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Assembling metals and clusters around an octaphosphine ligand based on *N*-substituted bis(diphenylphosphanyl)amines: structural characterization of dendrimer-like Co_{12} and Co_{16} branched clusters.†

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Experimental

General Considerations

All manipulations were carried out under inert dinitrogen atmosphere, using standard Schlenk-line conditions and dried and freshly distilled solvents. Multinuclear NMR spectra were recorded on a Bruker Avance 300 instrument (300.13 MHz for ^1H) at 298 K for **7** and **10-12** and on a Bruker Avance 400 instrument (400.13 MHz for ^1H) at 295 K for **8** and **9**. Chemical shifts are reported in ppm referenced to $SiMe_4$ (^1H and ^{13}C), 85% H_3PO_4 (^{31}P) and H_2PtCl_6 (^{195}Pt). Elemental C, H, and N analyses were performed by the "Service de microanalyses", Université Louis Pasteur, Strasbourg. The complex $[PtCl_2(cod)]$ (cod = 1,4-cyclooctadiene)[1] was prepared according to literature procedures and PPh_2Cl was freshly distilled before use. Other chemicals were commercially available and used as received.

Synthesis of 1,2,4,5-$(H_2NCH_2CH_2SCH_2)_4C_6H_2$

In our hands, the following procedure gave a better yield than the original one.[2] 2-Aminoethanethiol hydrochloride (5.93 g, 52.2 mmol) was added to a stirred solution of NaOEt (prepared from 2.42 g, 105.1 mmol of sodium in 200 mL ethanol) in one portion. After the resulting solution was boiled at reflux for 1 h, 1,2,4,5-$(BrCH_2)_4C_6H_2$ (5.86 g, 13.0 mmol) in EtOH/THF (1:1; 150 ml) was added dropwise to the white suspension, and the resulting solution was refluxed overnight. After it was cooled to room temperature, filtration, and evaporation of the solvent lead to a yellowish precipitate. The product 1,2,4,5-$(H_2NCH_2CH_2SCH_2)_4C_6H_2$ was obtained as a white waxy solid after extraction with dichloromethane and evaporation of the solvent under vacuum. Yield: 83% (4.70 g, 10.8 mmol). ^1H NMR ($CDCl_3$): δ 7.15 (s, 2H, aromatic), 3.84 (s, 8H, CH_2 benzylic), 2.85 (t, 8H, NCH_2CH_2S, ^3J = 6.4 Hz), 2.57 (t, 8H, NCH_2CH_2S, ^3J = 6.4 Hz), 1.27 (s, 8H, NH_2) ppm.

Synthesis of 1,2,4,5-[$CH_2SCH_2CH_2N(PPh_2)_2]_4C_6H_2$ (7)[3]

Et_3N (5.78 g, 57.14 mmol) was added to a stirred suspension of 1,2,4,5-($H_2NCH_2CH_2SCH_2)_4C_6H_2$ (2.81 g, 6.47 mmol) in diethylether (200 mL) at 0 °C. After 10 min, a solution of distilled PPh_2Cl (11.93 g, 54.07 mmol) in diethylether (50 mL) was added dropwise over 1 h at 0 °C. The mixture was further stirred at room temperature for 3 days after which a white sticky solid was formed. The solvent was evaporated under reduced pressure and the solid was washed with water (1 x 50 ml), ethanol (4 x 50 ml) and hexane (2 x 50 ml). Yield: 61% (7.54 g, 3.95 mmol). ^{1}H NMR ($CDCl_3$): δ 7.46–7.13 (m, 80H, P-phenyls), 6.80 (s, 2H, aromatic), 3.45 (m, 8H, NCH_2CH_2S), 3.30 (s, 8H, CH_2 benzylic), 1.97 (m, 8H, NCH_2CH_2S); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 63.3.

Synthesis of 1,2,4,5-[$CH_2SCH_2CH_2\{N(PPh_2)_2PtCl_2\}]_4C_6H_2$ (8)

A solution of ligand **7** (0.500 g, 0.26 mmol) in DMF (80 mL) was added dropwise over 1 h to a stirred solution of [$PtCl_2$(cod)] (0.389 g, 1.04 mmol) in DMF (50 mL) at room temperature. The resulting solution was further stirred at room temperature for 1 h. The solvent was removed under reduced pressure at 70 °C and the resulting off-white solid was dissolved in dichloromethane (50 mL). **8** was obtained as a white solid after precipitation with diethyl ether (100 mL), it was rapidly washed with dichloromethane (20 mL) to remove traces of **7** and [$PtCl_2$(cod)], further washed with diethylether (3×20 ml) and dried under vacuum. Yield: 86% (0.664 g, 0.22 mmol). Selected data: IR (KBr): 309 (m, ν_{Pt-Cl}), 292 (m, ν_{Pt-Cl}) cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 17.3 (s with ^{195}Pt satellites, $^1J_{P-Pt}$ = 3298 Hz); $^{195}Pt\{^1H\}$ NMR (CD_2Cl_2): δ −4028 (t, $^1J_{P-Pt}$ = 3298 Hz).

Synthesis of 1,2,4,5-[$CH_2SCH_2CH_2\{N(Ph_2P)_2PtCo_2(CO)_7\}]_4C_6H_2$ (9)

To a stirred suspension of Na[$Co(CO)_4$] (0.105 g, 0.541 mmol) in dichloromethane (50 mL), **8** (0.161 g, 0.054 mmol) was added in one portion. The colourless mixture turned brown and after 3 h the solvent was removed under reduced pressure. The brown solid was purified by percolation through silica and Celite using THF as eluent. The product **9** was obtained after evaporation of the solvent under reduced pressure as a brown solid. Yield: 81% (0.172 g, 0.044 mmol). Selected data: IR (KBr) ν(CO): 2054 (vs), 2010 (vs), 1966 (vs), 1756 (vs) cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 100.0 (br, Ph_2P-Co, **a**), 71.0 (d with ^{195}Pt satellites, $^2J_{P,P}$ = 23 Hz, $^1J_{P,Pt}$ = 3629 Hz, Ph_2P-Pt, **a**), 56.0 (s with ^{195}Pt satellites, $^1J_{P,Pt}$ = 3010 Hz, **b**); $^{195}Pt\{^1H\}$

NMR (CD_2Cl_2): δ –4129 (d, $^1J_{P,Pt}$ = 3629 Hz, **a**), –4330 (t, $^1J_{P,Pt}$ = 3010 Hz, **b**).

Reaction of [$Co_3(\mu_3$-CCl)(CO)$_9$] with 7 and formation of 1,2,4,5-[$CH_2SCH_2CH_2\{N(Ph_2P)_2Co_3(\mu_3$-CCl)(CO)$_7\}]_4C_6H_2$ (10).

Solid [$Co_3(\mu_3$-CCl)(CO)$_9$] (0.280 g, 0.781 mmol) and ligand **7** (0.372 g, 0.195 mmol) were placed in a Schlenk tube under nitrogen. Dry and degassed toluene (50 mL) was added and the reaction mixture was stirred at room temperature for 24 h during which time the reaction was monitored by TLC. During the course of the reaction, a red precipitate formed which was separated from the solution by filtration and purified by recrystallisation/precipitation from toluene/hexane (fine red powder). The red product was characterised by $^{31}P\{^1H\}$ NMR and IR spectroscopic methods. Yield: 0.433 g, 62%. IR (CH_2Cl_2) ν(CO): 2065 (s), 2014 (vs), 1997 (w) cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 109 (s). Further recrystallisation from CH_2Cl_2/MeOH/hexane in the presence of *p*-$C_6H_4(OH)_2$ (with the hope to favour formation of single crystals through H-bonding interactions, see J. T. Mague and S. E. Dessens)[4] (slow diffusion of a MeOH solution containing *p*-$C_6H_4(OH)_2$ into a CH_2Cl_2 solution of the cluster and layering with hexane) afforded crystals suitable for X-ray diffraction. It turned out that *p*-$C_6H_4(OH)_2$ was not incorporated in the crystalline material.

General procedures for the reactions of [$Co_4(CO)_{10}(\mu$-dppx)] with 7; formation of 11 (x = a) and 12 (x = m).

Method (A). Solid [$Co_4(CO)_{10}(\mu$-dppx)] and ligand **7** were placed in a Schlenk tube under nitrogen. Dichloromethane (50 mL) was added and the reaction mixture was stirred at reflux (60-70 °C) for 7 h during which time the evolution of the reaction was monitored by TLC. The reaction was stopped when no further change was observed. Since [$Co_4(CO)_{10}(\mu$-dppx)] was not totally consumed, the final product was purified by column chromatography on silica, using as eluent a mixture of CH_2Cl_2/hexane/MeOH with variable proportions to increase polarity. Four fractions were collected, evaporated to dryness under reduced pressure and the resulting green and red solids analysed by the usual characterisation techniques ($^{31}P\{^1H\}$ NMR and IR spectroscopic methods). The yields given below are based on **7**.

Method (B). Solid [$Co_4(CO)_{10}(\mu$-dppx)] was placed in a Schlenk tube equiped with an equalising dropping funnel and the whole system was purged with nitrogen. Dichloromethane (50 mL) was added to the solid through the top of the funnel and complete dissolution was reached. In a separated Schlenk tube, a CH_2Cl_2 solution (30 mL) of ligand **7** was prepared and transferred to the dropping funnel under a nitrogen purge. The solution of the ligand was added dropwise at room temperature to the cluster solution. The reaction was monitored by TLC and the mixture was stirred overnight. After 43 h, TLC showed no further changes and the reaction was stopped. Since $[Co_4(CO)_{10}(\mu\text{-dppx})]$ was not totally consumed, the final product was purified by column chromatography on silica, using as eluent a mixture of CH_2Cl_2/hexane/MeOH with variable proportions to increase polarity. Four fractions were collected, evaporated to dryness under reduced pressure and the resulting green and red solids analysed by $^{31}P\{^1H\}$ NMR and IR spectroscopic methods. The yields given below are based on reactant (**7**).

Method (C). As in *Method (B)* with the only difference that the CH_2Cl_2 solution of ligand **7** was added dropwise to a refluxing CH_2Cl_2 solution of $[Co_4(CO)_{10}(\mu\text{-dppx})]$. The reaction was stopped after 20 h. Work-up and products were as described in *Method (B).*

Spectroscopic Data

No excess of ligand was used to avoid the formation of mixtures of products with different degrees of substitution. Instead, we used an excess of $[Co_4(CO)_{10}(\mu\text{-dppx})]$. We have observed that when $[Co_4(CO)_{10}(\mu\text{-dppm})]$ is used, much less starting material remains at the end of the reaction. We have verified that ligand **7** is stable under our reaction conditions.

The three different reaction conditions described under A-C gave the same type and number of products as indicated by IR and $^{31}P\{^1H\}$ NMR spectroscopy. The only significant difference concerns the yields and reaction times since *Method (C)* required much longer reaction times and gave lower reaction yields when compared to *Method (A)* (see below).

In all cases, the first, red fractions collected from the column chromatography correspond by their colour, IR and ^{31}P NMR spectroscopic data to the starting material $[Co_4(CO)_{10}(\mu\text{-dppx})]$.

$[Co_4(CO)_{10}(\mu\text{-dppa})]$: IR ($CH_2Cl_2$): 2068 (s), 2029 (vs), 2015 (vs), 1988 (w) $\nu_{C\equiv O}$; 1823 (m), 1794 (m) $\nu_{C=O}$, cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 75.5 (s).

$[Co_4(CO)_{10}(\mu\text{-dppm})]$: IR ($CH_2Cl_2$): 2066 (s), 2022 (vs), 2015 (s), 1982 (w) $\nu_{C\equiv O}$; 1828 (m), 1794 (m) $\nu_{C=O}$, cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.2 (s).

The second, green fractions collected from the column chromatography turned out to be mixtures of $[Co_4(CO)_{10}(\mu\text{-dppx})]$ and free ligand since their $^{31}P\{^1H\}$ NMR spectra showed one peak corresponding to this cobalt cluster (at δ 74 for x = a and at δ 28 when x = m) and another peak at δ 60.2 corresponding to the free ligand (**7**). This is consistent with the IR data which show the same terminal and bridging CO bands as for $[Co_4(CO)_{10}(\mu\text{-dppx})]$.

The third, green fractions contain the major, expected reaction products. We have not been able to provide a detailed assignment of all the 5 different peaks present in the $^{31}P\{^1H\}$ NMR spectrum: the most intense one at δ 73.5 for the dppa derivative and at δ 29.0 for the dppm derivative and the other four (δ 84.7, 91.9, 96.5 and 105.6 for the dppa derivative and δ 88.0, 92.0, 97.4 and 102.7 for the dppm derivative) are weaker and broader. No trace of free ligand **7** was found and this indicates that no partial coordination of the ligand has occurred. The colour is once more in agreement with a doubly-disubstituted tetrahedral tetracobalt cluster (corresponding to two short-bite donor ligands).[5] Since the only significant difference between the $^{31}P\{^1H\}$ NMR data of the reactions performed with $[Co_4(CO)_{10}(\mu\text{-dppm})]$ or $[Co_4(CO)_{10}(\mu\text{-dppa})]$ deals with the peak at δ 28.7 or at δ 73.5, respectively, these signals should correspond to the P nuclei from the cluster-bound dppm and dppa ligands, respectively, the other four peaks belonging to the phosphorus atoms from cluster-bound ligand **7** that have become magnetically inequivalent owing to the lower symmetry of the product.

Attempts to characterize the products by mass spectrometry were unsuccessful (Note the high molecular weight of the desired products, 5289 for the dppa derivative and 5285 for the dppm derivative).

The IR spectra of products **11** and **12** have a similar shape to those of $[Co_4(CO)_{10}(\mu\text{-dppx})]$ with all the peaks shifted to lower wavenumbers, which is consistent with these molecules having retained the expected tetrahedral geometry.

$[\{Co_4(CO)_8(\mu\text{-dppa})\}_4(1,2,4,5\text{-}\{[(Ph_2P)_2NCH_2CH_2SCH_2]_4C_6H_2\})]$ (**11**): IR (CH_2Cl_2): 2010 (s), 1977 (vs), 1941 (w) $\nu_{C\equiv O}$; 1831 (w), 1793 (m), 1773 (m) $\nu_{C=O}$, cm^{-1}.

$[\{Co_4(CO)_8(\mu\text{-dppm})\}_4(1,2,4,5\text{-}\{[(Ph_2P)_2NCH_2CH_2SCH_2]_4C_6H_2\})]$ (**12**): IR (CH_2Cl_2): 2006 (s), 1973 (vs), 1953 (w) $\nu_{C\equiv O}$; 1832 (w), 1794 (m), 1769 (m) $\nu_{C=O}$, cm^{-1}.

Finally, the fourth, green fractions always appeared to be a mixture difficult to purify.

Amounts (yields are given for the 3rd fractions collected from the chromatography column):

Method (A):

- Reaction of [$Co_4(CO)_{10}$(μ-dppm)] (0.476 g, 0.529 mmol) with **7** (0.252 g, 0.132 mmol). Yield: 0.363 g, 52%.
- Reaction of [$Co_4(CO)_{10}$(μ-dppa)] (0.300 g, 0.333 mmol) with **7** (0.158 g, 0.083 mmol). Yield: 0.178 g, 40%.

Method (B):

- Reaction of [$Co_4(CO)_{10}$(μ-dppm)] (0.100 g, 0.111 mmol) with **7** (0.053 g, 0.028 mmol). Yield: 0.058 g, 39%.
- Reaction of [$Co_4(CO)_{10}$(μ-dppa)] (0.104 g, 0.115 mmol) with **7** (0.055 g, 0.029 mmol). Yield: 0.036 g, 24%.

Method (C):

- Reaction of [$Co_4(CO)_{10}$(μ-dppm)] (0.150 g, 0.167 mmol) with **7** (0.080 g, 0.042 mmol). Yield: 0.111 g, 50%.
- Reaction of [$Co_4(CO)_{10}$(μ-dppa)] (0.100 g, 0.111 mmol) with **7** (0.053 g, 0.028 mmol). Yield: 0.055 g, 37%.

X-ray data collection, structure solution and refinement for compounds 10·$4CH_2Cl_2 \cdot 2C_6H_{14}$ and **11**•$2CH_2Cl_2$.

Suitable crystals of **10**•$4CH_2Cl_2 \cdot 2C_6H_{14}$ for X-ray analysis were obtained as indicated above. Single crystals of **11**•$2CH_2Cl_2$ were obtained at room temperature by slow diffusion under argon atmosphere of hexane on a concentrated CH_2Cl_2 solution of **11**. The intensity data were collected at 173(2) K on a Kappa CCD diffractometer[6] (graphite monochromated MoK_α radiation, $\lambda = 0.71073$ Å) (Table S-1). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97)[7] with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXS-97 procedures) and refined *riding* on the corresponding parent atoms. Crystal data and refinement details are gathered in Tables S-1 and S-3. CCDC-xxx contains the supplementary crystallographic data that can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Comments on the structure of **10**·4CH_2Cl_2·2C_6H_{14}

An ORTEP view of the molecule is shown in Fig. S-1 and selected bond distances and angles are given in Table S-2. In this centrosymmetric molecule, each short-bite dppa-type ligand is attached to a Co_3 cluster and bridges an edge opposite to that spanned by the ancillary dppa ligand. All the CO ligands are terminal, and each Co_3 triangle is capped by a μ_3-C-Cl ligand, as in the precursor. The Co-Co bond distances are in the range: 2.40(1) - 2.50(1) Å.

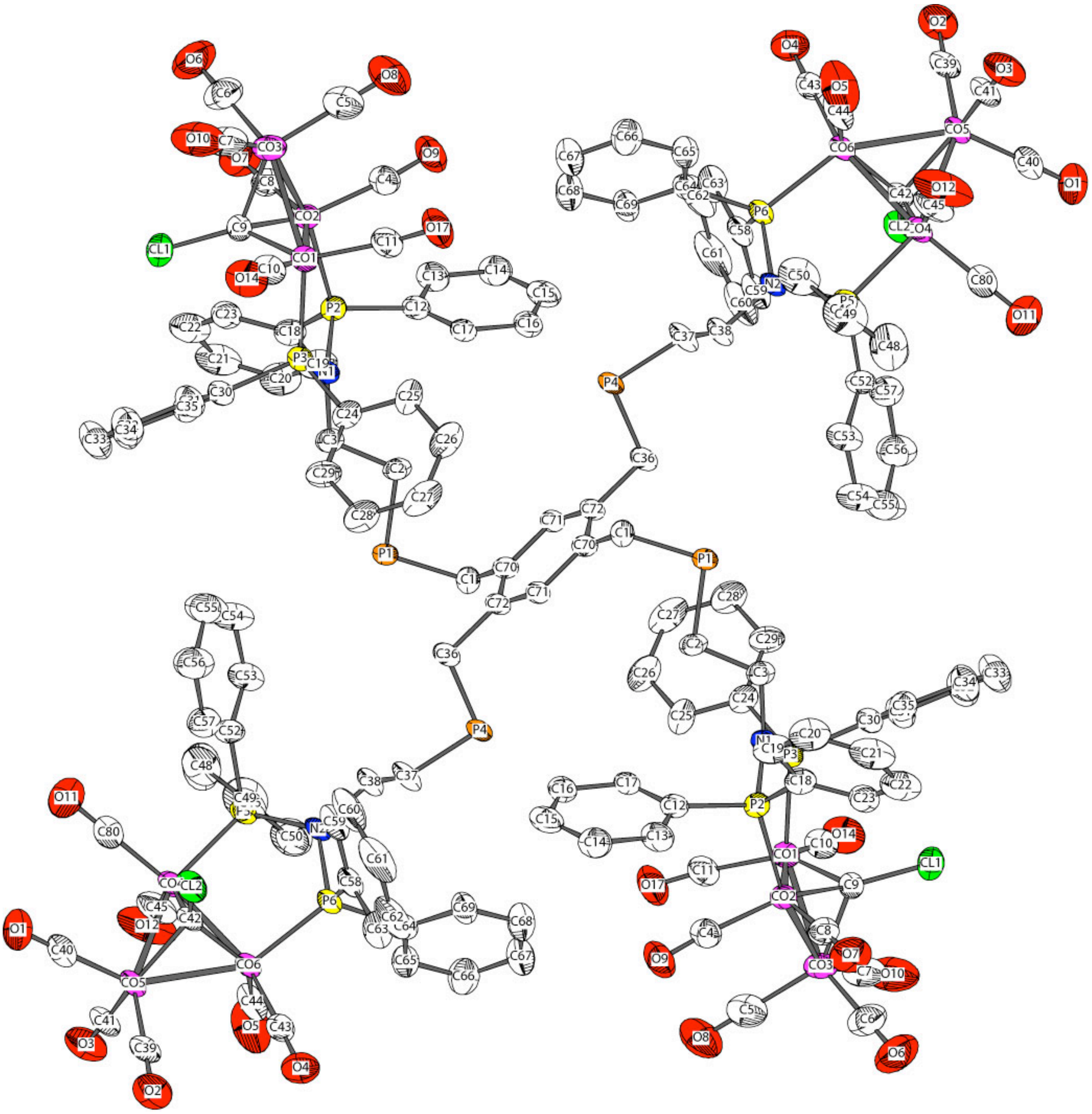

Figure S-1. ORTEP view of the crystal structure of **10** in **10**·4CH_2Cl_2·2C_6H_{14}. Ellipsoids enclose 50% of the electronic density. Symmetry operator for equivalent atoms (’) : -x, -y, -z+1.

Table S-1 : Data collection and refinement details for **10**·$4CH_2Cl_2 \cdot 2C_6H_{14}$

Formula	$C_{146}H_{106}Cl_4Co_{12}N_4O_{28}P_8S_4$, $4(CH_2Cl_2)$, $2(C_6H_{14})$
Formula weight	4101.36
Crystal system	monoclinic
Space group	$P\ 2_1/n$
a (Å)	21.034(5)
b (Å)	19.519(5)
c (Å)	23.247(7)
β (°)	111.493(10)
V (Å^3)	8881(4)
Z	2
Density (g.cm^{-3})	1.502
μ (Mo-Kα) (mm^{-1})	1.424
F(000)	4072
Data collection	
Temperature (K)	173(2)
Theta min - max	1.12 - 29.14
Data set[h, k, l]	-28/28, -26/25, -31/31
Tot., Uniq. Data, R(int)	23877, 14910, 0.0720
Observed data	$> 2\sigma(I)$
Refinement	
Nreflections, Nparameters	23877, 1035
R1, R2	0.0968, 0.1655
wR1, wR2	0.1745, 0.2051
GOF	1.227
Max. and Av. Shift/Error	0.001, 0.000
Min, Max. Resd Dens. (e-.A^{-3})	-0.926, 1.293

Table S-2 : Selected distances (Å) and angles (°) for **10**$\cdot 4CH_2Cl_2\cdot 2C_6H_{14}$

Distances			
Co1—P1	2.1740 (15)	Co4—P3	2.1833 (15)
Co1—Co2	2.4593 (11)	Co4—Co6	2.4420 (11)
Co1—Co3	2.4843 (11)	Co4—Co5	2.4700 (10)
Co2—P2	2.1946 (15)	Co5—Co6	2.4836 (12)
Co2—Co3	2.4715 (11)	Co6—P4	2.1797 (14)
Angles			
C10—Co1—Co2	153.2 (2)	C46—Co4—Co6	153.6 (3)
C11—Co1—Co2	97.05 (19)	C45—Co4—Co6	100.0 (2)
C9—Co1—Co2	49.11 (15)	C42—Co4—Co6	48.96 (16)
P1—Co1—Co2	96.20 (4)	P3—Co4—Co6	94.54 (5)
C10—Co1—Co3	99.36 (19)	C46—Co4—Co5	102.1 (2)
C11—Co1—Co3	98.52 (19)	C45—Co4—Co5	96.36 (18)
C9—Co1—Co3	49.65 (16)	C42—Co4—Co5	49.84 (14)
P1—Co1—Co3	147.73 (5)	P3—Co4—Co5	153.68 (5)
Co2—Co1—Co3	59.99 (3)	Co6—Co4—Co5	60.74 (3)
C8—Co2—Co1	149.76 (19)	C40—Co5—Co4	96.71 (19)
C4—Co2—Co1	104.97 (19)	C39—Co5—Co4	150.35 (18)
C9—Co2—Co1	48.79 (16)	C41—Co5—Co4	96.68 (17)
P2—Co2—Co1	93.83 (4)	C42—Co5—Co4	48.10 (15)
C8—Co2—Co3	100.93 (19)	C40—Co5—Co6	145.17 (19)
C4—Co2—Co3	96.49 (18)	C39—Co5—Co6	94.28 (18)
C9—Co2—Co3	49.87 (16)	C41—Co5—Co6	103.87 (18)
P2—Co2—Co3	153.69 (5)	C42—Co5—Co6	47.92 (16)
Co1—Co2—Co3	60.51 (3)	Co4—Co5—Co6	59.07 (3)
C6—Co3—Co2	97.2 (2)	C43—Co6—Co4	156.10 (18)
C7—Co3—Co2	147.4 (2)	C44—Co6—Co4	94.9 (2)
C5—Co3—Co2	97.2 (2)	C42—Co6—Co4	48.85 (16)
C9—Co3—Co2	48.68 (15)	P4—Co6—Co4	96.55 (5)
C6—Co3—Co1	148.5 (2)	C43—Co6—Co5	99.57 (17)
C7—Co3—Co1	93.4 (2)	C44—Co6—Co5	96.90 (18)
C5—Co3—Co1	101.8 (2)	C42—Co6—Co5	49.54 (14)
C9—Co3—Co1	48.15 (16)	P4—Co6—Co5	147.31 (5)
Co2—Co3—Co1	59.50 (3)	Co4—Co6—Co5	60.19 (3)

Comments on the structure of **11**•2CH_2Cl_2

An ORTEP view of the molecule is shown in Fig. S-2 and selected bond distances and angles are given in Table S-4. In this centrosymmetric molecule, each short-bite dppa-type ligand is attached to a Co_4 cluster and bridges an edge opposite to that spanned by the ancillary dppa ligand. Each tetrahedron attached to ligand **7** contains a cobalt atom bearing two terminal CO ligands, the other three have only one terminal CO and are also bridged by a CO ligand. For symmetry reasons, two clusters have the cobalt atom bearing the terminal CO ligands coordinated by a phosphorus from **7** whereas in the other two, this phosphorus comes from the ancillary dppa ligand. The Co-Co bond distances are in the range 2.40(1) - 2.60(1) Å.

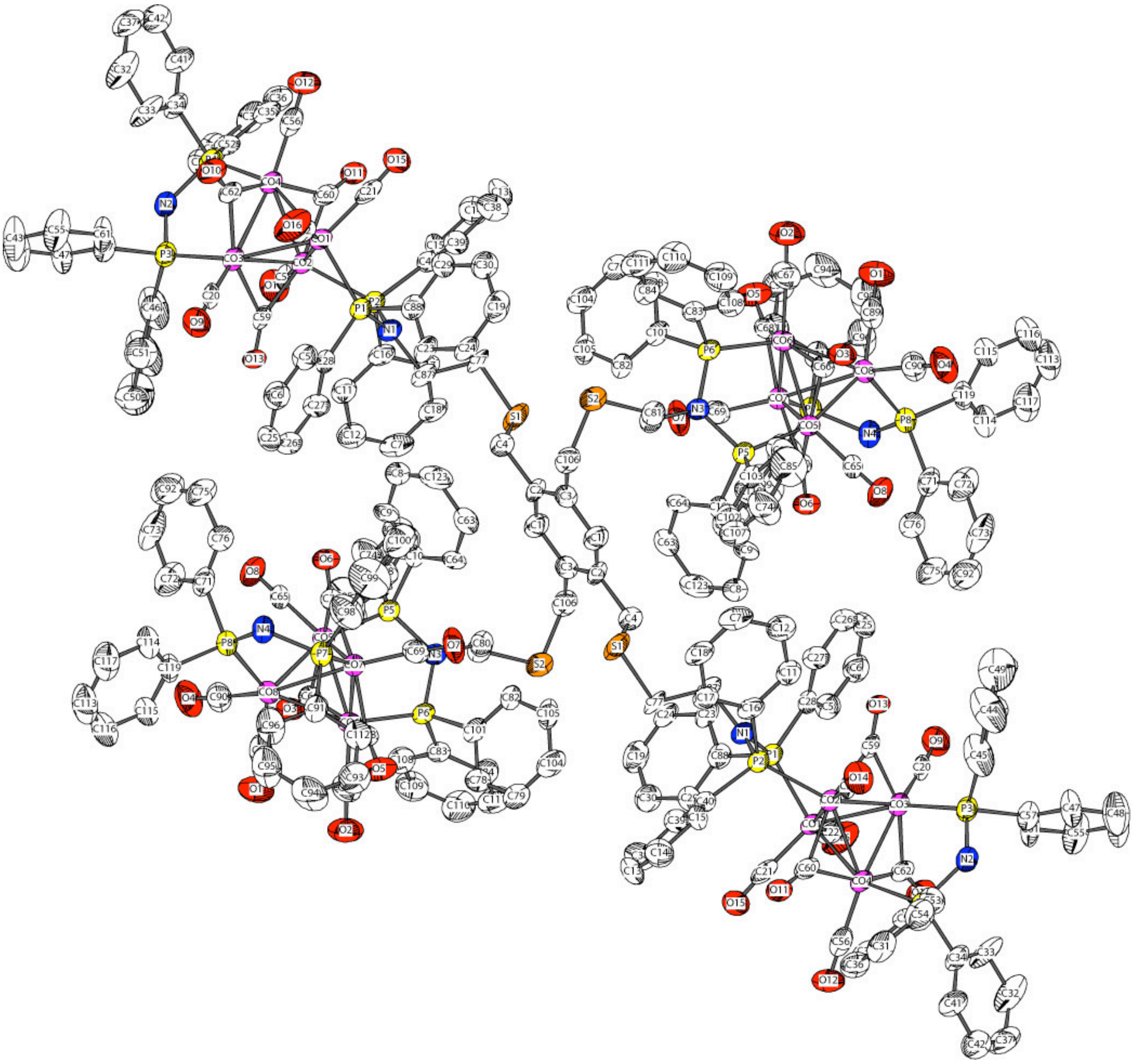

Figure S-2. ORTEP view of the crystal structure of **11**•2CH_2Cl_2. Ellipsoids enclose 50% of the electronic density. Symmetry operator for equivalent atoms (') = -x, -y-1, -z+1

Table S-3 : Data collection and refinement details for **11**•$2CH_2Cl_2$

Formula	$C_{242}H_{186}Co_{16}N_8O_{32}P_{16}S_4$, 2($CH_2Cl_2$)
Formula weight	5454.48
Crystal system	triclinic
Space group	*P* -1
a (Å)	18.7300(4)
b (Å)	19.7900(4)
c (Å)	20.4200(7)
α (°)	98.6200(9)
β (°)	97.8450(9)
γ (°)	116.4261(15)
V ($Å^3$)	6522.7(3)
Z	1
Density ($g.cm^{-3}$)	1.389
μ (Mo-Kα) (mm^{-1})	1.222
F(000)	2770
Data collection	
Temperature (K)	173(2)
Theta min - max	1.04 - 27.42
Data set[h, k, l]	-23/24, -25/25, -22/26
Tot., Uniq. Data, R(int)	29507, 12040, 0.1167
Observed data	>2 $\sigma(I)$
Refinement	
Nreflections, Nparameters	29507, 1486
R1, R2	0.1615, 0.3234
wR1, wR2	0.2633, 0.3302
Goof	1.229
Max. and Av. Shift/Error	0.001, 0.000
Min, Max. Resd Dens. (e-.A^{-3})	-0.896, 1.989

Table S-4 : Selected distances and angles for **11**•2CH_2Cl_2

Distances

Co1—P1	2.198 (4)	Co5—Co7	2.487 (3)
Co2—P2	2.191 (4)	Co5—Co8	2.503 (3)
Co2—Co3	2.479 (3)	Co6—P6	2.183 (4)
Co2—Co4	2.491 (2)	Co6—Co7	2.455 (3)
Co3—P3	2.164 (4)	Co6—Co8	2.563 (3)
Co3—Co4	2.407 (3)	Co7—P7	2.150 (5)
Co4—P4	2.171 (4)	Co7—Co8	2.550 (2)
Co5—P5	2.164 (4)	Co8—P8	2.216 (4)
Co5—Co6	2.401 (2)		

Angles

C22—Co1—Co3	92.8 (5)	C65—Co5—Co6	146.7 (5)
C21—Co1—Co3	142.3 (4)	C70—Co5—Co6	110.9 (4)
P1—Co1—Co3	109.28 (12)	C66—Co5—Co6	50.8 (5)
C22—Co1—Co4	109.9 (5)	P5—Co5—Co6	98.43 (12)
C21—Co1—Co4	85.3 (4)	C65—Co5—Co7	142.0 (5)
P1—Co1—Co4	152.20 (14)	C70—Co5—Co7	50.6 (4)
Co3—Co1—Co4	57.07 (7)	C66—Co5—Co7	109.2 (5)
C22—Co1—Co2	151.2 (5)	P5—Co5—Co7	104.92 (13)
C21—Co1—Co2	105.4 (5)	Co6—Co5—Co7	60.28 (8)
P1—Co1—Co2	93.47 (12)	C65—Co5—Co8	102.5 (4)
Co3—Co1—Co2	58.60 (7)	C70—Co5—Co8	84.4 (4)
Co4—Co1—Co2	58.76 (7)	C66—Co5—Co8	74.5 (5)
C58—Co2—Co3	115.9 (4)	P5—Co5—Co8	160.39 (13)
C59—Co2—Co3	50.7 (4)	Co6—Co5—Co8	62.99 (8)
C60—Co2—Co3	109.3 (5)	Co7—Co5—Co8	61.45 (8)
P2—Co2—Co3	133.38 (14)	C67—Co6—Co5	153.3 (5)
C58—Co2—Co4	115.9 (4)	C66—Co6—Co5	52.3 (4)
C59—Co2—Co4	108.6 (4)	C68—Co6—Co5	111.4 (4)
C60—Co2—Co4	51.3 (5)	P6—Co6—Co5	95.96 (12)
P2—Co2—Co4	135.71 (12)	C67—Co6—Co7	139.1 (5)
Co3—Co2—Co4	57.94 (7)	C66—Co6—Co7	111.9 (4)
C58—Co2—Co1	175.2 (4)	C68—Co6—Co7	49.9 (4)
C59—Co2—Co1	85.9 (4)	P6—Co6—Co7	101.60 (12)
C60—Co2—Co1	83.8 (4)	Co5—Co6—Co7	61.60 (8)
P2—Co2—Co1	88.14 (12)	C67—Co6—Co8	110.2 (5)
Co3—Co2—Co1	59.94 (7)	C66—Co6—Co8	73.6 (4)
Co4—Co2—Co1	60.10 (7)	C68—Co6—Co8	81.8 (4)
C20—Co3—Co4	148.4 (4)	P6—Co6—Co8	154.90 (12)
C62—Co3—Co4	50.5 (5)	Co5—Co6—Co8	60.45 (7)
C59—Co3—Co4	112.2 (4)	Co7—Co6—Co8	61.02 (7)
P3—Co3—Co4	97.80 (13)	C69—Co7—Co6	114.7 (5)
C20—Co3—Co2	137.4 (4)	C68—Co7—Co6	51.3 (5)
C62—Co3—Co2	110.1 (5)	C70—Co7—Co6	108.3 (5)
C59—Co3—Co2	51.0 (4)	P7—Co7—Co6	140.42 (13)
P3—Co3—Co2	105.72 (13)	C69—Co7—Co5	121.8 (5)
Co4—Co3—Co2	61.28 (7)	C68—Co7—Co5	109.3 (5)
C20—Co3—Co1	101.7 (4)	C70—Co7—Co5	50.2 (5)
C62—Co3—Co1	74.3 (4)	P7—Co7—Co5	129.70 (13)

C59—Co3—Co1	87.1 (4)	Co6—Co7—Co5	58.12 (7)
P3—Co3—Co1	158.93 (14)	C69—Co7—Co8	175.2 (4)
Co4—Co3—Co1	61.72 (7)	C68—Co7—Co8	82.9 (4)
Co2—Co3—Co1	61.46 (7)	C70—Co7—Co8	82.9 (4)
C56—Co4—Co3	147.5 (6)	P7—Co7—Co8	88.44 (12)
C62—Co4—Co3	52.3 (4)	Co6—Co7—Co8	61.58 (7)
C60—Co4—Co3	111.4 (4)	Co5—Co7—Co8	59.58 (7)
P4—Co4—Co3	96.57 (13)	C89—Co8—Co5	147.0 (5)
C56—Co4—Co2	141.4 (5)	C90—Co8—Co5	95.1 (5)
C62—Co4—Co2	111.3 (4)	P8—Co8—Co5	107.47 (13)
C60—Co4—Co2	50.6 (4)	C89—Co8—Co7	102.1 (5)
P4—Co4—Co2	105.44 (13)	C90—Co8—Co7	154.0 (5)
Co3—Co4—Co2	60.78 (7)	P8—Co8—Co7	94.33 (12)
C56—Co4—Co1	104.6 (5)	Co5—Co8—Co7	58.97 (7)
C62—Co4—Co1	74.7 (4)	C89—Co8—Co6	90.7 (5)
C60—Co4—Co1	84.1 (4)	C90—Co8—Co6	108.2 (5)
P4—Co4—Co1	157.32 (13)	P8—Co8—Co6	151.43 (13)
Co3—Co4—Co1	61.22 (7)	Co5—Co8—Co6	56.56 (7)
Co2—Co4—Co1	61.13 (7)	Co7—Co8—Co6	57.40 (7)

References

1 H. C. Clark and L. E. Manzer, *J. Organomet. Chem.*, 1973, **59**, 411.

2 P. Comba, J. Ensling, P. Gütlich, A. Kühner, A. Peters and H. Pritzkow, *Inorg. Chem.*, 1999, **38**, 3316.

3 K. G. Gaw, M. B. Smith and J. W. Steed, *J. Organomet. Chem.*, 2002, **664**, 294.

4 J. T. Mague and S. E. Dessens, *J. Organomet. Chem.*, 1984, **262**, 347.

5 P. Braunstein, H.-P. Kormann, W. Meyer-Zaika, R. Pugin and G. Schmid, *Chem. Eur. J.*, 2000, **6**, 4637.

6 Bruker-Nonius, Kappa CCD Reference Manual, Nonius BV, The Netherlands, 1998.

7 G. M. Sheldrick, *SHELXL-97*, *Program for crystal structure refinement*; University of Göttingen: Germany, **1997**.