

## Carbene Complexes from Coordinated Bis(diphenylphosphino)methane. Synthesis and X-Ray Structure Determination of the Remarkable Heterotrimetallic Derivative $[\{\text{Fe}(\text{CNPh})_4(\text{PPh}_2)_2\text{C}\}]_2\text{HgI}_2$

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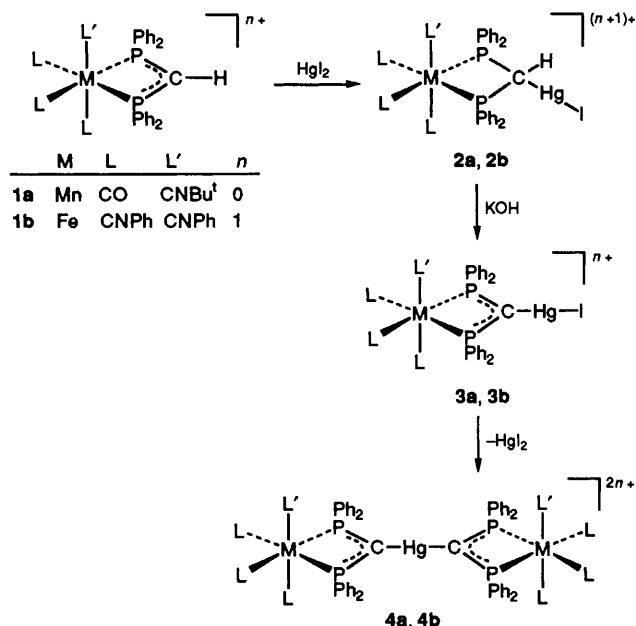
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The bis(diphenylphosphino)methanide complexes *fac*-[Mn(CNBut)(CO)<sub>3</sub>{(PPh<sub>2</sub>)<sub>2</sub>CH}] **1a** and [Fe(CNPh)<sub>4</sub>{(PPh<sub>2</sub>)<sub>2</sub>CH}]ClO<sub>4</sub> **1b** react with HgI<sub>2</sub> and KOH to give the heterotrimetallic bis(carbene)derivatives *fac*-[Mn(CNBut)(CO)<sub>3</sub>{(PPh<sub>2</sub>)<sub>2</sub>C}]<sub>2</sub>Hg] **4a** and  $[\{\text{Fe}(\text{CNPh})_4(\text{PPh}_2)_2\text{C}\}]_2\text{HgI}_2$  **4b**, respectively; the structure of **4b** has been determined by X-ray analysis.

The bidentate ligand bis(diphenylphosphino)methane (dppm) has widely been used in coordination and organometallic chemistry.<sup>1</sup> Its deprotonated form, bis(diphenylphosphino) methanide  $\{[(\text{PPh}_2)_2\text{CH}]^-\}$  has also received some attention because of its ability to act as a two-, four- or six-electron donor ligand, being a versatile building block for the construction of heterometallic species.<sup>2</sup> Despite its potential application in the preparation of polymetallic species, the doubly deprotonated form of dppm,  $[(\text{PPh}_2)_2\text{C}]^{2-}$ , has only been reported in a few cases.<sup>3</sup> The main reason appears to be the lack of valuable synthetic methodologies. Here, we report an easy way to obtain a new class of carbene complexes derived from double deprotonation of dppm coordinated to iron(II) and manganese(I) centres.

Neutral *fac*-[Mn(CNBut)(CO)<sub>3</sub>{(PPh<sub>2</sub>)<sub>2</sub>C}]<sub>2</sub>Hg] **4a**<sup>†</sup> and cationic  $[\{\text{Fe}(\text{CNPh})_4(\text{PPh}_2)_2\text{C}\}]_2\text{HgI}_2$  **4b**<sup>†</sup> trimetallic complexes have been prepared by treating dichloromethane solutions of the methanide derivatives *fac*-[Mn(CNBut)(CO)<sub>3</sub>{(PPh<sub>2</sub>)<sub>2</sub>CH}] **1a**<sup>4</sup> and [Fe(CNPh)<sub>4</sub>{(PPh<sub>2</sub>)<sub>2</sub>CH}]ClO<sub>4</sub>

<sup>†</sup> Spectroscopic data (IR in CH<sub>2</sub>Cl<sub>2</sub>, NMR in CD<sub>2</sub>Cl<sub>2</sub>) for **2a**: IR  $\nu_{\text{CO}}$  2037 and 1973,  $\nu_{\text{CN}}$  2184 cm<sup>-1</sup>; <sup>31</sup>P{<sup>1</sup>H}NMR:  $\delta$  26.94 (s, broad). For **2b**: IR  $\nu_{\text{CN}}$  2194w, 2154s cm<sup>-1</sup>; <sup>31</sup>P{<sup>1</sup>H}NMR:  $\delta$  19.62 (s, with <sup>199</sup>Hg satellites <sup>2</sup>J<sub>P-Hg</sub> 202 Hz). For **4a** IR  $\nu_{\text{CO}}$  2007, 1942, 1925,  $\nu_{\text{CN}}$  2168 cm<sup>-1</sup>; <sup>31</sup>P{<sup>1</sup>H}NMR:  $\delta$  5.0 (s, broad). For **4b**: IR  $\nu_{\text{CN}}$  2181w, 2137s cm<sup>-1</sup>; <sup>31</sup>P{<sup>1</sup>H}NMR:  $\delta$  -1.29 (s); <sup>31</sup>C NMR (except for phenyls):  $\delta$  62.28 (t, C-Hg, J<sub>P-C</sub> 36 Hz), 165.14 (s, broad, 2C, CNPh), 166.04 (t, 2C, CNPh, J<sub>P-C</sub> = 24 Hz).



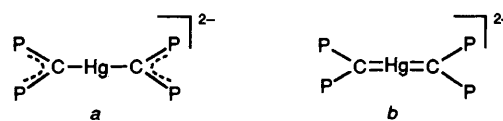
**Scheme 1** A possible mechanism for the formation of complexes type 4

**1b**<sup>3a</sup> with HgI<sub>2</sub> and further addition of KOH. A possible mechanism for the formation of complexes type 4 is shown in Scheme 1. Coordination of the central carbon atom of the methanide ligand to the mercury gives complexes **2**, which have been characterized spectroscopically,<sup>†</sup> its low thermal stability precluding a deeper structural analysis.<sup>‡</sup> Deprotonation of **2** with KOH can produce the proposed intermediate **3**, which is transformed to **4** by means of a symmetrization reaction analogous to that occurring in the haloalkylmercury derivatives.<sup>5</sup>

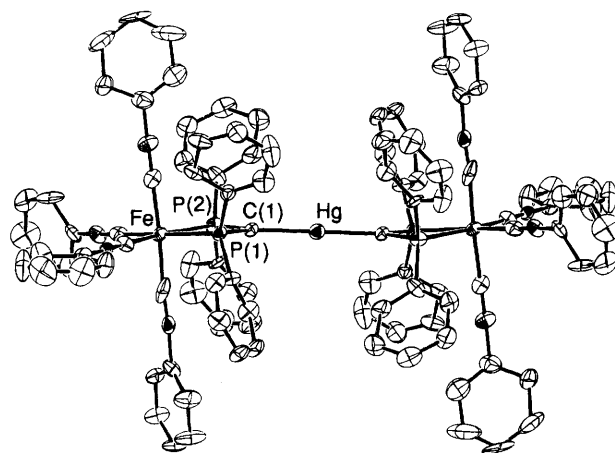
Type **4** complexes are very air sensitive in solution and readily absorb water to form their corresponding methanide precursors **1a** and **1b**. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **4a** and **4b** show only one peak due to the equivalent phosphorus of the diphosphine, but, surprisingly no <sup>199</sup>Hg satellites were observed. In order to fully structurally characterize these species, an X-ray analysis for **4b** has been carried out.<sup>§</sup> The molecular structure of the complex cation is shown in Fig. 1. The molecule is centrosymmetrical, the mercury being at the inversion centre. The four phosphorus atoms, the two central carbon atoms of the diphosphines and the mercury atom lie in the same plane, with the two iron atoms slightly deviating

<sup>‡</sup> Additional support for the structure of **2**: 1 equiv. of HgI<sub>2</sub> is needed to complete the conversion of **1a** to **2a**. The conductivity value of crude **2a** in acetone (5 × 10<sup>-4</sup> mol dm<sup>-3</sup>) is near the range for a 1:1 electrolyte (82 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>).

<sup>§</sup> *Crystal data*: complex **4b**: C<sub>106</sub>H<sub>80</sub>N<sub>8</sub>P<sub>4</sub>FeHgI<sub>2</sub>·2(CH<sub>2</sub>Cl<sub>2</sub>), *M* = 2919.7, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 13.91 (1), *b* = 21.27 (2), *c* = 18.56 (3) Å, β = 107.6 (2)°, *V* = 5232 (12) Å<sup>3</sup>, *Z* = 2, *D*<sub>x</sub> = 1.50 g cm<sup>-3</sup>, Mo-Kα radiation (λ = 0.71073 Å), μ(Mo-Kα) = 25.34 cm<sup>-1</sup>, crystal dimensions 0.26 × 0.23 × 0.10 mm. The structure was solved by Patterson interpretation and Phase Expansion using the program DIRDIF, and refined by isotropic least-squares analysis using SHELX76. Two dichloromethane solvent molecules were located and isotropically refined as an ideal group. All the hydrogen atoms were refined isotropically, except for the dichloromethane hydrogen atoms. For 2573 observed reflections [*I* > 3σ(*I*)] collected at room temperature on an Enraf-Nonius CAD4 diffractometer in the range 0° < θ < 25° the *R* value is 0.063. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



**Scheme 2**



**Fig. 1** View (ORTEP) of the complex cation of **4b**. Bond distances (Å): Fe–P(1), 2.273 (7); Fe–P(2), 2.281 (7); C(1)–P(1), 1.73 (2); C(1)–P(2), 1.67 (2); Hg–C(1), 2.10 (2). Bond angles (°): P(2)–Fe–P(1), 69. (1); P(1)–C(1)–Hg, 128. (1); P(2)–C(1)–Hg, 133. (1); P(2)–C(1)–P(1), 99. (1).

from this plane [Fe P(1) P(2) C(1) torsion angle = 173 (1)°]. The distance Hg–C(1) [2.10(2) Å] is similar to those normally found in diorganomercury(II) derivatives<sup>6</sup> and of the same order as that of the biscarbene complex {Hg{C(NPh)–C(H)=C(H)–NPh}<sub>2</sub>}(ClO<sub>4</sub>)<sub>2</sub> (2.06 Å).<sup>7</sup> The P(1)–C(1) [1.73(2) Å] and P(2)–C(1) [1.67(2) Å] bond lengths are shorter than the corresponding distances in dppm derivatives (1.84–Å)<sup>1</sup> and comparable with those existing in methanide complexes (1.74 Å).<sup>2</sup> All these structural features are consistent with the interpretation that form *a* in Scheme 2 is the main contributor in a valence bond description in complex **4b**. The eclipsed conformation of the fragment P<sub>2</sub>C–Hg–CP<sub>2</sub> is rather intriguing, because some degree of staggering should be expected either for steric reasons<sup>¶</sup> or for electronic considerations (supposing some contribution of an allene-like structure). This is the case in the isoelectronic diamide {Hg[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>}.<sup>8</sup>

Some of the remarkable features of type **4** complexes have to be emphasized. They are rare examples of bis(carbene) derivatives of mercury. On the other hand, they contain the doubly deprotonated form of dppm [(PPh<sub>2</sub>)<sub>2</sub>C]<sup>2-</sup>, which is very scarcely encountered in the literature. Finally, as long as they have three metal centres joined by two [(PPh<sub>2</sub>)<sub>2</sub>C]<sup>2-</sup> fragments with some degree of π-delocalization, they can serve as models for long-range indirect metal–metal interactions, an area of great interest owing to its potential application in the field of material science.<sup>9</sup>

Owing to the electron rich C–Hg–C skeleton, type **4** complexes are expected to be very reactive toward electrophilic agents, their reactivity being modulated by the high steric hindrance of the bulky diphenylphosphino substituents. In this last aspect we are focusing our current work.

<sup>¶</sup> The shortest interligand C–C distance for the eclipsed conformation is 3.82 Å. Rigid rotation into a 45° staggered conformation would lead to interligand C–C contacts of 4.33 Å or greater.

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