# SPECTROPHOTOMETRIC STUDIES OF THE REACTIONS OF TERTIARY BISDIPHENYLPHOSPHINES $Ph_2P(CH_2)_nPPh_2$ WITH n = 1, 2 AND 3 ON DIBROMO-BIS(TRIPHENYLPHOSPHINE)COBALT(II), IN BENZENE SOLUTION. FORMATION OF PENTA-COORDINATED COMPLEXES

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Abstract—The reactions of  $\operatorname{CoBr}_2(\operatorname{PPh}_3)_2$  at 25°C in benzene with  $\operatorname{Ph}_2\operatorname{P}(\operatorname{CH}_2)_n\operatorname{PPh}_2$  with n = 1 (dpm), n = 2 (dpe) and n = 3 (dpp) have been followed spectrophotometrically and by conductivity measurements in  $\operatorname{CH}_2\operatorname{Cl}_2$ . The addition and substitution steps of the bidentate bisphosphines L—L on the initial cobalt complex have been identified and the equilibrium constants calculated at different wavelengths using least squares methods. With dpm, binuclear species are formed in three steps with bridging dpm molecules. With dpc and dpp, two steps are observed with the formation of the final red penta-coordinated complexes [ $\operatorname{CoBr}(\operatorname{L}-\operatorname{L})_2$ ]Br; the intermediate complexes are different in each case. The overall constant for the equilibrium  $\operatorname{CoBr}_2(\operatorname{PPh}_3)_2 + 2\operatorname{L}-\operatorname{L} \rightleftharpoons [\operatorname{CoBr}(\operatorname{L}-\operatorname{L})_2]\operatorname{Br} + 2\operatorname{PPh}_3$  is  $1.06 \times 10^5$  for dpe and  $1.20 \times 10^3$  for dpp, and depends on the size of the chelate rings.

Cobalt(II) halogenide complexes with tertiary phosphines and diphosphines are well known.<sup>1,2</sup> nevertheless, their solution behaviour has not been extensively investigated. After study of the substitution of triphenylphosphine ligands on  $CoX_2(PPh_3)_2$  (X = Cl, Br, I and NCS) by triphenylphosphine oxide in benzene<sup>3</sup> or by triphenylphosphinesulphide,<sup>4</sup> we report here the of three tertiary interaction diphosphines  $Ph_2P(CH_2)_nPPh_2$ , with n = 1 (dpm), 2 (dpe) and 3 (dpp), on  $CoBr_2(PPh_3)_2$ , in benzene in order to establish the nature of the addition or substitution products, to estimate the corresponding equilibrium constants and to compare the chelating effect of the three diphosphines.

# **EXPERIMENTAL**

# Materials

 $CoBr_2(PPh_3)_2$  was prepared as previously described.<sup>5</sup>

The Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub> ligands (n = 1, 2 and 3), purchased from Interchim, were purified by recrystallization in benzene followed by vacuum sublimation. Benzene was distilled over P<sub>4</sub>O<sub>10</sub> and deaerated with a stream of nitrogen. Handling and preparations of solutions were carried out in a glove-box.

## Instrumentation

Electronic spectra were recorded on a Beckman 5240 spectrophotometer at  $25 \pm 0.2^{\circ}$ C. The conductivity measurements in CH<sub>2</sub>Cl<sub>2</sub> were made with a Tacussel CD 7 instrument at 1000 and 500 Hz.

# General procedure

To a benzene solution of  $CoBr_2(PPh_3)_2$ , increasing amounts of dpm, dpe or dpp were added and the evolution of the electronic spectra followed. The initial benzene solution of  $CoBr_2(PPh_3)_2$  always contains an excess of PPh<sub>3</sub> in order to minimize the perturbation due to traces of water, which may be present in the solvent for reasons previously explained.<sup>3a</sup>

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Moreover, for each equilibrium, the influence on the spectrum of dilution of a solution, with a given ratio R = diphosphine-cobalt, as well as the addition of PPh<sub>3</sub>, respectively, gave indications on the variation of the number of involved species, and the possible interference of PPh<sub>3</sub> in the equilibrium.

Conductivity measurements have been made in  $CH_2Cl_2$ , (the dielectric constant of benzene being too low), in order to check the stoichiometry of the reactions, taking care in comparing the spectra in  $CH_2Cl_2$  and benzene, to verify the presence or absence of the same species in both solvents.

Coleman, Varga and Mastin's graphical method<sup>6</sup> (further noted as the CVM method) was used to check the number of absorbing species involved in the equilibrium, and present in solution.

#### List of main symbols

C: analytical cobalt(II) concentration (mol  $1^{-1}$ ). R: ratio of analytical concentrations of diphosphine to cobalt.

*B*: analytical concentration of the excess of PPh<sub>3</sub> added in the initial solution (mol  $l^{-1}$ ).

 $\alpha$ ,  $\beta$ ,  $\gamma$ : proportion of cobalt engaged, respectively, in the first, second and third formed complex with exclusion of the initial CoBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.

 $\varepsilon$ : molar absorptivity of the solution based on C,  $\varepsilon = A/l \times C$ .

A: absorbance.

*l*: optical path in cm.

 $\varepsilon_p$ ,  $\varepsilon_1$ ,  $\varepsilon_2$ ,  $\varepsilon_3$ : molar absorptivities for CoBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, for the first, second and third complex, respectively.

#### **Calculations**

The type of calculations carried out is illustrated in the following example of substitution equilibria between two absorbing complexes 1 and 2 with respective extinction coefficients  $\varepsilon_1$  and  $\varepsilon_2$ . The ligands L and L' are non-absorbing

Complex 
$$1 + L \Longrightarrow$$
 Complex  $2 + L'$   
 $K = (\text{Complex 2})(L')/(\text{Complex 1})(L) = \frac{\alpha^2}{R(1-\alpha)^2}.$ 
(1)

For each wavelength  $\lambda$ :

$$\varepsilon = A/C \times l = \varepsilon_1(1-\alpha) + \varepsilon_2 \alpha_2$$

 $\varepsilon$  is a linear function of  $\alpha$ 

 $\varepsilon = \varepsilon_1 + (\varepsilon_2 - \varepsilon_1)\alpha = a\alpha + b.$ 

For a given solution  $\varepsilon$ , C and R are known.

K is calculated in order that the couples  $(\varepsilon, \alpha)$  give the best straight line at a given value of  $\lambda$ .  $\varepsilon_1$  and  $\varepsilon_2$  are obtained by the extrapolation of the straight line to  $\alpha = 0$  and  $\alpha = 1$ . Different arbitrary K values are used in relation (1) to yield, for a solution of analytical concentration C and ratio R, a value of  $\alpha$ . We then have a series of couples ( $\varepsilon$ ,  $\alpha$ ) for the n solutions.

By a least-squares method minimizing S, the best straight line going through the points  $(\varepsilon, \alpha)$  is calculated with  $S = \sum_{i=1}^{n} (1/\varepsilon^2)(\varepsilon - \varepsilon_{cal})^2$  where  $\varepsilon_{cal}$  is the calculated molar absorptivity at a given  $\lambda$ , from the straight line  $\varepsilon_{cal} = a\alpha + b$ . At the minimum of S,  $\partial S/\partial a = 0$  and  $\partial S/\partial b = 0$  yield a system of two relations with two unknowns, a and b:

$$\sum_{1}^{n} \frac{\alpha}{\varepsilon} = a \sum_{1}^{n} \frac{\alpha^{2}}{\varepsilon^{2}} + b \sum_{1}^{n} \frac{\alpha}{\varepsilon^{2}} \text{ and } \sum_{1}^{n} \frac{1}{\varepsilon} = a \sum_{1}^{n} \frac{\alpha}{\varepsilon^{2}} + b \sum_{1}^{n} \frac{1}{\varepsilon^{2}}.$$

For each value of K the calculation of  $S_{\text{minimum}}$  gives the standard deviation  $\sigma = \sqrt{S/n-2}$ .

The best K will be the one with the lowest  $\sigma$  value, so that the function  $\varepsilon = f(\alpha)$  will be the best straight line. Supposing that  $\sigma$ , near its minimum, is at first approximation a second order function of K, the minimum of that function (pit mapping) yields the final best value of K. The K given in the text is this mean value at different wavelengths.

## **RESULTS AND DISCUSSION**

*Reaction of* dpm *on*  $CoBr_2(PPh_3)_2$ 

The conductivity variation in  $CH_2Cl_2$  of a  $CoBr_2(PPh_3)_2$  solution (1.016 mM) by addition of increasing amounts of dpm, shows an increase in conductivity with three breaks at *R* values of 0.5, 1.2 and 2.4, indicating the possible formation of three successive ionic species, with a dpm/Co stoichiometry of 0.5, 1 and 2, beginning with a dinuclear complex. The conductivity remains close to 20  $\mu$ S cm<sup>-1</sup> for R = 1. The spectra in CH<sub>2</sub>Cl<sub>2</sub> are comparable to the spectra observed in benzene.

1st equilibrium. In benzene, the reaction is slow and the spectra are recorded 24 h after preparation of the solutions. The dilution of a  $\text{CoBr}_2(\text{PPh}_3)_2$ solution ( $C = 1.677 \times 10^{-4}$  mol  $1^{-1}$ ,  $B = 1.446 \times 10^{-3}$  mol  $1^{-1}$ ) with dpm (R = 0.255) does not obey Beer's law and the addition of PPh<sub>3</sub> to the solution does not modify the spectra.

The spectra given in Fig. 1 correspond to solutions with a constant cobalt concentration and increasing quantities of dpm. The presence of several isosbestic points (610, 686 and 740 nm) and the application of the CVM method,<sup>6</sup> both indicate the presence of only two absorbing species in equilibrium. The spectrum of the complex formed suggests a  $C_{3v}$  symmetry about cobalt.



Fig. 1. Solution spectra of  $\text{CoBr}_2(\text{PPh}_3)_2$  with increasing amounts of dpm in benzene  $(l = 5 \text{ cm}, T = 25^{\circ}\text{C})$ , C = 0.1677 mM, B = 1.446 mM. Values of R for each solution given in parentheses 0 (0), 1 (0.051), 2 (0.102), 3 (0.153), 4 (0.204), 5 (0.255), 6 (0.306), 7 (0.375), 8 (0.408).  $\bigcirc$  calculated spectrum of  $\text{Co}_2\text{Br}_4(\text{PPh}_3)_2(\text{dpm})$ .

The following equilibrium yielding a dinuclear complex with a bridged dpm, agrees with the preceeding observations:

ionic pairs is the fact that even if the dinuclear complex can be obtained in benzene and remains soluble, it becomes insoluble after it has been crystallized as an ionic compound,.

The expression of the equilibrium constant  $K_1$  is :

$$K_1 = \alpha/C^2(2R-\alpha)(1-\alpha)^2.$$
 (3)

The molar absorptivities of the solutions are:

$$\varepsilon = A/l \times C = \varepsilon_p(1-\alpha) + \varepsilon_1(\alpha/2).$$
 (4)

 $\varepsilon$  is a linear function of the ratio  $\alpha$  of the dinuclear compounds formed

$$\varepsilon = (\varepsilon_1/2 - \varepsilon_p)\alpha + \varepsilon_p. \tag{5}$$

A least-squares method gives the value of  $K_1$  at several wavelengths (see Table 1). The mean value is  $\bar{K}_1 = (1.73 \pm 0.14) \times 10^9 \text{ mol}^{-2} 1^2$ .

From the value of  $\bar{K}_1$ , the concentrations of the absorbing species in solution are calculated as well as the spectrum of  $\text{Co}_2\text{Br}_4(\text{PPh}_3)_2(\text{dpm})$  (Fig. 1).

2nd equilibrium. The recorded spectra of solutions with  $C = 1.749 \times 10^{-4} \text{ mol } 1^{-1}$ ,  $B = 1.293 \times 10^{-3} \text{ mol} 1^{-1}$  and different values for R = 0.766, 0.958, 1.149 and 1.341, show an isosbestic point at 598 nm. The microsymmetry around cobalt is  $C_{3v}$  for the two absorbing species, but their molar absorptivities are close, so dilution of the solution with 0.7 < R < 1.4and the addition of PPh<sub>3</sub> are not conclusive. The

$$2\begin{bmatrix}Br_{H_{2}}\\Br_{P}Ph_{3}\end{bmatrix} + Ph_{2}P-CH_{2}-PPh_{2} \xrightarrow{K_{1}} Ph_{3}P_{C} \xrightarrow{Br_{P}} \xrightarrow{Br_{P}} \xrightarrow{Ph_{3}P} \xrightarrow{Ph_{3}Ph_{2}} \xrightarrow{Ph_{3}Ph_{2}} \xrightarrow{Ph_{3}Ph_{2}} \xrightarrow{Ph_{3}Ph_{3}} \xrightarrow{Ph_{3}} \xrightarrow{Ph_{3}Ph_{3}} \xrightarrow{Ph_{3}Ph_{3}} \xrightarrow{Ph_{3}} \xrightarrow{Ph_{3}Ph_{3}} \xrightarrow{Ph_{3}} \xrightarrow{Ph_{3}$$

The formation of an ionic complex in benzene, undissociated in the form of an ionic pair, is likely in view of the low dielectric constant of the solvent

calculation carried out for the 1st equilibrium is not possible here.

The proposed equilibrium is shown in eq. (6)



(2.27). Hughes *et al.*<sup>7</sup> showed that at concentrations lower than  $10^{-3}$  mol  $1^{-1}$ , the ionic pairs remain undissociated. In CH<sub>2</sub>Cl<sub>2</sub> with a higher dielectric constant (9.08) these ionic compounds are slightly dissociated.

The conductivities of 26 different complexes, 1:1 electrolytes, in CH<sub>2</sub>Cl<sub>2</sub> or C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> are comparable (range 17–26  $\mu$ S cm<sup>-1</sup>)<sup>8</sup> with those observed for our compounds calculated on the basis of one metal atom (22.5  $\mu$ S cm<sup>-1</sup>).

Further evidence in favour of the existence of the

with

$$K_2 = \frac{2C\beta((B/C) + \beta)^2}{(1 - \beta)(2R - 1 - \beta)}.$$
 (7)

The molar absorptivities of the solutions are:

$$\varepsilon = A/l \times C = \varepsilon_1 \left(\frac{1-\beta}{2}\right) + \varepsilon_2 \frac{\beta}{2}.$$
 (8)

 $\varepsilon_1$  is known, and  $\varepsilon_2$  will be calculated from the next equilibrium (*vide infra*).  $\beta$  is obtained from the experimental  $\varepsilon$  value, using (8) and  $K_2$  is given by

Table 1. Values of  $K_1$  at various wavelengths

λ (nm)	637	650	665	703	715	762.5	
$K_1 ({ m mol}^{-2}{ m l}^2)$	$1.93 \times 10^{9}$	1.61 × 10°	$1.60 \times 10^{9}$	$1.65 \times 10^{9}$	1.94 × 10 <sup>9</sup>	1.64 × 10 <sup>9</sup>	

(7). For four solutions with  $\beta = 0.388, 0.567, 0.708$ and 0.795,  $\bar{K}_2 = (9.4 \pm 0.5) \times 10^{-2} \text{ mol } 1^{-1}$ .

3rd equilibrium. The spectra of solutions with 5.6 < R < 30.6 are given in Fig. 2. Application of the CVM method<sup>6</sup> indicates the presence of one equilibrium between two absorbing species. Dilution of solution 4 (Fig. 2) obeys Beer's law. The spectrum of the first species is characteristic for a  $C_{3v}$  symmetry, whereas the dark red second species is  $C_{4v}$  (square pyramid).

The equilibrium is shown in eq. (9)

The calculation on eight solutions is similar to that carried out for the first equilibrium. The values at several wavelengths (given in parentheses and in nm) are:  $K_3$ :  $1.02 \times 10^{-2}$  (450);  $1.01 \times 10^{-2}$  (462.5);  $1.03 \times 10^{-2}$  (475);  $1.05 \times 10^{-2}$  (487.5);  $1.01 \times 10^{-2}$  (500);  $1.03 \times 10^{-2}$  (512.5);  $1.09 \times 10^{-2}$  (525);  $9.84 \times 10^{-3}$  (537.5);  $9.24 \times 10^{-3}$  (550);  $1.02 \times 10^{-2}$  (625);  $1.22 \times 10^{-2}$  (637.5);  $1.20 \times 10^{-2}$  (650);  $1.02 \times 10^{-2}$  (750) and therefore  $\bar{K}_3 = (1.05 \pm 0.08) \times 10^{-2}$ .

The spectra of  $Co_2Br_2(dpm)_4$  and  $Co_2Br_4$ 



with the following relations

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$$K_{3} = \frac{\gamma(1+\gamma)^{2}}{(1-\gamma)(R-1-\gamma)^{2}}$$
(10)

$$\varepsilon = A/l \times C = \varepsilon_2 \left(\frac{1-\gamma}{2}\right) + \varepsilon_3 \frac{\gamma}{2}$$
 (11)

$$\varepsilon = \frac{(\varepsilon_3 - \varepsilon_2)}{2}\gamma + \frac{\varepsilon_2}{2}.$$
 (12)

 $(PPh_3)_2(dpm)_2$  are then calculated (Fig. 2).  $\varepsilon_2$  is used to estimate  $K_2$  (vide supra).

# Reactions of dpe on $CoBr_2(PPh_3)_2$

The conductivity in  $CH_2Cl_2$  of  $CoBr_2(PPh_3)_2$ solution (9.861 × 10<sup>-4</sup> mol 1<sup>-1</sup>) increases rapidly with the addition of dpe: ionic complexes are



Fig. 2. Solution spectra of  $\text{CoBr}_2(\text{PPh}_3)_2$  with increasing amounts of dpm in benzene  $(l = 5 \text{ cm}, T = 25^{\circ}\text{C}), C = 0.2119 \text{ mM}, B = 0$ . Values of R for each solution in parentheses 0 (5.627), 1 (7.411), 2 (9.196), 3 (10.980), 4 (14.549), 5 (21.687), 6 (25.256), 7 (30.609).  $\bigtriangledown$ : observed spectrum of  $\text{CoBr}_2(\text{PPh}_3)_2$ ;  $\bigcirc$ ,  $\triangle$ ,  $\square$ : calculated spectra for  $\text{Co}_2\text{Br}_4(\text{PPh}_3)_2(\text{dpm}), \text{Co}_2\text{Br}_4(\text{PPh}_3)_2(\text{dpm})_2$  and  $\text{Co}_2\text{Br}_4(\text{dpm})_4$ , respectively.



Fig. 3. Conductivity of a 0.9861 mM solution of CoBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> vs R in CH<sub>2</sub>Cl<sub>2</sub> (5000 Hz).

formed (Fig. 3). Breaks are observed at R values close to 1 and 2. The conductivity then remains practically constant for R > 2.2 (~ 18  $\mu$ S cm<sup>-1</sup>). This implies the formation of complexes with a stoichiometry of 1 and 2 dpe per cobalt. The spectrum in CH<sub>2</sub>Cl<sub>2</sub> for the final green complex (R =2.0) is similar to the one observed by Horrocks *et al.*,<sup>9</sup> with a trigonal bipyramidal coordination around the cobalt. The spectrum of the intermediate complex in CH<sub>2</sub>Cl<sub>2</sub> is similar to the one observed in C<sub>6</sub>H<sub>6</sub>.

1st equilibrium. The spectra for solutions with 0 < R < 1.286 are given in Fig. 4. Dilution of solution 5 obeys Beer's law; the addition of PPh<sub>3</sub> in this same solution moves the equilibrium towards the formation of the initial reagent CoBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. The isosbestic points at 601, 683 and 700 nm and the CVM method<sup>6</sup> indicate a simple equilibrium between two absorbing complexes. The proposed equilibrium is:

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Fig. 4. Solution spectra of  $\operatorname{CoBr}_2(\operatorname{PPh}_3)_2$  with increasing amounts of dpe  $(l = 5 \text{ cm}, T = 25^{\circ}\text{C}), C = 0.1789 \text{ mM}, B = 1.158 \text{ mM}.$  Values of R in parentheses 0 (0), 1 (0.161), 2 (0.321), 3 (0.482), 4 (0.643), 5 (0.804), 6 (0.964), 7 (1.125), 8 (1.286). Spectra of solutions 6, 7 and 8 are omitted for clarity of the graph.  $\bigoplus$  experimental spectrum of  $\operatorname{CoBr}_2(\operatorname{PPh}_3)_2$ ;  $\bigcirc$  calculated spectrum of  $\operatorname{CoBr}_2(\operatorname{PPh}_3)$ (dpe).

 $\varepsilon$  is a linear function of  $\alpha$ 

$$\varepsilon = (\varepsilon_1 - \varepsilon_p)\alpha + \varepsilon_p. \tag{16}$$

The values of  $K_1$  obtained by linear regression on nine solutions are (wavelengths in parentheses and in nm) K: 886 (662.5); 897 (700); 899 (712.5); 890 (725) and 895 (762.5) and a mean value  $\bar{K}_1 = 893 \pm 5$ .  $\bar{K}_1$  allows the calculation of the spectrum of CoBr<sub>2</sub>(PPh<sub>3</sub>)(dpe) (Fig. 4).

2nd equilibrium. The spectra of solutions with

$$\begin{array}{c} \begin{array}{c} PPh_{3} \\ PPh_{3} \end{array} + Ph_{2}P_{-}CH_{2}-CH_{2}-PPh_{2} \end{array} \xrightarrow{K_{1}} \begin{array}{c} Ph_{2} \\ P_{-}CH_{2} \\ Ph_{3}P \end{array} \xrightarrow{Ph_{2}} \begin{array}{c} Ph_{2} \\ P_{-}CH_{2} \\ Ph_{2} \end{array} + PPh_{3} \end{array}$$
(13)

with

$$K_1 = \frac{\alpha((B/C) + \alpha)}{(1 - \alpha)(R - \alpha)}$$
(14)

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$$= A/l \times C = \varepsilon_p(1-\alpha) + \varepsilon_1 \alpha.$$
 (15)

1.344 < R < 4.703 are given in Fig. 5. The final red complex is square-pyramidal. Again the isosbestic points at 622, 647, 685 and 757 nm and the CVM method<sup>6</sup> indicate a simple equilibrium. The equilibrium is concentration independent (solution 5 on Fig. 5 obeys Beer's law) whereas addition of PPh<sub>3</sub> regresses the equilibrium. It can be written as:





Fig. 5. Solution spectra of  $\operatorname{CoBr}_2(\operatorname{PPh}_3)_2$  with increasing amounts of dpe  $(l = 5 \text{ cm}, T = 25^{\circ}\text{C}), C = 0.1565 \text{ mM}, B = 1.125 \text{ mM}.$  Values of R given in parentheses 1 (1.344), 2 (1.680), 3 (2.015), 4 (2.351), 5 (3.359), 6 (4.031), 7 (4.703).  $\bigcirc$  calculated spectrum of  $\operatorname{CoBr}_2(\operatorname{PPh}_3)(\operatorname{dpe})$ ; + calculated spectrum of  $\operatorname{CoBr}_2(\operatorname{dpe})_2$ .

with

$$K_2 = \frac{\beta(1+\beta+(B/C))}{(1-\beta)(R-1-\beta)}$$
(18)

and

$$\varepsilon = A/l \times C = (\varepsilon_2 - \varepsilon_1)\beta + \varepsilon_1. \tag{19}$$

A linear regression on seven solutions gives the following  $K_2$  values (with wavelengths in parentheses and in nm)  $K_2$ : 114 (500); 110 (512.5); 127 (525); 130 (635); 119 (725) and 114 (737.5) and a mean value  $\vec{K}_2 = 119 \pm 8$ .

 $\bar{K}_2$  allows the calculation of the spectra of the two complexes (Fig. 5). The spectrum of the intermediate CoBr<sub>2</sub>(PPh<sub>3</sub>)(dpe) is the same as the one calculated for the 1st equilibrium (Fig. 4).



Fig. 6. Solution spectra of  $\operatorname{CoBr}_2(\operatorname{PPh}_3)_2$  with increasing amounts of dpp  $(l = 5 \text{ cm}, T = 25^{\circ}\text{C}), C = 0.1875 \text{ mM},$ B = 1.209 mM. Values of R given in parentheses 0 (0), 1 (0.106), 2 (0.212), 3 (0.318), 4 (0.425), 5 (0.531), 6 (0.637), 7 (0.743), 8 (0.849), 9 (0.955), 10 (1.062). Spectrum of solution 10 is omitted for clarity of the graph.  $\bigcirc$ calculated spectrum of  $\operatorname{CoBr}_2(\operatorname{dpp})$ .

complex corresponds to a green trigonal-bipyramidal complex, whereas the intermediate complex has a spectrum similar to the one observed in benzene solution.

1st equilibrium. The spectra for solutions with 0 < R < 1.062 are shown in Fig. 6. Dilution of solution 7 shifts the equilibrium forward and the addition of PPh<sub>3</sub> shifts the equilibrium towards the starting product, CoBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.

Again the presence of isosbestic points at 627.5, 694, 758 and 817.5 nm as well as the CVM method<sup>6</sup> indicate an equilibrium involving two absorbing species. The spectrum of the final product corresponds to the same  $C_{2v}$  microsymmetry as the starting material.

The equilibrium is:

$$\begin{array}{c} B_{F_{1}} & P_{Ph_{3}} \\ B_{P} & P_{Ph_{3}} \end{array} + Ph_{2}P_{-}CH_{2}-CH_{2}-CH_{2}-PPh_{2} \end{array} \xrightarrow{K_{1}} \begin{array}{c} B_{F_{1}} & Ph_{2}-CH_{2} \\ B_{P} & CH_{2} + 2PPh_{3} \end{array}$$

$$\begin{array}{c} Ph_{2} \\ P-CH_{2} \\ Ph_{2} \end{array}$$

$$\begin{array}{c} Ph_{2} \\ P-CH_{2} \\ Ph_{3} \end{array}$$

## Reaction of dpp with CoBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>

The conductivity measurements in  $CH_2Cl_2$  show at the beginning, the formation of a non-ionic complex. Starting with R = 1, an ionic complex, only slightly dissociated, is formed and a break for R = 2is observed. dpp/Co stoichiometries of 1 and 2 can be proposed. The spectrum in  $CH_2Cl_2$  of the final with a constant

$$K_1 = \frac{\alpha(2\alpha + (B/C))^2 C}{(R-\alpha)(1-\alpha)}$$
(21)

and

$$\varepsilon = A/l \times C = (\varepsilon_1 - \varepsilon_p)\alpha + \varepsilon_p.$$
 (22)

A linear regression method gives  $\alpha$  and  $K_1$  on 10 solutions.



Fig. 7. Solution spectra of CoBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> with increasing amounts of dpp (*l* = 5 cm, *T* = 25°C), *C* = 0.1762 mM. Values of *R* given in parentheses 1 (1.103), 2 (1.274), 3 (1.787), 4 (2.812), 5 (4.520), 6 (6.228), 7 (9.645), 8 (14.770), 9 (25.020). Spectra of solutions 1, 2 and 3 are omitted for reasons of clarity. ○ calculated spectrum of CoBr<sub>2</sub>(dpp); △ calculated spectrum of CoBr<sub>2</sub>(dpp)<sub>2</sub>.

 $K_1$ : 3.75 (640 nm); 3.91 (650 nm); 3.62 (662.5 nm) and 4.02 (664 nm) with a mean value  $\bar{K}_1 = 3.83 \pm 0.25 \text{ mol } 1^{-1}$ .

The spectra calculated using  $\bar{K}_1$  are given in Fig. 6.

2nd equilibrium. Spectra of solutions with 1.103 < R < 25.02 are shown in Fig. 7. Dilution of solution 5 shifts the equilibrium toward the starting material whereas the addition of PPh<sub>3</sub> has no influence on the spectrum.

A new equilibrium between two absorbing species is observed by the presence of isosbestic points at 597.5, 680, 726 and 765 nm and the application of the CVM method.<sup>6</sup> The final spectrum corresponds to a square-pyramidal complex of  $C_{4v}$  microsymmetry.

The equilibrium inferred from the preceding observations is:

 $\varepsilon$  is a linear function of  $\beta$ .

$$\varepsilon = A/l \times C = (\varepsilon_2 - \varepsilon_1)\beta + \varepsilon_1. \tag{25}$$

The values of  $K_2$  for seven solutions are shown in Table 2, with a mean value  $\bar{K}_2 = 312 \pm 10 \text{ mol}^{-1} \text{ l.}$ 

This  $\bar{K}_2$  value allows the calculation of the spectrum of the two complexes involved in equilibrium (23). The spectrum of  $\text{CoBr}_2(\text{dpp})$  is identical to the spectrum calculated for the 1st equilibrium.

#### CONCLUSIONS

The three bidentate ligands show a different behaviour when they react with  $\text{CoBr}_2(\text{PPh}_3)_2$  in benzene. With a long hydrocarbonic chain, as in dpp (n = 3) or in dpe (n = 2), coordination around the metal with a six- or five-membered ring is fav-

$$\begin{array}{c} Br \\ P - CH_2 \\ Br \\ Ph_2 \end{array} + Ph_2 P- CH_2 - CH_2 \\ Ph_2 \\ Ph_2 \end{array} + Ph_2 Ph_2 Ph_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 \\ Ph_2 \\$$

with

$$K_2 = \frac{\beta}{(1-\beta)(R-1-\beta)C}.$$
 (24)

oured, whereas with a short one as in dpm (n = 1), a bridging mode of coordination on two metal atoms occurs, followed by the formation of a four-mem-

Table 2. Values o	$f K_2$ at	various	wave	lengths
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l (nm)	525	537.5	550	619	640	662.5	664	748	750	812.5	825
$K_2 ({ m mol}^{-1} { m l})$	298	289	284	329	323	340	272	312	329	312	335

bered ring without breaking of the established bridges.

The steric hindrance of the diphosphines cannot explain the difference in reactivity. The Tolman cone angles<sup>10</sup> increase only slightly from dpm to dpp (dpm: 121°, dpe 125° and dpp 127°). Nevertheless, dpm is less favoured for chelation than dpe or dpp, because the four-membered ring produced on chelation is considerably strained.

The values of the equilibrium constants,  $K_{\rm T} = K_1 \times K_2$ , corresponding to the formation of the final penta-coordinated complex starting with CoBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> are, respectively,  $1.06 \times 10^5$  for dpe and  $1.20 \times 10^3$  for dpp. This order is that expected based on the size of the chelating rings.

In all cases, the final red complex is pentacoordinated with a square-pyramidal geometry containing the  $CoBrP_4$  chromophore. These red compounds, obtained in benzene, are no longer soluble after they have been crystallized, owing to their ionic nature in  $[CoBr(diphos)_2]^+Br^-$ . The square-pyramidal structure allows a close approach of the halogen ion in benzene favouring ion-pair formation.

The interpretation of the electronic spectra will be given in a later publication.

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