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Preliminary communication

DEPROTONATED BIS(DIPHENYLPHOSPHINO)METHANE AS A MONODENTATE C-BONDED LIGAND: PREPARATION AND $^{31}P/^{199}Hg$ NMR CHARACTERISATION OF $Hg[CH(PPh_2)_2]_2$

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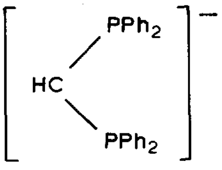
Summary

$HgCl_2$ reacts with 2 equivalents of $(PPh_2)_2CHLi$ to yield the title compound. The deprotonated dppm ligands are monodentate and bonded through the methine carbon atoms as shown by ^{31}P and ^{199}Hg NMR spectroscopy.

Deprotonated dppm (**1**) * is known to act as bidentate or tridentate ligand [1]. In the tridentate bonding mode the carbon atom as well as the phosphorus atoms are coordinated [1–5]. Bidentate deprotonated dppm is ambidentate; usually, P,P-bonding is observed [1], but there are at least two examples of P,C-bonding [6]. We report here on the preparation and characterisation of $Hg[CH(PPh_2)_2]_2$, which has been shown in solution to involve a novel coordination mode of the deprotonated dppm. The synthesis of the related compound $[Hg\{CH(PPh_2)_2\}Br]$ has previously been reported, but the bonding mode of the ligand was not established [7].



(1)

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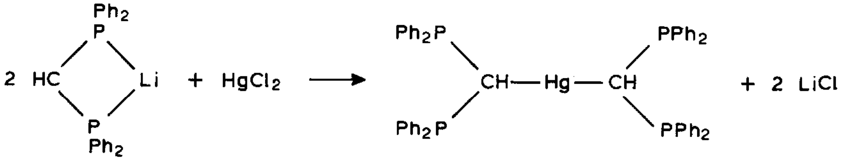
* In structural formulae only the connectivity is shown. There is no attempt to define bond orders.

Lithiated dppm [7] (from dppm and BuLi in THF) reacts with $HgCl_2$ in THF at 0°C quantitatively according to eq. 1:



(2)

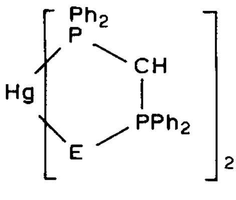
(1)

Complex **2** is readily soluble in apolar organic solvents (e.g. THF or toluene) and is moisture sensitive.

The mode of coordination of the ligands in **2** has been established by ^{31}P and ^{199}Hg NMR spectroscopy: the $^{199}Hg\{^1H\}$ NMR spectrum consist of a 1/4/6/4/1 quintet at 1725 ppm (solvent THF, reference aqueous $Hg(ClO_4)_2$ (2 mmol HgO/ml 60% $HClO_4$), instrument: Bruker WP-80) with a coupling constant of 92 Hz. The ^1H coupled ^{199}Hg NMR spectrum is a quintet of triplets. The coupling patterns are clear at ambient temperature and are attributed to coupling of ^{199}Hg to 4 equivalent phosphorus atoms and 2 equivalent hydrogen atoms (J(Hg,H) 137 Hz). The magnitude of J(Hg,P) clearly indicates a two bond coupling. This implies coordination of the ligand via the methine carbon, which is in keeping with the kinetic stability of Hg–C bonds on the NMR time scale at ambient temperature, and consistent with the value of the Hg–H coupling constant.

The $^{31}P\{^1H\}$ NMR spectrum of **2** consists of one signal at −7.8 ppm (solvent THF, reference 85% H_3PO_4) with ^{199}Hg satellites of appropriate intensity and displacement. Coordination of phosphorus atoms to mercury is unlikely since diorganomercurials are weak acceptors unless the organic groups are strong electron-withdrawing groups, and absence of such coordinated is confirmed by the position of the ^{31}P resonance.

The bonding mode of $[CH(PPh_2)_2]^-$ in **2** is not thought to arise from a preference of mercury for carbon in an ambidentate system with P and C as potential donor sites, since, for example, the compounds $Hg(EPPh_2CHPPh_2)_2$ have the structure **3** (E = S, Se, Te) [8]; in which the deprotonated dppm chalcogenides



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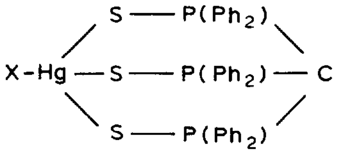
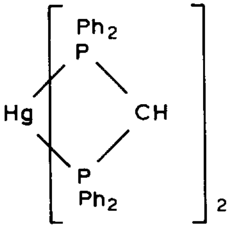


(4)

(which involve a potentially ambidentate C,E,P-system) act as P,E-bonded chelates [8]. A further example is provided by the mercury complexes of deprotonated $HC[P(S)Ph_2]_3$ (**4**), in which mercury is coordinated through three S donor atoms but not through the methine carbon [9].

We suggest that the bonding mode of the ligand in **2** is caused by steric factors. The most probable (vide supra) alternative structure of **2** would involve chelating bidentate ligands as sketched in structure **5**.



(5)

Four-membered chelate rings are strained, especially when metals in tetrahedral coordination geometry are involved [1]. Although $[Hg(\eta^2\text{-dppm})_2]^{2+}$, the dppm analogue of **5**, exists [10], the presence of ring strain is demonstrated by the ease of ring opening by rather weak ligands [11]. Thus dppm will tend to avoid the formation of 4-membered chelate rings by adopting other modes of coordination (e.g. bridging bidentate or monodentate). The same factor is believed to lead the deprotonated dppm in **2** to adopt the novel monodentate carbon bonding mode.

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