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OBSERVATION OF DIASTEREOMERS BY ^{199}Hg NMR

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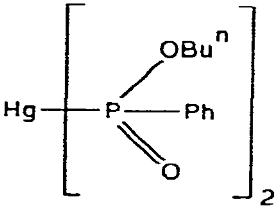
Summary

The diastereomeric parts of Hg—P bonded $Hg[P(O)(OBu^n)Ph]_2$ give rise to different ^{199}Hg NMR patterns. No enantiomeric discrimination occurs in the synthesis. Ligand redistribution reactions prevent the separation of the diastereomers.

Whilst the ^{199}Hg NMR spectrum of the Hg—P bonded bis[*O*-n-butyl-*P*-



(I)

phenylphosphonito]mercury (I) in pyridine consists as expected of a 1/2/1 triplet, in toluene or tetrahydrofurane two triplets are displayed (Fig. 1).

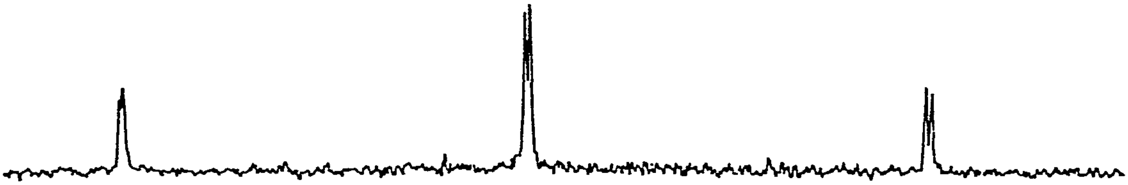


Fig. 1. ^{199}Hg NMR spectrum of $Hg[P(O)(OBu^n)Ph]_2$ in tetrahydrofuran (0.25 mmol/cm^3) recorded on a Bruker WP-80: $\delta(^{199}Hg)$: 1134.4 $^1J(^{31}P—^{199}Hg)$: 5275 Hz; $\delta(^{199}Hg)$: 1138.3, $^1J(^{31}P—^{199}Hg)$: 5264 Hz (chemical shifts in ppm to high frequency of aqueous $Hg(ClO_4)_2$ (2 mmol HgO/cm^3 60% $HClO_4$)).

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Molecular weight measurements for I in benzene indicate a dimeric structure (as observed for bis(phosphito)mercury compounds [1]), and on the basis of the X-ray structure of $Hg[P(O)(OMe)_2]_2$ [1], association by Hg—O bonds seems likely. On the other hand the ^{31}P NMR spectrum of I at ambient temperature displays only one ^{31}P species and no $^2J(^{31}P—^{199}Hg)$ coupling pattern. This demonstrates the kinetic lability of the Hg—O bonds of I on the NMR time scale, as has been suggested for bis(phosphito)mercury compounds [1]. NMR detectable molecular association of I is however observed below 183 K. Hence the appearance of the two triplets (Fig. 1) cannot be explained by molecular association but seems to be due to the diastereomeric parts of I (containing two optically active P centers). The observation of two triplets shows the kinetic stability of the Hg—P bonds on this NMR time scale.

Compound I is formed via an enantiomeric intermediate eq. (1):

$$\mathrm{LH} + \mathrm{Hg(OAc)_2} \rightarrow \mathrm{HOAc} + \mathrm{AcOHgL} \quad \mathrm{L} = \mathrm{OP(OBu^n)Ph} \qquad (1)$$

$$\mathrm{AcOHgL} + \mathrm{LH} \rightarrow \mathrm{HgL_2} + \mathrm{HOAc}$$

No enantiomeric discrimination is however observed upon formation of I from this intermediate, as shown by the almost equal intensities of the two ^{199}Hg triplets (Fig. 1). No separation of the diastereomers is possible because of the occurrence of the ligand redistribution reaction shown in eq. 2 on the preparative time scale.

$$\mathrm{L}\mathit{HgL} + \mathrm{HgL_2} \rightleftharpoons \mathit{L}\mathrm{HgL} + \mathit{Hg}\mathrm{L_2} \quad \mathrm{L} = \mathrm{OP(OBu^n)Ph} \qquad (2)$$

This is the first report of the detection of diastereomers by ^{199}Hg NMR spectroscopy, taking advantage of the large range of chemical shifts of this nucleus [2] which makes it possible to distinguish rather similar chemical environments. This may be of considerable interest for the stereochemical investigations of compounds containing kinetically stable Hg—E bonds (e.g. E = C). An example of the use of ^{95}Mo NMR spectroscopy for the observation of diastereomers appeared very recently [3].

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