

Preliminary communication

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

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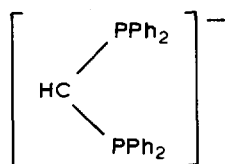
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(Received July 1st, 1986)

Summary

HgCl_2 reacts with 2 equivalents of $(\text{PPh}_2)_2\text{CHLi}$ 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

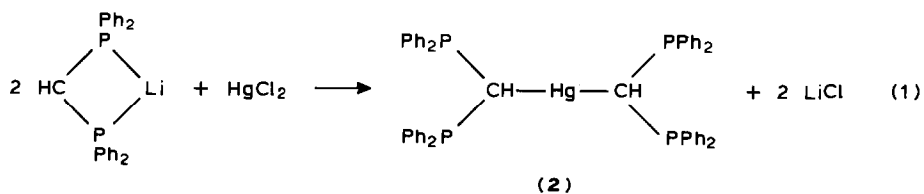


(1)

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 $\text{Hg}[\text{CH}(\text{PPh}_2)_2]_2$, which has been shown in solution to involve a novel coordination mode of the deprotonated dppm. The synthesis of the related compound $[\text{Hg}\{\text{CH}(\text{PPh}_2)_2\}\text{Br}]$ has previously been reported, but the bonding mode of the ligand was not established [7].

* 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:

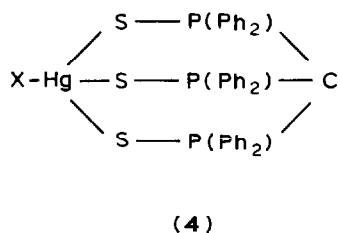
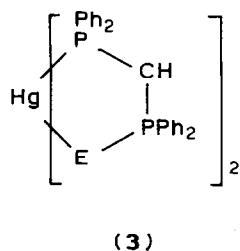


Complex **2** is readily soluble in apolar organic solvents (e.g. THF or toluene) and is moisture sensitive.

The mode of coordination of the ligands in **2** has been established by ^{31}P and ^{199}Hg NMR spectroscopy: the $^{199}\text{Hg}\{^1\text{H}\}$ NMR spectrum consist of a 1/4/6/4/1 quintet at 1725 ppm (solvent THF, reference aqueous $\text{Hg}(\text{ClO}_4)_2$ (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 ($J(\text{Hg},\text{H})$ 137 Hz). The magnitude of $J(\text{Hg},\text{P})$ 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 $\text{Hg}-\text{C}$ bonds on the NMR time scale at ambient temperature, and consistent with the value of the $\text{Hg}-\text{H}$ coupling constant.

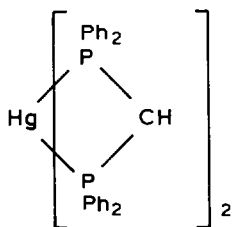
The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** consists of one signal at -7.8 ppm (solvent THF, reference 85% H_3PO_4) with ^{199}Hg satellites of appropriate intensity and displacement. Coordination of phosphorus atoms to mercury is unlikely since diorganomercurials are weak acceptors unless 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 $[\text{CH}(\text{PPh}_2)_2]^-$ 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 $\text{Hg}(\text{EPPH}_2\text{CHPPH}_2)_2$ have the structure **3** (E = S, Se, Te) [8]; in which the deprotonated dppm chalcogenides



(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 $\text{HC}[\text{P}(\text{S})\text{Ph}_2]_3$ (**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 $[\text{Hg}(\eta^2\text{-dppm})_2]^{2+}$, 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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