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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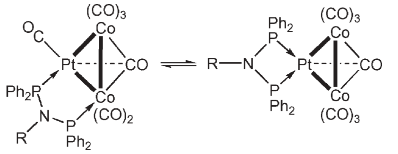
A polypodal ligand based on an aromatic ring decorated by four dppa-type diphosphine moieties has been used to prepare Pt(II) complexes and to assemble four tricobalt or tetracobalt carbonyl clusters, leading to centrosymmetric Co_{12} and Co_{16} «clusters of clusters» which were characterized by X-ray diffraction.

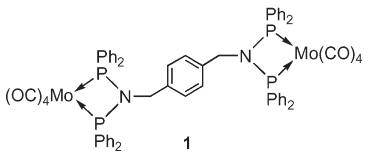
Short-bite ligands, *i.e.* which contain a single atom as spacer between the donor atoms, continue to attract much attention in fundamental and applied coordination chemistry and are particularly useful as assembling ligands in di- and polynuclear chemistry, including cluster chemistry.[1] Such bidentate ligands can coordinate to metal centres in monodentate, chelating or bridging modes and relatively minor changes in the ligand substituents or in the coligands may alter their bonding modes or, alternatively, render their interconversions energetically readily accessible. A recent example is shown in eqn (1) where relatively bulky *N*-substituents result in a higher chelating power of the PNP ligand owing to entropic factors, thus making the energy of the chelate form comparable with that of the bridged form.[2]



(1)

Whereas $Ph_2PCH_2PPh_2$ (dppm) has been used for decades,[1] the analogous ligand $Ph_2PNHPPh_2$ (dppa) has been less exploited, although recent results have demonstrated its remarkable properties, and those of its *N*-substituted derivatives, in the chromium catalyzed selective trimerization or tetramerization of ethylene.[3] We have described the first dppa-bridged heterometallic complexes and prepared and characterized, using X-ray diffraction, a number of homo- and heterometallic complexes and clusters with this and related ligands,[4] and examined the catalytic properties of some of the Fe-Pd complexes for the dehydrogenative coupling of stannanes.[5] *N*-Functionalization of dppa, which is easier than that of dppm owing to the enhanced acidity of the NH proton, allows the synthesis of alkoxysilyl derivatives for the anchoring of clusters into mesoporous alumina or silica supports and the subsequent formation of highly dispersed metallic nanoparticles confined in the matrix.[6,7]

More complex structures containing interconnected metal centres or clusters each bonded to a dppa-type donor set could be attractive targets in order to examine the possible occurrence of cooperative effects and to generate new steric environments that are susceptible to change of the properties associated with only one of the metal centres or clusters. Furthermore, molecular clusters organised around an organic core could form nano-objects with novel properties and applications.[8] We thus turned our attention to multidentate bis(diphenylphosphanyl)amine systems, such as the structurally characterized complexes **1**[9] and **2**.[10]



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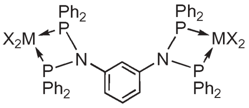
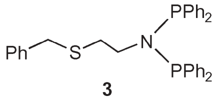


$MX_2 = NiBr_2, PdCl_2$
2

Our aim was to extend this type of arrangement to a ligand core decorated with four $–N(PPh_2)_2$ donors and form metal-richer molecules. Furthermore, introduction of sulfur in the spacer could allow subsequent deposition of the molecule on a Au surface and selective formation of metallic monolayers.

A thioether function has been recently introduced in dppa-type ligands (see **3** and **4**) and the Pt(II) complex **5** and Co_2Pt cluster **6** have been structurally characterized.[2] Our attention was therefore attracted by ligand **7**[9] and we describe here its first cluster derivatives **9**–**12**.



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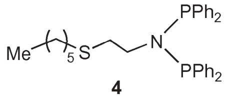

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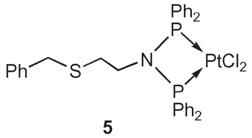

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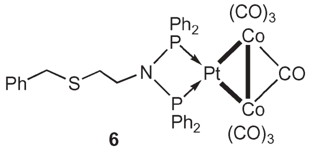

6

We first set out to coordinate $PtCl_2$ moieties to **7** in order to react them subsequently with $[Co(CO)_4]^-$ and form four Co_2Pt clusters by extension of the procedure used to obtain **6** from **5**.[2]

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† Electronic supplementary information (ESI) available: Detailed experimental data and ORTEP plots for **10** and **11**. See DOI: 10.1039/b713540h

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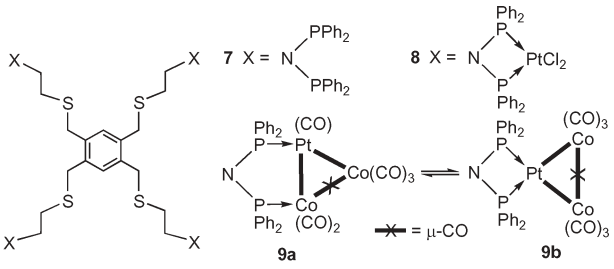
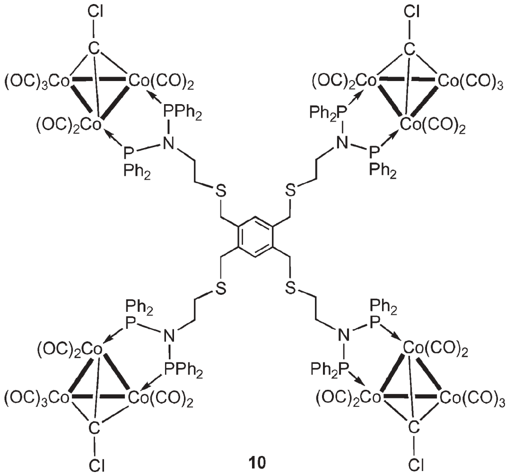


Reaction of **7** with [$PtCl_2$(cod)] (cod = 1,4-cyclooctadiene) (4 equiv.) in CH_2Cl_2 resulted in complete consumption of the ligand and rapid precipitation of a white solid whose poor solubility in common organic solvents (THF, CH_2Cl_2 or acetone) prevented characterization by NMR spectroscopy. However, when a DMF solution of **7** was added dropwise over 1 h to a stirred DMF solution of [$PtCl_2$(cod)] and the reaction mixture further stirred for 1 h, a white solid was obtained after work-up.† It was characterized in the $^{31}P\{^1H\}$ NMR spectrum by a singlet at δ 17.3 with satellites ($^1J_{P-Pt}$ = 3298 Hz) and in the $^{195}Pt\{^1H\}$ NMR spectrum by a triplet at δ −4028 ($^1J_{P-Pt}$ = 3298 Hz). These data, together with the ν(Pt–Cl) IR absorptions at 309 and 292 cm^{-1}, are consistent with the formulation shown for **8**. The insoluble species obtained by the former procedure (and during many other attempts) are likely to be polymeric and ionic species (bis-chelation at Pt with displacement of the chloride ligands often results when ligand addition is not slow enough).[2]

Reaction of **8** with 8 equiv. of Na[Co(CO)$_4$] in CH_2Cl_2 at room temp. for 3 h afforded after work-up a brown solid whose spectroscopic data are consistent with species **9**. Its $^{31}P\{^1H\}$ NMR spectrum contains a broad signal at δ 100.0 for the Co-bound P nucleus, and a doublet with ^{195}Pt satellites at δ 71.0 (J_{P-P} = 23 Hz, $^1J_{P-Pt}$ = 3629 Hz) and a singlet with ^{195}Pt satellites at δ 56.0 ($^1J_{P-Pt}$ = 3010 Hz) for the Pt-bound P in the bridged (**a**) and chelate forms (**b**), respectively. Accordingly, the $^{195}Pt\{^1H\}$ NMR spectrum contains a broad doublet at δ −4129 ($^1J_{P-Pt}$ = 3629 Hz) and a triplet at δ −4330 ($^1J_{P-Pt}$ = 3010 Hz) for isomers **a** and **b**, respectively. Very strong IR absorptions at 2054, 2010, 1966, 1756 cm^{-1} indicate the presence of terminal and bridging CO groups.†

As an alternative to building the clusters stepwise, we then used [$Co_3(\mu_3$-CCl)(CO)$_9$] as a precursor, anticipating its stabilization by the short-bite ligand moieties of **7**.[11] A high yield reaction in toluene yielded, after recrystallization/precipitation from CH_2Cl_2–toluene–hexane, a fine red powder. Recrystallization from toluene–MeOH–hexane afforded crystals suitable for X-ray diffraction.† Product **10** is characterized by a $^{31}P\{^1H\}$ NMR singlet at δ 109 and IR absorptions indicating the presence of only terminal CO ligands.† An X-ray diffraction study established its centrosymmetric structure (Fig. 1) with each short-bite site of ligand **7** bridging an edge of a Co_3 triangle to form a molecule with four Co_3 branches.¶ A related topology has been recently described with a polyalkynylalkene core.[12]



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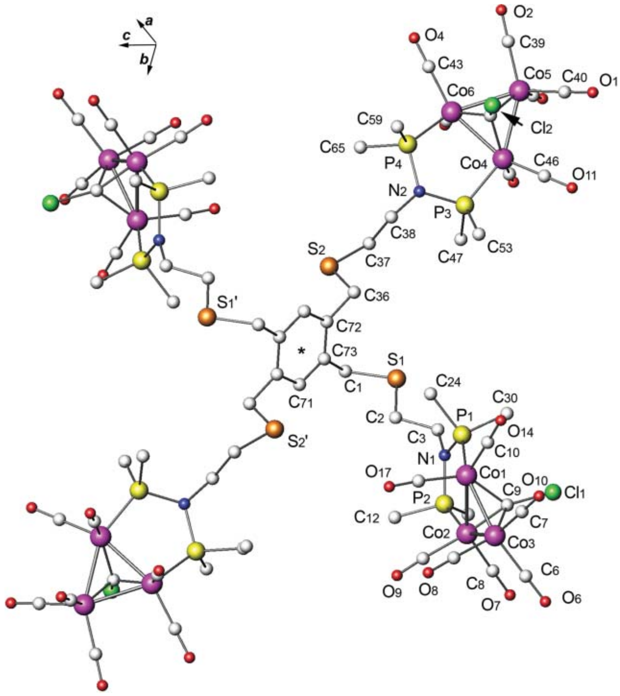
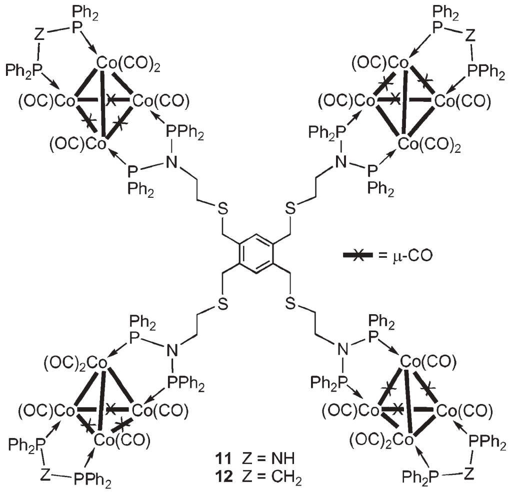


Fig. 1 View of the molecular structure of **10** in **10**·4CH_2Cl_2·2C_6H_{14}. Symmetry operator for equivalent atoms ($'$): $-x$, $-y$, $-z + 1$. For clarity, only the P-phenyl *ipso* carbons are represented.

To expand the scope of this approach, we then turned to tetracobalt carbonyl clusters which appeared promising since derivatives of [$Co_4(CO)_{12}$] with dppa and its alkoxysilyl derivatives have been characterized, anchored inside nanoporous alumina membranes,[6] and used for the synthesis of Co_2P nanoparticles within a SBA-15 matrix.[7] Such phosphides are of considerable interest for their electronic, magnetic and catalytic properties.[13] The reaction of [$Co_4(CO)_{12}$] with **7** afforded a deep-green, poorly soluble compound which could only be analyzed by IR† and could correspond to a polymeric material because of the possibility for dppa-type units from different molecules of **7** to span two edges of Co_4 tetrahedra. We found earlier that short-bite ligand cluster stabilization is achieved in [$Co_4(CO)_{10}(\mu$-dppx)] (x = a or m) compared to [$Co_4(CO)_{12}$] and allows a more selective substitution chemistry.[14] Thus, in the reaction product of [$Co_4(CO)_{10}(\mu$-dppa)] with another dppa-type ligand, two opposite Co–Co edges of the tetrahedron are selectively spanned.[6,14] Therefore, **7** was reacted with [$Co_4(CO)_{10}(\mu$-dppx)] and purification by column chromatography afforded four fractions.† The third, major fraction was the desired product but we have not been able to assign all the broad resonances in the $^{31}P\{^1H\}$ NMR spectrum (Co quadrupolar broadening). Its colour is consistent with tetrahedral tetracobalt carbonyl clusters substituted by two short-bite ligands, as shown in **11** and **12**.†



11 Z = NH
12 Z = CH_2

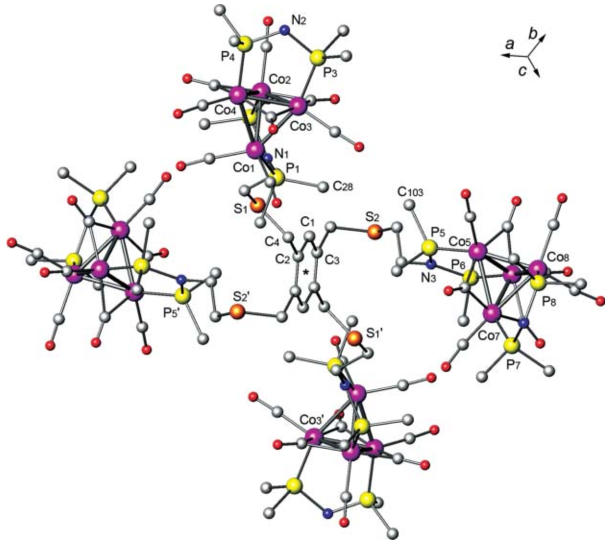


Fig. 2 View of the molecular structure of **11** in **11**·$2CH_2Cl_2$. Symmetry operator for equivalent atoms ('): $-x$, $-y - 1$, $-z + 1$. For clarity, only the P-phenyl *ipso* carbons are represented.

The crystal structure of **11**·$2CH_2Cl_2$¶ established that four Co_4 clusters have indeed been branched around the organic core (Fig. 2). As anticipated, the ancillary dppa ligand has prevented further, uncontrolled CO substitution and played the role of a stopper.

Future objectives are to deposit such dendrimer-like nano-objects on surfaces,[15] prepare metal particles and compare their physical properties with those of nanoparticles obtained from the isolated tetrahedral carbonyl clusters.[16]

In conclusion, we have reported a stepwise strategy to assemble dendrimer-like Co_{12} and Co_{16} metal clusters around a polypodal ligand. To the best of our knowledge, **11** is the largest molecule of its kind to have been characterized by X-ray diffraction. Clusters **10** and **11** form disk-like molecules with a thickness of *ca.* 11 Å and a diameter of *ca.* 23 and 30 Å, respectively.

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¶ CCDC 659619 and 659620. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b713540h

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