

Preliminary communication

# Bidentate phosphines of heteroarenes: effective stabilization of the $\text{Co}_2(\text{CO})_6$ fragment by 4,6-bis(diphenylphosphino)dibenzofuran<sup>1</sup>

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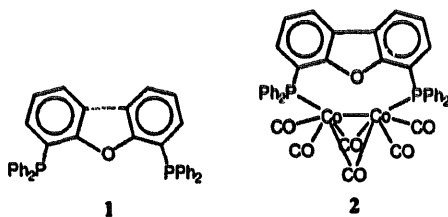
## Abstract

Reaction of  $\text{Co}_2(\text{CO})_8$  with 4,6-bis(diphenylphosphino)dibenzofuran (**1**) in diethylether gives the dinuclear complex 4,6-bis(diphenylphosphino)dibenzofurandicobalthexacarbonyl (**2**). The solid state structures of **1** and **2** have been established by X-ray crystallography. Low temperature  $^{13}\text{C}$ -NMR spectroscopy was used to analyse **2** in solution.

**Keywords:** Cobalt; Bidentate phosphine; Dinuclear phosphine complex; X-ray structure; Carbonyl; Dibenzofuran

## 1. Introduction

In pursuing our concept of designing stabilized homo- or heterobinuclear metal complexes, we previously reported the synthesis of 4,6-bis(diphenylphosphino)dibenzofuran (**1**) [3]. Bidentate phosphine ligands like **1** containing a rigid backbone should favour the stabilization of dimetallic fragments, since the two phosphorus centres are just too far apart to chelate one metal centre.



There has been some interest in dinuclear metal carbonyl complexes of bidentate phosphine ligands [4–10]. The major part of this work involves dicobalt fragments [6–10]. Structural investigations of dinuclear cobalt complexes are of interest in connection with various catalytic applications and intermediates in catalytic cycles of dicobaltoctacarbonyl and its derivatives, e.g. in the Pauson–Khand reaction [11], and in other

processes [12]. Here we present the X-ray crystal structures of the ligand **1** and its dicobalthexacarbonyl complex **2**. We also report some results on the dynamic behaviour of **2** in solution.

## 2. Results and discussion

Crystals of 4,6-bis(diphenylphosphino)dibenzofuran (**1**), the free ligand, were grown from dichloromethane/isopropanol solution. The result of the X-ray analysis [13] is shown in Fig. 1. The distance P(1)–P(2) is 5.741(1) Å, and compares well with one of the values calculated by Kranenburg et al. [14]: P(1)–P(2) = 5.760 Å, MM calculations; P(1)–P(2) = 5.956 Å, PM3 calculations. The difference in the distances O–P(1) = 3.071(2) Å and O–P(2) = 3.311(2) Å is due to the different steric strain around the dibenzofuran *ipso* carbon atoms, resulting in different angles C(6)–C(5)–P(1) = 119.1(2)° and C(7)–C(8)–P(2) = 127.9(2)°. This strain is caused by the conformation of the diphenylphosphino groups: two phenyl groups C(19)–C(24) and C(25)–C(30) are almost coplanar, one phosphorus lone pair is pointing away from the oxygen, the other is directed more towards the oxygen. This conformational arrangement is probably due to the packing in the crystal.

The dicobalt complex **2** was prepared by adding a solution of 4,6-bis(diphenylphosphino)dibenzofuran (**1**)

<sup>1</sup> Ref. [1]. Dedicated to the memory of Professor H. Takaya.

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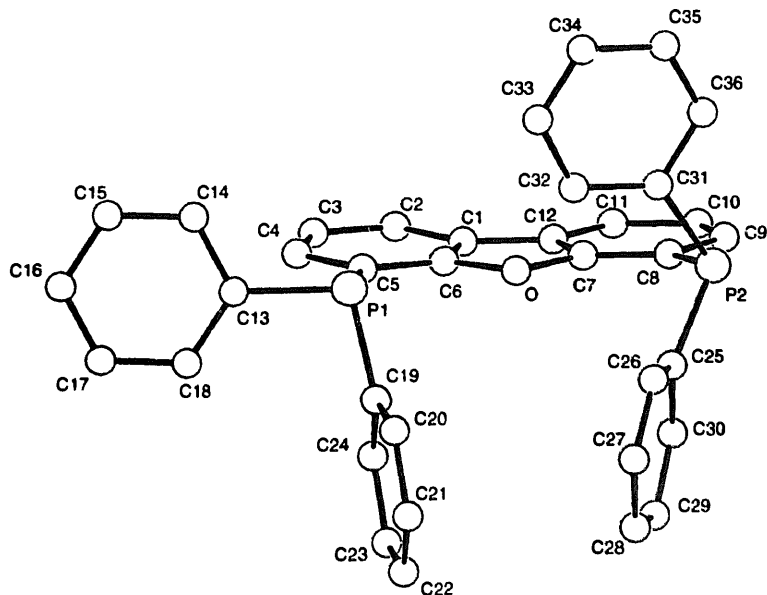


Fig. 1. The molecular structure of 4,6-bis(diphenylphosphino)dibenzofuran (1). Selected bond lengths (Å), angles (°) and distances (Å) are as follows: C(5)–P(1) 1.831(2), C(8)–P(2) 1.829(3), C(6)–O 1.390(3), C(7)–O 1.378(3), C(4)–C(5)–P(1) 126.5(2), C(9)–C(8)–P(2) 118.3(2), C(6)–O–P(1) 105.8(2), C(6)–C(5)–P(1) 119.1(2), C(7)–C(8)–P(2) 127.9(2), P(1)–P(2) 5.741(1), O–P(1) 3.071(2), O–P(2) 3.311(2).

in diethylether to a stirred solution of dicobaltoctacarbonyl in diethylether (reactant molar ratio 1:1) at  $-50^{\circ}\text{C}$ . On allowing the mixture to warm to room temperature, the evolution of gas was observed. After filtration, the dark brown solution was overlaid with hexane. Dark red crystals [15], suitable for X-ray analysis, were isolated in moderate yield (20%).

The molecular structure of 4,6-bis(diphenylphosphino)dibenzofurandicobalthexacarbonyl (2) [16] is

shown in Figs. 2 and 3. The phosphorus atoms of the ligand are each coordinated to one of the cobalt atoms, resulting in the formation of a non-planar, nine-membered ring. When designing 1 we also raised the questions whether the oxygen atom of the furan unit would participate in coordination to a metal and whether that could eventually improve or alter the compound's catalytic activity. In turn, the oxygen of the furan ring could show some changes in bond lengths or hybridiza-

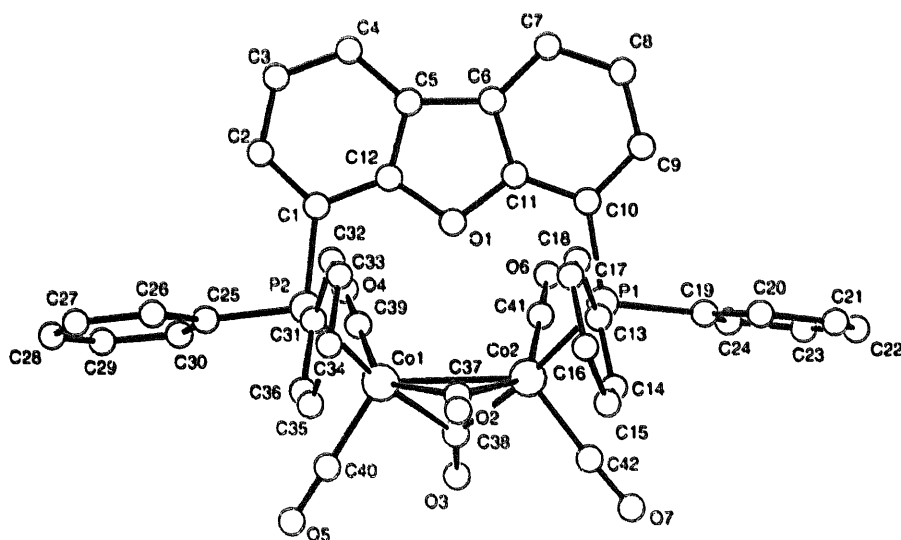
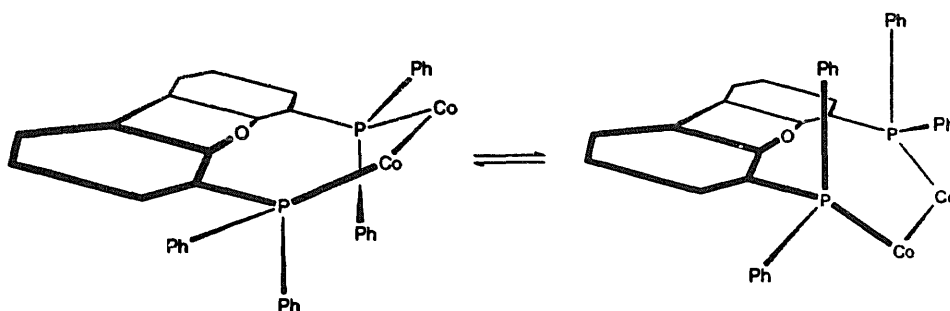


Fig. 2. The molecular structure of 4,6-bis(diphenylphosphino)dibenzofurandicobalthexacarbonyl (2). Top view of dibenzofuran unit. Selected bond lengths (Å), angles (°) and distances (Å) are as follows: C(1)–P(2) 1.822(3), C(10)–P(1) 1.831(4), C(12)–O(1) 1.377(4), C(11)–O(1) 1.383(4), P(2)–Co(1) 2.290(1), P(1)–Co(2) 2.285(1), Co(1)–Co(2) 2.573(1), C(2)–C(1)–P(2) 127.4(3), C(9)–C(10)–P(1) 127.1(3), C(12)–O(1)–C(11) 105.3(2), C(1)–P(2)–Co(1) 115.5(1), C(10)–P(1)–Co(2) 115.2(1), P(2)–Co(1)–Co(2) 124.7(1), Co(1)–Co(2)–P(1) 126.8(1), C(12)–C(1)–P(2) 118.2(2), C(11)–C(10)–P(1) 117.8(3), P(1)–P(2) 5.246(1), P(1)–O(1) 3.006(2), P(2)–O(1) 3.010(3), Co(1)–O(1) 3.345(3), Co(2)–O(1) 3.302(2).



Scheme 1.

tion, caused by electronic effects. As can be seen in Fig. 2, the oxygen atom is not involved in the coordination to any of the cobalt atoms and therefore the geometry of the dibenzofuran unit is essentially as in 1.

The cobalt atoms are not located in the plane defined by the dibenzofuran unit (Fig. 3). This crystal structure raises two questions on a possible dynamic behaviour in solution: (a) whether the phosphine ligand still provides enough flexibility to allow the metal atoms to flip between two energetically equal conformations, and (b) whether there is still a rapid equilibrium between the terminal and the bridging carbon monoxide ligands. To investigate **2** in solution we recorded its  $^{13}\text{C}$ -NMR spectra at low temperatures [15]. At  $-30\text{ }^\circ\text{C}$  the broad signal for rapid exchange of carbon monoxide ligands, which is observed at room temperature ( $\delta = 212\text{ ppm}$ ), disappears. At  $-80\text{ }^\circ\text{C}$  three new signals with an intensity ratio of 4:1:1 can be observed ( $\delta = 200\text{ ppm}$ ,  $\delta = 229\text{ ppm}$ ,  $\delta = 249\text{ ppm}$ ) for the carbon monoxide ligands. In addition, the signal for the *o*-phenyl carbon

atoms is split into two signals ( $\delta = 134.4\text{ ppm}$ ,  $\delta = 135.2\text{ ppm}$ ) at that temperature.

These results suggest that at room temperature rapid scrambling of all six carbon monoxide ligands takes place. A similar case was reported earlier by Cotton and Troup [5]. At the same time the dinuclear metal fragment must be undergoing a fast process of ring flipping, as shown in Scheme 1. Hence, chemical shift differences between axial and equatorial phenyl groups are averaged.

From the coalescence phenomenon of the *ortho* phenyl carbon atom at around  $-30\text{ }^\circ\text{C}$  (75.5 MHz), the mean free energy of activation for this process can be estimated as  $\Delta G^\ddagger \approx 40\text{ kJ mol}^{-1}$  [17]. At  $-80\text{ }^\circ\text{C}$  the nine-membered ring containing the two metal atoms is no longer fluxional. The exchange of terminal and bridged carbon monoxide ligands is slow compared with the NMR time scale. Only the terminal carbon monoxide groups on each metal are apparently exchanging rapidly with each other below  $-80\text{ }^\circ\text{C}$ .

The thermal stability of compound **2** is remarkable. As a result of differential scanning calorimetry, two endothermic effects can be found ( $182\text{ }^\circ\text{C}$ ,  $68\text{ J g}^{-1}$ ;  $205\text{ }^\circ\text{C}$ ,  $315\text{ J g}^{-1}$ ). Currently, **2** is being tested for possible applications in homogenous catalysis [11,12,18]. It does not, however, show significant catalytic activity in the water-gas shift reaction [18].

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### References and notes

- [1] Phosphine ligands, **5**; for part 4 see Ref. [2]. This work is part of the planned doctoral thesis of E.M. Vogl, to be submitted to the University of Düsseldorf.

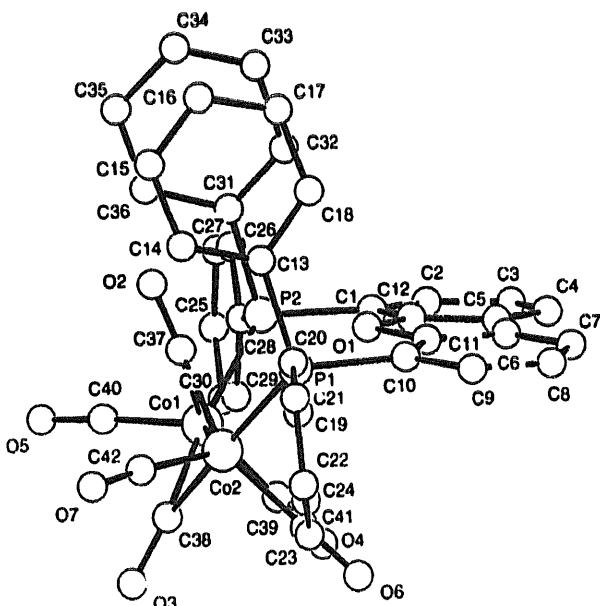


Fig. 3. The molecular structure of **2**. Side view of dibenzofuran unit (on the right).

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- [13] Crystal data for **1**:  $C_{36}H_{26}OP_2$ , molar mass 536.6, crystal size  $0.24 \times 0.46 \times 0.58 \text{ mm}^3$ ,  $a = 11.638(1) \text{ \AA}$ ,  $b = 20.976(1) \text{ \AA}$ ,  $c = 13.071(1) \text{ \AA}$ ,  $\beta = 116.28(1)^\circ$ ,  $V = 2681.2 \text{ \AA}^3$ ,  $T = 20 \text{ }^\circ\text{C}$ ,  $d_{\text{calc}} = 1.25 \text{ g cm}^{-3}$ ,  $\mu = 15.78 \text{ cm}^{-1}$ ,  $Z = 4$ , monoclinic, space group  $P2_1/n$  (No. 14), Enraf-Nonius CAD4 diffractometer,  $\lambda = 1.54178 \text{ \AA}$ , 6333 measured reflections [ $\pm h, + k, + l$ ],  $[\sin\theta/\lambda]_{\text{max}} = 0.63 \text{ \AA}^{-1}$ , 5887 independent and 4754 observed reflections [ $I > 2\sigma(I)$ ], 352 refined parameters, H-atom positions found and kept fixed in the final stage of refinement,  $R = 0.057$ ,  $R_w = 0.073$  [ $w = 1/\sigma^2(F_o)$ ], max. residual electron density  $0.68 \text{ e \AA}^{-3}$ . Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.
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- [15] Spectral data for complex **2**: IR (KBr)  $\text{cm}^{-1}$ : 1787 (CO bridged), 1796 (CO bridged), 1851 (CO bridged), 1867 (CO bridged), 1962 (CO term), 1990 (CO term), 2028 (CO term).  $^{31}\text{P}$ -NMR ( $\text{CDCl}_3$ , 81 MHz):  $\delta = 34.9$ .  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 6.77$  (m, 2H, H3, H7),  $\delta = 7.28$  (dd, 2H, H2, H8,  $^3J_{\text{H2H1}} \approx ^3J_{\text{H2H3}} \approx 8 \text{ Hz}$ ),  $\delta = 7.31$ – $7.40$  (m, 20H),  $\delta = 8.09$  (d, 2H, H1, H9,  $^3J_{\text{H1H2}} = 8 \text{ Hz}$ ).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 100.6 MHz, RT):  $\delta(\text{coupling to } ^{31}\text{P}) = 117.7$  ('t', C4, C6,  $\sum J_{\text{CP}} = 33.5 \text{ Hz}$ ),  $\delta = 123.3$  ('t', C1a, C9a,  $\sum J_{\text{CP}} = 6.7 \text{ Hz}$ ),  $\delta = 123.6$  ('t', C1, C9,  $\sum J_{\text{CP}} = 4.7 \text{ Hz}$ ),  $\delta = 123.9$  (s, C2, C8),  $\delta = 128.4$  ('t', phenyl-C<sub>meta</sub>,  $\sum J_{\text{CP}} = 9.6 \text{ Hz}$ ),  $\delta = 129.7$  (s, C3, C7),  $\delta = 130.1$  (s, phenyl-C<sub>para</sub>),  $\delta = 131.0$  ('t', phenyl-C<sub>ipso</sub>,  $\sum J_{\text{CP}} = 40 \text{ Hz}$ ),  $\delta = 133.6$  ('t', phenyl-C<sub>ortho</sub>,  $\sum J_{\text{CP}} = 9.6 \text{ Hz}$ ),  $\delta = 157.9$  ('t', C4a, C6a,  $\sum J_{\text{CP}} = 10.5 \text{ Hz}$ ),  $\delta = 211.7$  (br, C=O).  $^{13}\text{C}$ -NMR ( $\text{CD}_2\text{Cl}_2$ , 75.5 MHz, 185 K):  $\delta = 134.4$  (br, phenyl-C<sub>ortho</sub>),  $\delta = 135.2$  (br, phenyl-C<sub>ortho</sub>),  $\delta = 200$  (br, term C=O),  $\delta = 229$  (br, bridged C=O),  $\delta = 246$  (br, bridged C=O).
- [16] Crystal data for **2**:  $C_{42}H_{26}P_2Co_2O_7$ , molar mass 822.5, crystal size  $0.25 \times 0.56 \times 0.60 \text{ mm}^3$ ,  $a = 11.741(1) \text{ \AA}$ ,  $b = 13.248(2) \text{ \AA}$ ,  $c = 14.557(2) \text{ \AA}$ ,  $\alpha = 73.51(1)^\circ$ ,  $\beta = 88.39(1)^\circ$ ,  $\gamma = 68.61(1)^\circ$ ,  $V = 2014.4 \text{ \AA}^3$ ,  $T = 20 \text{ }^\circ\text{C}$ ,  $d_{\text{calc}} = 1.36 \text{ g cm}^{-3}$ ,  $\mu = 9.45 \text{ cm}^{-1}$ ,  $Z = 2$ , triclinic, space group  $P\bar{1}$  (No. 2), Enraf-Nonius CAD4 diffractometer,  $\lambda = 0.71069 \text{ \AA}$ , 9531 measured reflections [ $\pm h, \pm k, + l$ ],  $[\sin\theta/\lambda]_{\text{max}} = 0.65 \text{ \AA}^{-1}$ , 9169 independent and 6895 observed reflections [ $I > 2\sigma(I)$ ], 478 refined parameters, H-atom positions calculated and not included in least-squares refinement,  $R = 0.051$ ,  $R_w = 0.160$  [ $w = 1/(\sigma^2(F_o^2) + (0.100P)^2 + 0.000P)$ ], with  $P = (F_o^2 + 2F_c^2)/3$ , max. residual electron density  $2.60 \text{ e \AA}^{-3}$ . Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.
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