet. Chem.*, 1965, **3**, 113.

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