

## Novel 6- and 8-Membered Hg-P Rings

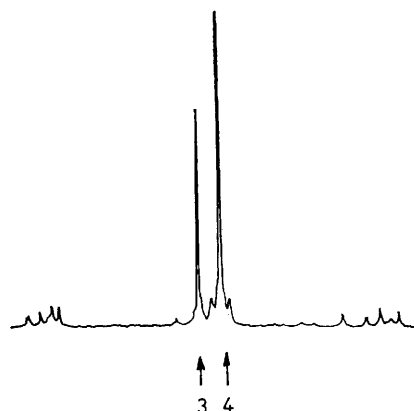
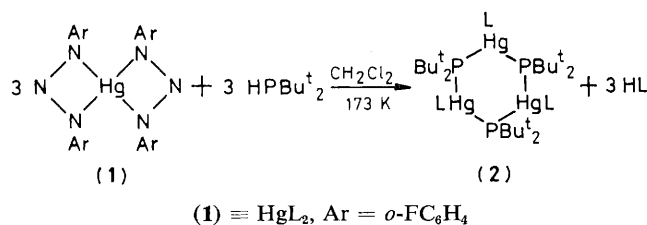
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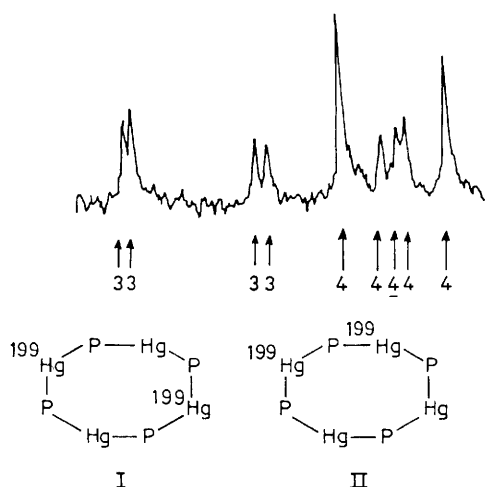
Reaction of  $\text{HgL}_2$  [HL = 1,3-bis(*o*-fluorophenyl)triazene] with secondary phosphines yields the first monocyclic 6- and 8-membered M-P rings [ $\text{Hg}_n(\mu_2\text{-R}_2\text{P})_n\text{L}_n$ ] ( $n = 3$ , R = Bu<sup>t</sup> or cyclohexyl; ( $n = 4$ , R = cyclohexyl or Ph) which are characterized by  $^1\text{H}$ ,  $^{31}\text{P}$ , and  $^{199}\text{Hg}$  n.m.r. spectroscopy.

Four-membered monocyclic structures (M-P)<sub>2</sub> are well known in transition and main group metal phosphido compounds; furthermore some (M-P)<sub>3</sub> rings with or without metal-metal bonds have been described.<sup>1</sup> We report here the first (mono)cyclic  $\mu$ -phosphido mercury complexes with six- and eight-membered Hg-P ring structures.

Reaction of equimolar amounts of  $\text{HgL}_2$  (**1**) and  $\text{HPBu}_2^t$  leads to stable orange crystals, m.p. 182–187 °C, in almost quantitative yield. Chemical analysis and mass spectra indicate substitution of one L by  $\text{PBu}_2^t$  (highest *m/e* 578,  $\text{LHgPBu}_2^t$ ). A  $^1\text{H}$  n.m.r. pseudo-triplet of the Bu<sup>t</sup> groups



**Figure 1.**  $^{31}\text{P}\{^1\text{H}\}$  N.m.r. spectrum of an equilibrium mixture of [ $\text{Hg}_3(\mu_2\text{-Cy}_2\text{P})_3\text{L}_3$ ], labelled 3 and [ $\text{Hg}_4(\mu_2\text{-Cy}_2\text{P})_4\text{L}_4$ ], labelled 4. The n.m.r. spectra were measured on a multinuclear Bruker WP-80 FT spectrometer and calculated using PANIC on a Bruker aspect 2000 computer.



**Figure 2.**  $^{199}\text{Hg}$  Satellite pattern of the right-hand side of the  $^{31}\text{P}$  n.m.r. spectrum in Figure 1. Peaks labelled 3 belong to  $[\text{Hg}_3(\mu_2\text{-Cy}_2\text{P})_3\text{L}_3]$ , those labelled 4 to  $[\text{Hg}_4(\mu_2\text{-Cy}_2\text{P})_4\text{L}_4]$  (isotopomer with one  $^{199}\text{Hg}$  atom in each case). The peak marked 4 is attributed to the isotopomer I ( $p = 3.9\%$ ) containing two  $^{199}\text{Hg}$  atoms; the isotopomer II is not resolved. (Substituents are omitted from the drawings of the isotopomers.)

indicates a P–Hg–P bond sequence,<sup>2</sup> in agreement with the  $^{199}\text{Hg}$  n.m.r. spectrum. The intensity of the  $^{199}\text{Hg}$  satellite bands in the  $^{31}\text{P}$  n.m.r. spectrum indicates an Hg–P–Hg structural element and both arguments combine to suggest a  $(\text{Hg-P})_n$  ring system. All n.m.r. spectra are consistent with those calculated for  $[\text{Hg}_3(\mu_2\text{-Bu}^t\text{P})_3\text{L}_3]$ , the novel six-membered ring (2);  $\delta$  ( $^{31}\text{P}$ ) 102 and  $\delta$  ( $^{199}\text{Hg}$ ) 1954 p.p.m. to high frequency of 85%  $\text{H}_3\text{PO}_4$  or aqueous  $\text{Hg}(\text{ClO}_4)_2$  (2 mmol  $\text{HgO}$  in 1 ml 60%  $\text{HClO}_4$ ), respectively;  $^2J$  ( $^{31}\text{P}$ – $^{31}\text{P}$ ) 162,  $^1J$  ( $^{31}\text{P}$ – $^{199}\text{Hg}$ ) 2313, and  $^3J$  ( $^{31}\text{P}$ – $^{199}\text{Hg}$ ) –9 Hz; spectra measured

in toluene for the isotopomer with one  $^{199}\text{Hg}$  atom,  $p_1 = 34.9\%$ . A second equivalent of  $\text{HPBu}^t_2$  does not co-ordinate or form  $\text{Hg}(\text{PBu}^t_2)_2$  under the same conditions.

The reaction of (1) with  $\text{HPCy}_2$  (Cy = cyclohexyl) yields, first the analogous product  $[\text{Hg}_3(\mu_2\text{-Cy}_2\text{P})_3\text{L}_3]$ , (3) [ $\delta$  ( $^{31}\text{P}$ ) 50 and  $\delta$  ( $^{199}\text{Hg}$ ) 2148 p.p.m.;  $^2J$  ( $^{31}\text{P}$ – $^{31}\text{P}$ ) 178,  $^1J$  ( $^{31}\text{P}$ – $^{199}\text{Hg}$ ) 2352, and  $^3J$  ( $^{31}\text{P}$ – $^{199}\text{Hg}$ ) 2 Hz; in tetrahydrofuran (THF)]. This ring system rearranges to give another product (4) whose n.m.r. spectra (Figures 1 and 2) are compatible with the novel monocyclic eight-membered Hg–P ring system  $[\text{Hg}_4(\mu_2\text{-Cy}_2\text{P})_4\text{L}_4]$ , (4) [ $\delta$  ( $^{31}\text{P}$ ) 45 and  $\delta$  ( $^{199}\text{Hg}$ ) 2062 p.p.m.;  $^2J$  ( $^{31}\text{P}$ – $^{31}\text{P}$ ) 138,  $^4J$  ( $^{31}\text{P}$ – $^{31}\text{P}$ ) ca. 0,  $^1J$  ( $^{31}\text{P}$ – $^{199}\text{Hg}$ ) 2562, and  $^3J$  ( $^{31}\text{P}$ – $^{199}\text{Hg}$ ) 18 Hz; in THF, isotopomer with one  $^{199}\text{Hg}$  atom,  $p_1 = 38.7\%$ ]. Reaction of (1) with  $\text{HPPh}_2$  yields the eight-membered ring compound  $[\text{Hg}_4(\mu_2\text{-Ph}_2\text{P})_4\text{L}_4]$  (5) exclusively [ $\delta$  ( $^{31}\text{P}$ ) 28 p.p.m.;  $^2J$  ( $^{31}\text{P}$ – $^{31}\text{P}$ ) 157,  $^4J$  ( $^{31}\text{P}$ – $^{31}\text{P}$ ) ca. 0,  $^1J$  ( $^{31}\text{P}$ – $^{199}\text{Hg}$ ) 2903, and  $^3J$  ( $^{31}\text{P}$ – $^{199}\text{Hg}$ ) 9 Hz; toluene]. Solutions of (3)–(5) are quite stable below 253 K in contrast with the respective symmetric compounds  $\text{Hg}(\text{PPh}_2)_2$  and  $\text{Hg}(\text{PCy}_2)_2$ .<sup>3</sup>

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