# Chelating versus bridging bonding modes of N-substituted bis(diphenylphosphanyl)amine ligands in Pt complexes and Co<sub>2</sub>Pt clusters

Vito Gallo,<sup>a,b</sup> Piero Mastrorilli,\*<sup>a</sup> Cosimo F. Nobile,<sup>a</sup> Pierre Braunstein\*<sup>b</sup> and Ulli Englert<sup>c</sup>

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N-Substituted dppa ligands  $Ph_2P-NR-PPh_2$  [ $R = -CH_2CH_2SCH_2C_6H_5$  (1),  $-CH_2CH_2S(CH_2)_5CH_3$  (2),  $-(CH_2)_9CH_3$  (3),  $-C_6H_5$  (4)] were used for the synthesis of *cis*-[PtCl<sub>2</sub>{Ph<sub>2</sub>PN(R)PPh<sub>2</sub>}] complexes [R = -CH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> (**5**), -CH<sub>2</sub>CH<sub>2</sub>S(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub> (**6**), -(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub> (**7**), -C<sub>6</sub>H<sub>5</sub> (**8**)] and heterotrinuclear clusters of formula [PtCo<sub>2</sub>(CO)<sub>7</sub>{Ph<sub>2</sub>PN(R)PPh<sub>2</sub>}][R =  $-CH_2CH_2SCH_2C_6H_5$  (9),  $-CH_2CH_2S(CH_2)_5CH_3$  $(10), -(CH_2)_9CH_3$  (11),  $-C_6H_5$  (12)]. The presence of relatively bulky substituents on N resulted in a higher chelating power of the ligands. The thermodynamic study of the equilibrium between the chelate and the bridged forms of clusters 9-11 showed that the bridged form is favoured by enthalpic factors whereas entropic factors favour chelation. The structures of 5 and 9 were determined by single crystal X-ray diffraction.

## Introduction

Diphosphanes containing a single atom as spacer between the donor atoms, such as dppm [dppm = bis(diphenylphosphanyl)methane] and dppa [dppa = bis(diphenylphosphanyl)amine] belong to the category of short-bite ligands and their coordination chemistry has attracted much interest.<sup>1</sup> Such bidentate ligands can coordinate to metal centres in monodentate, chelating or bridging modes and interconversions between them are often observed as a result of seemingly minor changes in the ligand substituents or in the coligands bound to the metal centre(s). These aspects and, in particular, their bridging vs. chelating behaviour, are still a matter of discussion. For instance, it has been reported that dppa exhibits a strong chelating ability in Pt(II) complexes,<sup>2</sup> but no chelation is observed when it is used in the synthesis of dinuclear Pd(I) complexes.<sup>3</sup> The coordination mode of these ligands depends on the nature of both the substituents on the phosphorus atom and the bridging backbone. The propensity to form chelate complexes increases with the bulkiness of the groups on phosphorus.<sup>4</sup> The replacement of one or two hydrogen atoms of the methylene carbon of dppm with alkyl groups results in a greater tendency to form stable four-membered chelate rings.<sup>5</sup> A similar effect has been observed upon replacement of the N-H hydrogen atom of dppa. Such results were readily explained invoking the Thorpe-Ingold (gem-dimethyl) effect in small organic rings,<sup>6</sup> *i.e.* the accelerated rate of cyclization due to the "angle compression" generated by the alkyl substitution. In studies on Ag complexes, Hill<sup>7</sup> reported that the effect of an alkyl group bound to the N atom of the ligand on the cyclization has steric origins and can be rationalized by evaluating two factors, one enthalpic and one entropic. The first one involves the gauche

interactions that occur on chelation: N-alkylated ligands undergo stronger interactions than unsubstituted dppa. The entropy factor is explained by comparing the degrees of freedom associated with rotation about the P-N bond in the free ligand with those in the coordinated ligand. In the free ligand, N-substituted dppa has a more hindered rotation about the P-N bond due to the steric interaction of the substituent on nitrogen with the phenyl groups on the P atoms. Consequently, the decrease of internal rotational entropy that occurs on chelation is less in the N-substituted dppa than in dppa.

N-substituted dppa-type ligands represent an attractive class of ligands for at least two reasons: they are isoelectronic to dppm but possess slightly different electronic properties and they can be easily derivatized on the nitrogen. This latter feature fuels the stimulating research on dppa-derivatives8 which already covers interesting applications in the fields of catalysis9 and nanomaterials.<sup>10</sup> Funtionalized dppa ligands were shown to be suitable for the anchoring of carbonyl clusters on supports owing to their propensity to bridge an edge of the cluster.<sup>10</sup>

Herein we report on the behaviour shown by N-substituted dppa ligands Ph<sub>2</sub>PN(R)PPh<sub>2</sub> (1-4) when used for the synthesis of new Pt(II) complexes of formula *cis*-[PtCl<sub>2</sub>{Ph<sub>2</sub>PN(R)PPh<sub>2</sub>}][R = -CH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> (5), -CH<sub>2</sub>CH<sub>2</sub>S(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub> (6), -(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub> (7),  $-C_6H_5$  (8)] and of heterotrinuclear clusters of formula  $[PtCo_{2}(CO)_{7}\{Ph_{2}PN(R)PPh_{2}\}] [R = -CH_{2}CH_{2}SCH_{2}C_{6}H_{5} (9),$  $-CH_2CH_2S(CH_2)_5CH_3$  (10),  $-(CH_2)_9CH_3$  (11),  $-C_6H_5$  (12)]. The obtained results allowed to correlate the bulkiness of R with



<sup>&</sup>lt;sup>a</sup>Dipartimento di Ingegneria delle Acque e di Chimica del Politecnico di Bari, via Orabona 4, I-70125 Bari, Italy. E-mail: p.mastrorilli@poliba.it; Fax: +39 080 5963611

<sup>&</sup>lt;sup>b</sup>Laboratoire de Chimie de Coordination, UMR 7513 CNRS Université Louis Pasteur 4, rue Blaise Pascal, F-67070 Strasbourg, France. E-mail: braunst@chimie.u-strasbg.fr; Fax: +33 390241322

<sup>&</sup>lt;sup>e</sup>Institut für Anorganische Chemie der RWTH, Landoltweg 1, D-52074 Aachen, Germany

the chelating ability of the ligand. Moreover thermodynamic determinations clarified the relative importance of enthalpic and entropic factors in the chelating *vs.* bridging bonding mode of the N-substituted dppa ligands.

### **Results and discussion**

N-substituted dppa ligands can be synthesised following two different procedures: (*i*) the deprotonation of the acidic NH proton of dppa and the subsequent derivatization of the nitrogen atom by the required electrophile; (*ii*) the reaction of the suitable amine and two equivalents of chlorodiphenylphosphane. In the present work, we have chosen the second method since the starting amines were easily available: decylamine and aniline are commercially available and the amines needed for ligands 1 and 2 can be obtained by reaction of 2-aminoethanethiol with the relevant alkyl halide. All pure ligands used for the synthesis of the complexes 5–8 were characterized by IR and multinuclear spectroscopic methods. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of 1–4 showed the expected signals downfield shifted with respect to free dppa ( $\delta$  43.5). In particular, 1–3 gave a singlet in the range  $\delta$  62.2–62.9 while a singlet centred at  $\delta$  68.6 was found for 4.

Although the synthesis of dichloro-bisphosphanyl Pt(II) complexes is generally easy and fast, a clean preparation of complexes **5–8** was not straightforward, due to complications originating from concomitant formation of undesired bis-chelated species.

Taking the synthesis of 5 as a model for those of 5-8 (Scheme 1), it was observed that when the addition of 1 was not sufficiently slow, the reaction mixture contained at the end of reaction the cationic bis-chelated Pt(II) complex  $[Pt(1)_2]Cl_2$  (13) along with 5 and unreacted  $[PtCl_2(cod)]$ . Complex 13 is characterized by a singlet flanked with satellites ( $\delta$  29.7,  ${}^{1}J_{P,Pt}$  2373 Hz) in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum and a quintet ( $\delta$  –4383, <sup>1</sup>J<sub>PPt</sub> 2373 Hz) in the <sup>195</sup>Pt{<sup>1</sup>H} NMR spectrum. The absence of absorption bands assignable to Pt-Cl stretching modes in the IR spectrum confirms the ionic nature of the complex. Leaving complex 13 in  $CD_2Cl_2$  at room temperature for one week resulted in the slow isomerization to the PhCH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>N(PPh<sub>2</sub>)<sub>2</sub> bridged dinuclear complex 14 depicted in Scheme 2. The  ${}^{31}P{}^{1}H$  and  ${}^{195}Pt{}^{1}H$  NMR spectra of the aged solution showed the progressive disappearance of the signals ascribable to 13 with a contemporary growing of the AA'XX' spin system for 14 where A ( $\delta$  65.6) is the P nucleus of the bridging ligands and X ( $\delta$  42.4) that of the chelating ligands. In agreement with the proposed structure, the <sup>195</sup>Pt{<sup>1</sup>H} NMR spectrum of 14 showed a triplet of triplets centred at  $\delta$  -4682  $[{}^{1}J_{P(A),Pt}$  2698 Hz,  ${}^{1}J_{P(X),Pt}$  1908 Hz].

Pure 5 could be obtained in 89% yield when the dropwise addition of 1 to [PtCl<sub>2</sub>(cod)] (both as dichloromethane solutions,



Scheme 1 Synthesis of Pt(II) complexes.



 $R = -CH_2CH_2SCH_2Ph$ 

Scheme 2 Isomerization of 13.

1/Pt molar ratio = 1 : 1) lasted for at least 2 h. <sup>31</sup>P{<sup>1</sup>H} and <sup>195</sup>Pt{<sup>1</sup>H} NMR spectroscopic features were fully consistent with the bidentate ligand chelating the Pt atom. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum contained one singlet flanked with satellites centred at  $\delta$  17.8 (<sup>1</sup>J<sub>P,Pt</sub> 3304 Hz) while the <sup>195</sup>Pt{<sup>1</sup>H} NMR spectrum showed a triplet at  $\delta$  –4037 (<sup>1</sup>J<sub>P,Pt</sub> 3304 Hz). The value of the <sup>1</sup>J<sub>P,Pt</sub> coupling constant is consistent<sup>11</sup> with the presence of Cl atoms *trans* to P. The IR bands due to the Pt–Cl stretching vibrations were found at 305 and 288 cm<sup>-1</sup>.<sup>12</sup>

The crystal structure of complex **5** is shown in Fig. 1 and selected bond distances and angles are collected in Table 1. The geometry around the platinum atom is distorted square planar in order to fulfil the constraints imposed by ligand **1**. The plane defined by the Pt, P(1) and P(2) atoms is almost coincident with that defined by N, P(1) and P(2) (the sum of the internal angles in the Pt–P(1)– N–P(2) ring is 359.92°). The average Pt–P bond length [2.2115 Å] as well as the P–Pt–P [72.06(3)°] and P–N–P [99.34(13)°] angles in **5** are comparable to those found for [PtCl<sub>2</sub>(dppaMe)] [dppaMe = bis(diphenylphosphanyl)methylamine, average Pt–P = 2.206(4) Å; P–N–P = 71.8(1)° and 100.0(6)°].<sup>13</sup> Interestingly, the sum of angles at nitrogen ( $\Sigma \theta$  = 354.4°) is lower than that in [PtCl<sub>2</sub>(dppaMe)]



Fig. 1 ORTEP view of the crystal structure of 5.

 Table 1
 Selected bond distances and angles for 5

Bond lengths/Å		Bond angles/°	
Pt(1)-P(2) Pt(1)-P(1) Pt(1)-Cl(1) Pt(1)-Cl(2) P(1)-N(1) P(2)-N(1)	2.2099(9) 2.2131(9) 2.3637(9) 2.3636(10) 1.710(3) 1.703(3)	$\begin{array}{l} P(2)-Pt(1)-P(1)\\ P(2)-Pt(1)-Cl(1)\\ P(1)-Pt(1)-Cl(2)\\ Cl(1)-Pt(1)-Cl(2)\\ N(1)-P(1)-Pt(1)\\ N(1)-P(2)-Pt(1)\\ P(2)-N(1)-P(1)\\ C(13)-N(1)-P(2)\\ C(13)-N(1)-P(1)\\ \end{array}$	72.06(3) 96.28(3) 98.98(3) 92.44(3) 94.11(9) 94.41(9) 99.34(13) 126.4(2) 128.7(2)

**Table 2** Percentage of pyramidal character (P.P.C.%) and geometrical<br/>parameters for dppa-based ligands in their Pt complexes

Complex	$\Sigma \theta / ^{\circ}$	P.P.C./%
PtCl <sub>2</sub> (dppaMe) <sup>14</sup> [Pt(dppaMe) <sub>2</sub> ] <sup>2+ 14</sup> <b>5</b>	357.1 355.0 354.4	9.2 14.6 17.7

 $(\Sigma \theta = 357.1^{\circ})$  indicating a higher pyramidal character of the nitrogen atom (compare with  $\Sigma \theta_{plan} = 360^{\circ}$  for an ideally planar nitrogen centre and  $\Sigma \theta_{tetr} = 328.5^{\circ}$  for an ideally tetrahedral nitrogen centre).

According to Farrar,<sup>14</sup> the pyramidal character of the nitrogen atom can be evaluated by means of the percentage pyramidal character (P.P.C.%, defined as in eqn (1) where  $\Sigma \theta$  is the sum of the three angles at nitrogen) and can be taken as a measure of the Pt–P– N–P ring strain (the higher the pyramidal character of N the higher the Pt–P–N–P ring strain). In fact, on going from [PtCl<sub>2</sub>(dppaMe)] to the higher ring strained complex [Pt(dppaMe)<sub>2</sub>]<sup>2+</sup> the P.P.C.% went from 9.2% to 14.6%.<sup>14</sup> In our case, the P.P.C.% of 17.7% calculated for **5** (Table 2) indicates a ring strain which is higher than those of both [PtCl<sub>2</sub>(dppaMe)] and [Pt(dppaMe)<sub>2</sub>]<sup>2+</sup>. The reason for the increased ring strain has to be associated with the nature of the N-substituent.

P.P.C. (%) = 
$$\frac{\left[(\Sigma \theta)_{\text{plan}} - (\Sigma \theta)\right]}{\left[(\Sigma \theta)_{\text{plan}} - (\Sigma \theta)_{\text{terr}}\right]} \cdot 100 = \frac{\left[360^{\circ} - (\Sigma \theta)\right]}{31.5^{\circ}} \cdot 100$$
(1)

The bis-chelate complex 13 is expected to show an even higher ring strain with respect to 5, therefore its tendency to give 14 could be conceived as a way to reduce the strain while retaining (for one ligand) chelation. In other words, the thermodynamically stable species 14 represents a compromise between the strong tendency of ligand 1 to chelate (as demonstrated by the inevitable formation of 13 unless the reaction was carried out by slow addition of the reagent), and the high ring strain imposed by a bis-chelation.

The procedure which gave **5** selectively, *i.e.* the slow, dropwise addition of one equivalent of the relevant ligand to  $[PtCl_2(cod)]$  in dichloromethane, allowed the synthesis of **6–8** in good yields. The spectroscopic data for complexes **5–8** are collected in Table 3 from which it is apparent the similarity between all complexes bearing the N-alkyl substituted ligand **5–7**. Complex **8** showed the highest <sup>31</sup>P{<sup>1</sup>H}NMR chemical shift, the highest <sup>1</sup>J<sub>P,Pt</sub> coupling and the lowest IR wavenumbers for the Pt–Cl stretching vibrations, all indicative of a stronger bond between the phosphorus atoms and Pt.

All the heterotrinuclear clusters with a PNP short-bite ligand and the [PtCo<sub>2</sub>] core<sup>8a,b</sup> were prepared by reaction of the Pt(II) complexes **5–8** with two equivalents of NaCo(CO)<sub>4</sub> in dichloromethane at room temperature. The resulting brown solids obtained after work-up gave, in solution, NMR signals ascribable to species **9a–** 

Table 3 Selected  $^{31}P\{^{1}H\}$  NMR,  $^{195}Pt\{^{1}H\}$  NMR and IR spectroscopic features of complexes 5-8

Complex	$\delta_{ extsf{P}}/ extsf{ppm}$	$^{1}J_{\mathrm{P,Pt}}/\mathrm{Hz}$	$\delta_{ ext{Pt}}/ ext{ppm}$	v <sub>Pt-Cl</sub>	/cm <sup>-1</sup>
5	17.8	3304	-4037	288	305
6	17.7	3308	-4038	289	308
7	17.1	3296	-4038	286	306
8	20.7	3330	-4060	276	300

**12a** and **9b–12b** of Scheme 3. This was rather surprising, given that analogous clusters bearing dppa ( $[PtCo_2(CO)_7{Ph_2PN(H)PPh_2}]$ , **15**) or dppaMe ( $[PtCo_2(CO)_7{Ph_2PN(CH_3)PPh_2}]$ , **16**) are known to have, both in the solid state and in solution, exclusively the bridged structure **a**.<sup>8a,b</sup> Furthermore, the strong propensity of the PCP ligand dppm to bridge the edge of an analogous PtCo<sub>2</sub> cluster has also been demonstrated.<sup>15</sup>



In order to identify the most stable structure in the solid state, an XRD analysis of the crystals obtained by slow diffusion of hexane into a dichloromethane solution of 9 at room temperature was undertaken. The crystal structure (Fig. 2) shows that in the solid state the complex crystallises as 9b, thus confirming the unusual stability of the four membered ring formed by ligand 1 in these  $[PtCo_2]$  clusters.



Fig. 2 ORTEP view of the crystal structure of 9b.

Selected bond distances and angles are collected in Table 4. The metal core forms a nearly equilateral triangle with the Co atoms bridged by the C(1)O(4) ligand. This confers an 18 electron and a 16 electron environment to the Co and Pt atoms, respectively. The Pt–C(1) distance of 2.733(4) Å is longer than those found for clusters **15** [2.55(1) Å] and [Co<sub>2</sub>Pt( $\mu_3$ -CO)(CO)<sub>7</sub>(PPh<sub>3</sub>)] [2.57(1) Å]<sup>16</sup> thus indicating that the  $\mu_2$ -CO ligand does not interact with platinum. The geometry around the platinum is distorted square planar (sum of the angles at Pt = 359.0°). The P–Pt bond distances are slightly longer than those of the Pt(II) precursor **5** while the P–N–P angle is slightly larger.

The mixture of clusters having structures  $\mathbf{a}$  and  $\mathbf{b}$  formed also varying the experimental procedure, namely carrying out

Table 4 Selected bond distances and angles for 9b

Bond distances/	Å	Bond angles/°	
Bond distances/ <i>i</i> Pt(1)–P(2) Pt(1)–P(1) Pt(1)–Co(1) Pt(1)–Co(2) Co(1)–Co(2) Co(1)–C(1) Co(1)–C(1) Co(1)–C(5) Co(1)–C(6) Co(1)–C(7) Co(2)–C(1) Co(1)–C(2) Co(1)–C(2) Co(1)–C(3) Co(1)–C(4) Pt(1)–C(1)	A 2.2351(9) 2.2427(9) 2.5587(5) 2.55426(5) 2.5511(7) 1.922(4) 1.807(4) 1.792(4) 1.772(4) 1.928(4) 1.759(4) 1.823(4) 1.784(4) 2.733(4)	Bond angles/° P(2)-Pt(1)-P(1) P(1)-Pt(1)-Co(1) P(2)-Pt(1)-Co(1) P(1)-Pt(1)-Co(2) P(2)-Pt(1)-Co(2) Co(1)-Pt(1)-Co(2) Co(2)-Co(1)-Pt(1) Pt(1)-Co(2)-Co(1) N(1)-P(1)-Pt(1) N(1)-P(2)-Pt(1) P(2)-N(1)-P(1) C(20)-N(1)-P(1)	$\begin{array}{c} 71.53(3)\\ 114.99(3)\\ 170.07(2)\\ 171.10(2)\\ 112.44(3)\\ 60.010(16)\\ 59.681(16)\\ 60.309(15)\\ 93.28(10)\\ 93.77(10)\\ 100.21(15)\\ 126.1(2)\\ 133.2(2) \end{array}$
P(1)-N(1) P(2)-N(1) N(1)-C(20)	1.710(3) 1.702(3) 1.487(4)		

the reactions (*i*) in different solvents (toluene, acetone or THF); (*ii*) at different temperatures (in the range 25–50 °C); (*iii*) using a NaCo(CO)<sub>4</sub>/Pt(II) molar ratio higher than 2. The increase of temperature or of the NaCo(CO)<sub>4</sub>/Pt(II) molar ratio had an accelerating effect on the reaction.

The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of complexes **9a–12a** contain a broad signal around  $\delta$  100 ascribable to P bound to Co and a higher field doublet flanked with satellites ascribable to P bound to <sup>195</sup>Pt. The corresponding <sup>195</sup>Pt{<sup>1</sup>H} NMR signals are doublets of doublets centred near  $\delta$  –4100. Structures **b**, where the two phosphorus atoms are equivalent, gave a singlet flanked with satellites in the <sup>31</sup>P{<sup>1</sup>H} NMR and a triplet in the <sup>195</sup>Pt{<sup>1</sup>H} NMR spectra.

The relative amount of compounds **a** and **b** was found to depend on both the solvent in which the reaction products were dissolved, and the temperature, hence suggesting the existence of an equilibrium between **a** and **b** (Reaction 1, Fig. 3). As to the role of the solvent, the **b/a** molar ratio assessed on the basis of the <sup>31</sup>P NMR integrals<sup>17</sup> of the acetone solution of **11** at 295 K was 2.9 (sample  $\alpha$ ), while those calculated in 1,2-dichlorobenzene and in THF were 2.1 and 1.8, respectively. The **b/a** value calculated for sample  $\alpha$  after acetone evaporation and redissolution in dichloromethane was 1.5 (Fig. 3). Further evaporation of dichloromethane and redissolution in acetone brought the **b/a** molar ratio back to 2.9.

A similar effect was observed performing <sup>31</sup>P VT-NMR experiments. When a 1,2-dichlorobenzene solution of **11** was heated to 375 K, the **b/a** ratio became 5.5. Upon cooling the solution down to 295 K the **b/a** ratio was 2.1 again.

Considering that the volume of the solution is the same for **b** and **a**, the **b**/**a** molar ratio represents the thermodynamic equilibrium constant  $K_e = [\mathbf{b}]/[\mathbf{a}] = \mathbf{b}/\mathbf{a}$ . Table 5 reports the values of  $K_e$ 

 Table 5
 Thermodynamic data of clusters 9–11

Cluster	$K_{e}{}^{a}$	$\Delta H^{\circ b}/\mathrm{kJ} \mathrm{mol}^{-1}$	$\Delta S^{\circ b}/J \ K^{-1} \ mol^{-1}$
9	1.4	$7.8 \pm 0.5$	$31 \pm 2$
10	1.0	12.8 ± 0.6	$47 \pm 2$
11	1.5	11.3 ± 0.6	$44 \pm 2$
12	5.9	n.d.	n.d.

<sup>*a*</sup> Solvent:  $CH_2CI_2$ , T = 295 K. <sup>*b*</sup> Solvent: 1,2-dichlorobenzene, temperature range 295–375 K.



Fig. 3 <sup>31</sup>P NMR spectrum of 11 after dissolution in CH<sub>2</sub>Cl<sub>2</sub>.

obtained in dichloromethane at 295 K for clusters 9–12. It is apparent that clusters 9–11 bearing alkyl substituents on the nitrogen atom of the ligand have similar  $K_e$  while that bearing the phenyl group has a higher  $K_e$  indicating, for 12, a stronger preference for the chelate structure **b**.

It has already been mentioned that the existence of an equilibrium between the chelating and the bridging forms **a** and **b** for clusters bearing alkyl or phenyl substituents on N of the dppa ligand was not observed in related clusters bearing dppa or dppa-Me. In order to gain a deeper insight into the contributions of enthalpy and entropy to  $\Delta G^{\circ}$ , we have calculated  $\Delta G^{\circ}$  of reaction (1) ( $\Delta G^{\circ} = -RT \ln K_e$ ) in the temperature range 295–375 K in 1,2-dichlorobenzene. The plot of  $\Delta G^{\circ}$  vs. T (Fig. 4) was found linear for clusters **9–11** and allowed to calculate  $\Delta H^{\circ}$  as the intercept and  $-\Delta S^{\circ}$  as the slope of the line ( $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ ). Accurate



**Fig. 4**  $\Delta G^{\circ}$  vs. T plot. **9**, R = 0.995; **10**, R = 0.996, **11**, R = 0.997.

measurements of  $\Delta G^{\circ}$  vs. *T* (and obviously of  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$ ) for **12** were prevented by the relatively large errors made when integrating the weak NMR signal of the Pt-bound P of **12a**.

The positive values of  $\Delta H^{\circ}$  found for the isomerization of **a** into **b** (reaction 1) indicate that the bridged structure **a** is favoured with respect to the chelate structure **b** in terms of bond energy balance. This is rationalized by considering the higher stability of five membered cycles with respect to four membered cycles and can explain that clusters 15 and 16 only exist in the bridged form. However, the positive  $\Delta S^{\circ}$  values found for clusters 9–11 (Table 5) render the  $T\Delta S^{\circ}$  term predominant with respect to  $\Delta H^{\circ}$ , resulting in a negative  $\Delta G^{\circ}$  which accounts for equilibrium (1). A comparison with clusters 15 and 16 tends to indicate a relationship between the bulkiness of the substituent on nitrogen and the entropic contribution to  $\Delta G^{\circ}$  of reaction (1). In fact the number of microstates of coordinated dppa(s) bearing bulkier substituents on N (such as those of ligands 1-4) should increase when the P^P bite angle decreases (entropic factor). In the case of clusters 15 (H on N) and 16 (CH<sub>3</sub> on N) the number of microstates could be thought independent of the  $P^{A}P$  bite angle due to the less steric demand of the substituents on N, so that the higher stability of the less strained five-membered cycle (enthalpic factor) renders unfavorable the isomerization  $\mathbf{a} \rightarrow \mathbf{b}$ .

In conclusion, the presence of relatively bulky substituents on N results in a higher chelating power of dppa(s), due to entropic factors. In the case of mononuclear Pt complexes it justifies the tendency to give bis-chelate species, whereas in the case of  $PtCo_2$  clusters it renders the energy of the chelate form **b** comparable with that of the bridged form **a**, resulting in equilibrium (1).

## Experimental

#### General

All the manipulations were conducted under an inert gas (argon) using standard Schlenk techniques. Flash-chromatography was performed on SiO<sub>2</sub> Kieselgel 230–400 mesh. Multinuclear NMR spectra were recorded with a Bruker AX400 spectrometer (400 MHz for <sup>1</sup>H) at 295.0 K; chemical shifts are reported in ppm referenced to SiMe<sub>4</sub> for <sup>1</sup>H and <sup>13</sup>C, H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P and  $H_2PtCl_4$  for <sup>195</sup>Pt. J values are given in Hz. C, H, N elemental analyses were carried out with a Eurovector CHNS-O Elemental Analyser. Pt and Co analyses were performed with a Perkin Elmer SIMAA6000 Atomic Absorption spectrometer after mineralization. The chloride content of the complexes was determined by a potentiometric automatic titration using a Metrohm 716 DMS Titrino. The IR spectra were recorded with a Bruker Vector 22 FT-IR spectrometer. GC-MS analyses were performed with an HP6890-HP5973MSD instrument equipped with an HP-5MS capillary column (30 m  $\times$  250  $\mu$ m  $\times$  0.25  $\mu$ m). All commercial reagents were used as received without further purification. Solvents were dried and distilled under nitrogen according to standard procedures. PtCl<sub>2</sub>(cod)<sup>18</sup> was synthesised according to literature procedures.

## Synthesis of NaCo(CO)<sub>4</sub>

To a stirred deep brown solution of dicobalt octacarbonyl in THF  $(1.53 \text{ g}, 4.5 \text{ mmol in } 80 \text{ cm}^3)$ , a little drop of mercury and pieces

of sodium (overall amount: 2.05 g) were added. After 24 h, the resulting black suspension was filtered (sintered glass filter no. 4) and the resulting colorless solution gave NaCo(CO)<sub>4</sub> as a white solid (1.47 g, 84%) after evaporation of the solvent under reduced pressure.  $v_{max}$ (THF)/cm<sup>-1</sup> 1890 (CO).

#### Synthesis of PhCH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>

To a solution of EtONa in ethanol, obtained by gradual addition of sodium metal (overall amount: 2.29 g, 99.5 mmol in 200 cm<sup>3</sup>), 2-aminoethanethiol hydrochloride (8.52 g, 49.8 mmol) was added. After the resulting solution was boiled at reflux for 1 h, benzyl bromide (5.66 g, 49.8 mmol) was added drop-wise, and the resulting solution was refluxed overnight. Cooling to room temperature, filtration, and evaporation of the solvent led to an off-white solid from which the waxy white amine was obtained by extraction with dichloromethane (3 × 100 cm<sup>3</sup>);  $\delta_{\rm H}$ (CDCl<sub>3</sub>): 7.60–7.35 (5H, m, C<sub>6</sub>H<sub>5</sub>), 3.91 (2H, s, Ph–CH<sub>2</sub>–S), 3.01 (2H, m, S–CH<sub>2</sub>–CH<sub>2</sub>– NH<sub>2</sub>), 2.72 (2H, m, S–CH<sub>2</sub>–CH<sub>2</sub>–NH<sub>2</sub>) and 1.85 (2H, s, –NH<sub>2</sub>);  $\delta_{\rm C}$ (CDCl<sub>3</sub>) 138.4 (C<sub>6</sub>H<sub>5</sub>, C<sub>ipso</sub>), 128.8 (C<sub>6</sub>H<sub>5</sub>, C<sub>orthol/meta</sub>), 128.5 (C<sub>6</sub>H<sub>5</sub>, C<sub>meta/ortho</sub>), 127.0 (C<sub>6</sub>H<sub>5</sub>, C<sub>para</sub>), 40.7 (Ph–CH<sub>2</sub>–S), 35.8 (s, S–CH<sub>2</sub>– CH<sub>2</sub>–NH<sub>2</sub>), 35.3 (s, S–CH<sub>2</sub>–CH<sub>2</sub>–NH<sub>2</sub>).

#### Synthesis of CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>SCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>

To a solution of EtONa in ethanol, obtained by gradual addition of sodium metal (overall amount: 1.93 g, 84.1 mmol in 80 cm<sup>3</sup>), 2-aminoethanethiol hydrochloride (4.76 g, 41.9 mmol) was added. After the resulting solution was boiled at reflux for 1 h, a THF solution of hexyl bromide (6.91 g, 41.9 mmol in 50 cm<sup>3</sup>) was added drop-wise, and the resulting solution was refluxed overnight. Cooling to room temperature and evaporation of the solvent led to a pale yellow suspension. Addition of dichloromethane (50 cm<sup>3</sup>), filtration on Celite and evaporation of the solvent gave the amine as a dense pale yellow liquid (5.27 g, 78%);. m/z (EI) 161 (M<sup>+</sup>, 11%), 144 (9), 132 (100), 117 (97) and 84 (46);  $v_{\text{max}}(\text{CsI})/\text{cm}^{-1}$  3358br, 3287br, 2954s, 2926s, 2857s, 1592w, 1467w, 1378w, 1260w, 1068w, 1014w, 813w, 721w.  $\delta_{\rm H}(\rm CDCl_3)$ : 0.65 (3H, t, -CH<sub>3</sub>), 1.00-1.10 (6H, -NH<sub>2</sub> and CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>-), 1.14 (2H, m, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S-), 1.33 (2H, m, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S-), 2.25 (2H, t, -CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>), 2.36 (2H, t, -SCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>) and 2.61 (2H, br,  $-CH_2NH_2$ );  $\delta_c(CDCl_3)$ : 41.0 ( $-CH_2NH_2$ ), 36.2 (-SCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>), 31.6 (-CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>), 31.2 (CH<sub>3</sub>CH<sub>2</sub>-CH2-), 29.6 (-CH2CH2CH2S-), 28.4 (-CH2CH2CH2S-), 22.4  $(CH_{3}CH_{2}CH_{2})$  and 13.8  $(-CH_{3})$ .

#### Synthesis of 1 and 2

To a vigorously stirred suspension of the amine PhCH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> (7.14 g, 42.8 mmol) and triethylamine (11.91 g, 117.9 mmol) in diethyl ether (100 cm<sup>3</sup>) kept at 0 °C, a solution of chlorodiphenylphosphane in diethyl ether (23.54 g, 107.0 mmol in 100 cm<sup>3</sup>) was added dropwise in 90 min. After the mixture was stirred for 2 days at room temperature, the solvent and the excess triethylamine were removed under reduced pressure. The resulting solid was washed with water (5 × 60 cm<sup>3</sup>), methanol (5 × 20 cm<sup>3</sup>) and hexane (5 × 20 cm<sup>3</sup>) and dried under reduced pressure.

The same procedure was followed for the synthesis of 2.

1. (14.18 g, 62%). (Found C, 74.45; H, 6.1; N, 2.75.  $C_{33}H_{31}NP_2S$ requires C, 74.0; H, 5.8; N, 2.6);.  $\nu_{max}$ (KBr)/cm<sup>-1</sup> 3053w, 2919w, 2903w, 1584w, 1493w, 1478w, 1452w, 1433s, 1091s, 1058vs, 1024s, 1008w, 998w, 867s, 833vs, 743vs, 722w, 695vs, 677s, 626s, 615w, 562w, 539w, 518w, 510w, 493s, 459s, 435w, 415w, 358w;  $\delta_{H}$ (CDCl<sub>3</sub>): 7.54–7.11 (25H,  $-N[P(C_6H_5)_2]_2$  and  $-SCH_2C_6H_5)$ , 3.48 (2H, m,  $-SCH_2CH_2N-$ ), 3.44 (2H, s, PhCH<sub>2</sub>S–) and 2.12 (2H, m,  $-SCH_2CH_2N-$ );  $\delta_{C}$ (CDCl<sub>3</sub>): 139.1 [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P, C<sub>ipso</sub>], 138.4 [(C<sub>6</sub>H<sub>5</sub>)CH<sub>2</sub>S, C<sub>ipso</sub>], 132.7 [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P, C<sub>ortho</sub>], 129.0 [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P, C<sub>para</sub>], 128.8 [(C<sub>6</sub>H<sub>5</sub>)CH<sub>2</sub>S, C<sub>ortho/meta</sub>], 128.5 [(C<sub>6</sub>H<sub>5</sub>)CH<sub>2</sub>S, C<sub>meta</sub>], 126.9 [(C<sub>6</sub>H<sub>5</sub>)CH<sub>2</sub>S, C<sub>para</sub>], 52.6 (t,  $-SCH_2CH_2N-$ , <sup>2</sup> $J_{C,P}$  10.4), 36.4 [(C<sub>6</sub>H<sub>5</sub>)CH<sub>2</sub>S] and 32.4 (t,  $-SCH_2CH_2N-$ , <sup>3</sup> $J_{C,P}$  3.4);  $\delta_{P}$ (CDCl<sub>3</sub>): 62.9 (s).

**2.** (6.79 g, 47%); CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>SCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, 4.40 g, 27.3 mmol. (Found C, 73.1; H, 7.6; N, 2.4.  $C_{32}H_{37}NP_2S$  requires C, 72.6; H, 7.0; N, 2.6); found  $\nu_{max}(KBr)/cm^{-1}$  3069w, 3057w, 2920s, 2852w, 1484s, 1427s, 1091s, 1055s, 846s, 742vs, 697vs, 508s, 452s;  $\delta_{\rm H}$ (CDCl<sub>3</sub>): 7.50–7.30 (20H, –N[P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>), 3.47 (2H, m, S–CH<sub>2</sub>–CH<sub>2</sub>–N), 2.21–2.11 (4H, m, CH<sub>2</sub>–S–CH<sub>2</sub>–CH<sub>2</sub>–N), 1.36–1.25 (8H, m), 0.91 (3H, t, –CH<sub>3</sub>);  $\delta_{\rm C}$ (CDCl<sub>3</sub>): 139.2 [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P–, C<sub>*ipso*], 132.7 [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P–, C<sub>*ortha*], 129.0 [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P–, C<sub>*para*], 128.3 [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P–, C<sub>*meta*], 53.1 (t, –SCH<sub>2</sub>CH<sub>2</sub>N–, <sup>2</sup>J<sub>C,P</sub> 10.2), 32.5 (t, –SCH<sub>2</sub>CH<sub>2</sub>N–, <sup>3</sup>J<sub>C,P</sub> 3.5), 32.1, 31.4, 29.8, 28.5, 22.6 and 14.1 (–CH<sub>3</sub>);  $\delta_{\rm P}$ (CDCl<sub>3</sub>): 62.9 (s).</sub></sub></sub></sub>

## Synthesis of 3

To a vigorously stirred suspension of the decylamine (1.98 g, 12.6 mmol) and triethylamine (2.54 g, 25.2 mmol) in diethyl ether  $(50 \text{ cm}^3)$  kept at 0 °C, a solution of chlorodiphenylphosphane in diethyl ether (5.43 g, 24.6 mmol in 50 cm<sup>3</sup>) was added dropwise in 90 min. After 24 h stirring at room temperature, the solvent and the excess triethylamine were removed under reduced pressure. The resulting solid was dissolved in dichloromethane (30 cm<sup>3</sup>) and the resulting solution was washed with deionized water (30 cm<sup>3</sup>), dried with MgSO<sub>4</sub> and purified by flash chromatography (petroleum ether 40–60 °C : methylene chloride, 7 : 3). The product was obtained as a white solid after evaporation of the solvents under reduced pressure (3.89 g, 59%). (Found C, 77.9; H, 8.0; N, 2.6.  $C_{34}H_{41}NP_2$  requires C, 77.7; H, 7.9; N, 2.7);  $v_{max}(KBr)/cm^{-1}$  2960w, 2924w, 2853w, 1619w, 1462s, 1385s, 1261w, 1084s, 1032s, 873w, 801w, 697w, 533w;  $\delta_{\rm H}$ (CDCl<sub>3</sub>): 7.47–7.32 (20H, [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P]<sub>2</sub>N), 3.27 (2H, m, -CH<sub>2</sub>N), 1.35-0.95 (16H, m, -(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>) and 0.92  $(3H, t, -CH_3, {}^{3}J_{H,H}, 7.0); \delta_{C}(CDCl_3): 139.7 [(C_6H_5)_2P, C_{ipso}], 132.8$ [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P, C<sub>ortho</sub>], 128.7 [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P, C<sub>para</sub>], 128.1 [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P, C<sub>meta</sub>], 53.1 (-CH<sub>2</sub>N, t, <sup>2</sup>J<sub>C,P</sub> 10.8), 31.9, 31.4 (-CH<sub>2</sub>CH<sub>2</sub>N, t, <sup>3</sup>J<sub>C,P</sub> 3.2), 29.5, 29.4, 29.3, 29.1, 26.8, 22.7 and 14.2 ( $-CH_3$ );  $\delta_P(CDCl_3)$ : 62.2 (s).

### Synthesis of 4

To a vigorously stirred suspension of aniline (2.36 g, 25.3 mmol) and triethylamine (5.26 g, 52.1 mmol) in diethylether (50 cm<sup>3</sup>) kept at 0 °C, was added dropwise over 90 min to a solution of chlorodiphenylphosphane in diethyl ether (11.28 g, 51.1 mmol in 70 cm<sup>3</sup>). After stirring for 48 h at room temperature, the solvent and excess triethylamine were removed under reduced pressure. The resulting solid was dissolved in dichloromethane (30 cm<sup>3</sup>) and the solution was washed with deionized water (30 cm<sup>3</sup>), dried

with MgSO<sub>4</sub> and the solvent removed under reduced pressure. The solid was purified by flash chromatography (petroleum ether 40–60 °C : ethyl ether, 6 : 4) and further washed with hexane (4 × 20 cm<sup>3</sup>). The product was obtained as a white solid after evaporation of the solvent (4.79 g, 41%). (Found C, 78.3; H, 5.6; N, 3.0;  $C_{30}H_{25}NP_2$  requires C, 78.1; H, 5.5; N, 3.0);  $v_{max}(KBr)/cm^{-1}$  3084w, 3056w, 3041w, 3028w, 3013w, 2999w, 1493s, 1438s, 1209vs, 937vs, 908w, 866vs, 737vs, 695vs, 524s, 511s, 465w;  $\delta_{H}(CDCl_3)$ : 7.45–7.28 (20H, [( $C_6H_5$ )<sub>2</sub>P]<sub>2</sub>N–), 7.05–6.95 (m, 3H, –NC<sub>6</sub>H<sub>5</sub>) and 6.71 (m, 2H, –NC<sub>6</sub>H<sub>5</sub>);  $\delta_{C}(CDCl_3)$ : 147.5 ( $C_6H_5N$ –, t,  $C_{ipso}$ , <sup>2</sup> $J_{C,P}$  2.6), 139.3 [( $C_6H_5$ )<sub>2</sub>P,  $C_{ipso}$ ], 133.3 [( $C_6H_5$ )<sub>2</sub>P,  $C_{ortho}$ ], 129.1 [( $C_6H_5$ )<sub>2</sub>P,  $C_{meta}$ ] and 125.1 [( $C_6H_5$ )N–];  $\delta_{P}(CDCl_3)$ : 68.6 (s).

#### Synthesis of 5, 6, 7 and 8

To a vigorously stirred solution of  $[PtCl_2(cod)]$  in dichloromethane (1.01 g, 2.7 mmol in 60 cm<sup>3</sup>) a solution of 1 (1.45 g, 2.7 mmol in 20 cm<sup>3</sup>) was added dropwise in 2 h. After 5 h, the solution was concentrated (to 30 cm<sup>3</sup>) and the product was obtained by precipitation with diethyl ether (60 cm<sup>3</sup>). The white solid was washed with diethyl ether (3 × 20 cm<sup>3</sup>) and the solvent evaporated to dryness.

The same procedure was followed for the synthesis of **6**, **7** and **8**.

**5.** (89%). (Found C, 49.65; H, 4.0; Cl, 8.55; N, 1.6; Pt, 23.5.  $C_{33}H_{31}Cl_2NP_2PtS$  requires C, 49.45; H, 3.9; Cl, 8.85; N, 1.75; Pt 24.3);  $v_{max}(KBr)/cm^{-1}$  3050w, 2928w, 1480vs, 1435w, 1299w, 1103vs, 1018w, 999w, 878w, 848s, 749s, 694vs, 665s, 579s, 510vs, 492s, 454w, 305w (Pt–Cl), 288w (Pt–Cl);  $\delta_{H}(CDCl_{3})$ : 7.85–7.48 (20H,  $[(C_{6}H_{5})_{2}P]_{2}N-)$ , 7.25–6.87 (5H,  $C_{6}H_{5}CH_{2}S-)$ , 3.40 (2H, s, PhC $H_{2}S-)$ , 2.95 (2H, m, S–CH<sub>2</sub>–CH<sub>2</sub>–N) and 2.00 (2H, m, S–CH<sub>2</sub>–CH<sub>2</sub>–NH<sub>2</sub>);  $\delta_{C}(CDCl_{3})$ : 137.4 ( $C_{6}H_{5}CH_{2}S-$ ,  $C_{ipso}$ ), 133.4 [ $(C_{6}H_{5})_{2}P-$ ], 128.5 ( $C_{6}H_{5}CH_{2}S-$ ), 127.3 ( $C_{6}H_{5}CH_{2}S-$ ,  $C_{para}$ ), 126.9 [ $(C_{6}H_{5})_{2}P-$ ,  $C_{ipso}$ ], 49.1 (–SCH<sub>2</sub>CH<sub>2</sub>N–), t, <sup>2</sup>J<sub>CP</sub> 9.0), 36.3 [ $(C_{6}H_{5})CH_{2}S-$ ] and 29.6 (–SCH<sub>2</sub>CH<sub>2</sub>N–);  $\delta_{P}(CDCl_{3})$ : 17.8 (s, <sup>1</sup>J<sub>PPt</sub> 3304);  $\delta_{Pt}(CDCl_{3})$ : –4037 (t, <sup>1</sup>J<sub>PPt</sub> 3304).

**6.** (87%). (Found C, 48.5; H, 4.8; Cl, 8.5; N, 1.7; Pt, 23.8.  $C_{32}H_{37}Cl_2NP_2PtS$  requires C, 48.3; H, 4.7; Cl, 8.9; N, 1.8; Pt 24.5);  $\nu_{max}(KBr)/cm^{-1}$  3056w, 2951w, 2924w, 2858w, 1437s, 1260s, 1129s, 1101vs, 1025s, 804s, 747s, 719s, 691s, 577w, 520s, 511s, 492w, 381w, 308w (Pt–Cl), 289w (Pt–Cl);  $\delta_{H}(CDCl_{3})$ : 7.90–7.25 (20 H,  $[(C_6H_5)_2P]_2N-)$ , 3.13 (2 H, m), 2.16 (2 H, m), 2.01 (2 H, m), 1.35–1.10 (8 H, m) and 2.01 (3 H, –CH<sub>3</sub>);  $\delta_{C}(CDCl_{3})$ : 133.4  $[(C_6H_5)_2P-]$ , 133.3  $[(C_6H_5)_2P-, C_{paral}]$ , 129.5  $[(C_6H_5)_2P-]$ , 127.1  $[(C_6H_5)_2P-, C_{ipso}]$ , 49.4 (–SCH<sub>2</sub>CH<sub>2</sub>N–), 32.2, 31.3, 30.6, 29.3, 28.3, 22.5 and 14.0;  $\delta_{P}(CDCl_{3})$ : 17.7 (s, <sup>1</sup> $J_{PPt}$  3308);  $\delta_{Pt}(CDCl_{3})$ : –4038 (t, <sup>1</sup> $J_{PPt}$  3308).

7. (84%). (Found C, 51.4; H, 5.4; Cl, 8.5; N, 1.6; Pt, 24.0.  $C_{34}H_{41}Cl_2NP_2Pt$  requires C, 51.6; H, 5.2; Cl, 9.0; N, 1.8; Pt 24.6);  $v_{max}(KBr)/cm^{-1}$  3053w, 2933w, 1480w, 1435vs, 1306w, 1102vs, 878w, 848s, 749s, 721w, 694vs, 664s, 575s, 522vs, 508vs, 492s, 306w (Pt–Cl), 286w (Pt–Cl);  $\delta_{H}(CDCl_3)$ : 7.87–7.56 (20H,  $[(C_6H_5)_2P]_2N-)$ , 2.93 (2H, m,  $-CH_2N-)$  and 1.20–0.80 (19H, m,  $-(CH_2)_8CH_3$ );  $\delta_C(CDCl_3)$ :128.9  $[(C_6H_5)_2P-]$ , 128.7  $((C_6H_5)_2P-]$ ,  $C_{para}$ ), 124.8  $[(C_6H_5)_2P-]$ , 122.8  $[(C_6H_5)_2P, C_{ipso}]$ , 45.3 (t,  $-CH_2N-$ ,  ${}^2J_{C,P}$  8.1), 27.3, 26.4, 24.9, 24.7, 24.6, 24.2, 22.2, 22.1 and 18.1

 $(-CH_3)$ ;  $\delta_P(CDCl_3)$ : 17.1 (s, <sup>1</sup> $J_{P,Pt}$  3296);  $\delta_{Pt}(CDCl_3)$ : -4038 (t, <sup>1</sup> $J_{P,Pt}$  3296).

**8.** (88%). (Found C, 49.8; H, 3.7; Cl, 9.6; N, 2.0; Pt, 27.0.  $C_{30}H_{25}Cl_2NP_2Pt$  requires C, 49.5; H, 3.5; Cl, 9.75; N, 1.9; Pt, 26.8);  $\nu_{max}$ (KBr)/cm<sup>-1</sup> 3084w, 3059w, 3042w, 3029w, 3012w, 2999w, 1591w, 1580w, 1485s, 1479s, 1439s, 1431s, 1207s, 1100w, 1023w, 930vs, 902s, 871vs, 735vs, 692vs, 659w, 529s, 517s, 300w (Pt-Cl), 276w (Pt-Cl);  $\delta_{H}$ (CDCl<sub>3</sub>): 7.88 (8H, [( $C_6H_5$ )<sub>2</sub>P]<sub>2</sub>N-), 7.63 (4H, [( $C_6H_5$ )<sub>2</sub>P]<sub>2</sub>N-,  $H_{para}$ ), 7.51 (8H, [( $C_6H_5$ )<sub>2</sub>P]<sub>2</sub>N-), 7.21 (1H, ( $C_6H_5$ )N,  $H_{para}$ ), 7.09 (2H, ( $C_6H_5$ )N,  $H_{meta}$ ) and 6.48 (2H, ( $C_6H_5$ )N,  $H_{ortha}$ );  $\delta_{P}$ (CDCl<sub>3</sub>): 20.7 (s, <sup>1</sup>J<sub>PPt</sub> 3330);  $\delta_{Pt}$ (CDCl<sub>3</sub>): -4060 (t, <sup>1</sup>J<sub>PPt</sub> 3330).

#### Synthesis of the clusters 9-12

To a stirred suspension of NaCo(CO)<sub>4</sub> in dichloromethane (180 mg, 0.93 mmol in 80 cm<sup>3</sup>), **5** (365 mg, 0.46 mmol) was added in one portion. The colorless mixture turned to brown and after 4 h (24 h for **12**) the solvent was removed under reduced pressure. The brown solid was purified by percolation on silica and Celite using THF as eluent. The product was obtained after evaporation of the solvent under reduced pressure as a brown solid affording **9** in 82% yield.

The same procedure was followed for the synthesis of **10**, **11** and **12**.

**9.** (Found C, 46.7; H, 3.4; Co, 11.0; N, 1.1; Pt, 18.0.  $C_{40}H_{31}Co_2NO_7P_2PtS$  requires C, 46.0; H, 3.0; Co, 11.3; N, 1.3; Pt, 18.7);  $\nu_{max}(KBr)/cm^{-1}$  (CO): 2049vs, 2006vs, 1977vs, 1970vs, 1956s, 1941s, 1755s;  $\delta_P(CH_2Cl_2)$ : 99.5 (br,  $Ph_2P$ –Co, **9a**), 70.3 (d,  $Ph_2P$ –Pt,  $J_{PP}$  26,  ${}^{1}J_{PPt}$  3604, **9a**) and 55.2 (s,  $Ph_2P$ –Pt,  ${}^{1}J_{PPt}$  3019,

**Table 6**Crystal data and structure refinement for **5** and **9b** 

**9b**);  $\delta_{Pl}$ (THF): -4120 (dd,  ${}^{1}J_{P,Pt}$  3589,  ${}^{2}J_{P,Pt} + {}^{3}J_{P,Pt}$  | 78, **9a**), -4325 (t,  ${}^{1}J_{P,Pt}$  3006, **9b**).

**10.** (81%). (Found C, 45.3; H, 3.9; Co, 11.2; N, 1.2; Pt, 18.1.  $C_{39}H_{37}Co_2NO_7P_2PtS$  requires C, 45.1; H, 3.6; Co, 11.35; N, 1.35; Pt 18.8);  $\nu_{max}(KBr)/cm^{-1}$  (CO): 2047s, 2033vs, 2006s, 1955vs, 1913vs, 1882s, 1761w;  $\delta_P(CH_2Cl_2)$ : 98.4 (br, Ph<sub>2</sub>*P*–Co, **10a**), 69.5 (d, Ph<sub>2</sub>*P*–Pt,  $J_{PP}$  28,  ${}^{1}J_{P,Pt}$  3604, **10a**) and 54.3 (s, Ph<sub>2</sub>*P*–Pt,  ${}^{1}J_{P,Pt}$  3015, **10b**);  $\delta_{Pt}(CH_2Cl_2)$ : -4136 (dd,  ${}^{1}J_{P,Pt}$  3604,  ${}^{2}J_{P,Pt} + {}^{3}J_{P,Pt}$  | 80, **10a**), -4333 (t,  ${}^{1}J_{P,Pt}$  3015, **10b**).

**11.** (83%). (Found C, 48.0; H, 4.3; Co, 11.1; N, 1.2; Pt, 18.3.  $C_{41}H_{41}Co_2NO_7P_2Pt$  requires C, 47.6; H, 4.0; Co, 11.4; N, 1.35; Pt, 18.85);  $\nu_{max}(KBr)/cm^{-1}$  (CO): 2048vs, 2004vs, 1976vs, 1969vs, 1757s;  $\delta_P(CH_2Cl_2)$ : 96.6 (br, Ph<sub>2</sub>*P*-Co, **11a**), 68.1 (d, Ph<sub>2</sub>*P*-Pt, <sup>2+3</sup>*J*<sub>PP</sub> 28, <sup>1</sup>*J*<sub>PPt</sub> 3603, **11a**) and 52.2 (s, Ph<sub>2</sub>*P*-Pt, <sup>1</sup>*J*<sub>PPt</sub> 3013, **11b**);  $\delta_{Pt}(CDCl_3)$ : -4149 (dd, <sup>1</sup>*J*<sub>Pt,Pt</sub> 3612,  $|{}^2J_{PPt} + {}^3J_{PPt}|$  77, **11a**) and -4337 (t, <sup>1</sup>*J*<sub>Pt,Pt</sub> 3009, **11b**).

12. (73%). (Found C, 45.9; H, 2.8; Co, 11.8; N, 1.1; Pt, 19.6.  $C_{37}H_{25}Co_2NO_7P_2Pt$  requires C, 45.8; H, 2.6; Co, 12.15; N, 1.4; Pt, 20.1);  $\nu_{max}(KBr)/cm^{-1}(CO)$ : 2048vs, 2002vs, 1986vs, 1971vs, 1934s, 1741vs;  $\delta_P(CH_2Cl_2)$ : 104.4 (br, Ph<sub>2</sub>*P*-Co, **12a**), 73.9 (d, Ph<sub>2</sub>*P*-Pt,  $J_{P,P}$  30,  ${}^{1}J_{P,Pt}$  3607, **12a**) and 60.7 (s, Ph<sub>2</sub>*P*-Pt,  ${}^{1}J_{P,Pt}$  3042, **12b**);  $\delta_{Pt}(CH_2Cl_2)$ : -4143 (dd,  ${}^{1}J_{Pt,Pt}$  3607,  ${}^{2}J_{P,Pt} + {}^{3}J_{P,Pt}$ | 74, **12a**) and -4358 (t,  ${}^{1}J_{Pt,Pt}$  3042, **12b**).

# X-Ray data collection, structure solution, and refinement of 5 and 9b<sup>19</sup>

Crystal data, parameters for intensity data collection and convergence results are compiled in Table 6. Crystals were studied at 110 K with a BRUKER-AXS SMART APEX diffractometer.

	5	9
Empirical formula	C <sub>33</sub> H <sub>31</sub> Cl <sub>2</sub> NP <sub>2</sub> PtS	$C_{40}H_{31}Co_2NO_7P_2PtS$
Molecular mass	801.58	1044.61
Crystal size	$0.27 \times 0.23 \times 0.06 \text{ mm}$	$0.38 \times 0.15 \times 0.12 \text{ mm}$
Temperature/K	110(2)	110(2)
Wavelength/Å	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_{1}/c$	Pbca
Unit cell dimensions		
a/Å	11.4712(19)	20.0857(19)
b/Å	16.585(3)	19.929(2)
c/Å	17 909(3)	19 9610(19)
B/°	111.516(9)	
$V/Å^3$	3169.8(9)	7990.1(13)
Z	4	8
$D_{\rm calcd}/{\rm Mg}~{\rm m}^{-3}$	1.680	1.737
Absorption coeff./mm <sup>-1</sup>	4.786	4.495
$\theta$ Range for data coll./°	2.44-28.10	2.04-29.62
Reflections collected	31456	52751
Independent reflections	7584	11065
Indep. observed reflections		
$(I > 2\sigma(I))$	6462	
Data/parameters	7584/361	11065/487
Goodness of fit on $F^2$	1.020	1.013
$R^a (I > 2\sigma(I))$	0.0289	0.0344
$wR2^{b}$ (all data)	0.0668	0.0790
Largest diff. Peak/hole [e Å <sup>-3</sup> ]	1.532, -0.592	1.900, -0.764

 ${}^{a} R = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}| . {}^{b} w R_{2} = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{o}^{2})^{2}]^{1/2}.$ 

5. An empirical absorption correction<sup>20</sup> was applied before averaging symmetry related reflections. The structure was solved by direct methods<sup>21</sup> and refined on  $F^{2,22}$  In the final refinement, all non-hydrogen atoms were assigned anisotropic displacement parameters and hydrogen atoms were included as riding in standard geometry.

**9b.** A semi-empirical absorption correction based on equivalents (min. *trans.* 0.280, max. *trans* 0.615) was applied before averaging symmetry equivalent data [R(int) = 0.0565]. After merging 11065 independent reflections remained for structure solution by direct methods.<sup>21</sup> The structure model was completed by Fourier difference syntheses and refined with full-matrix least-squares on  $F^{2}$ .<sup>22</sup>

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