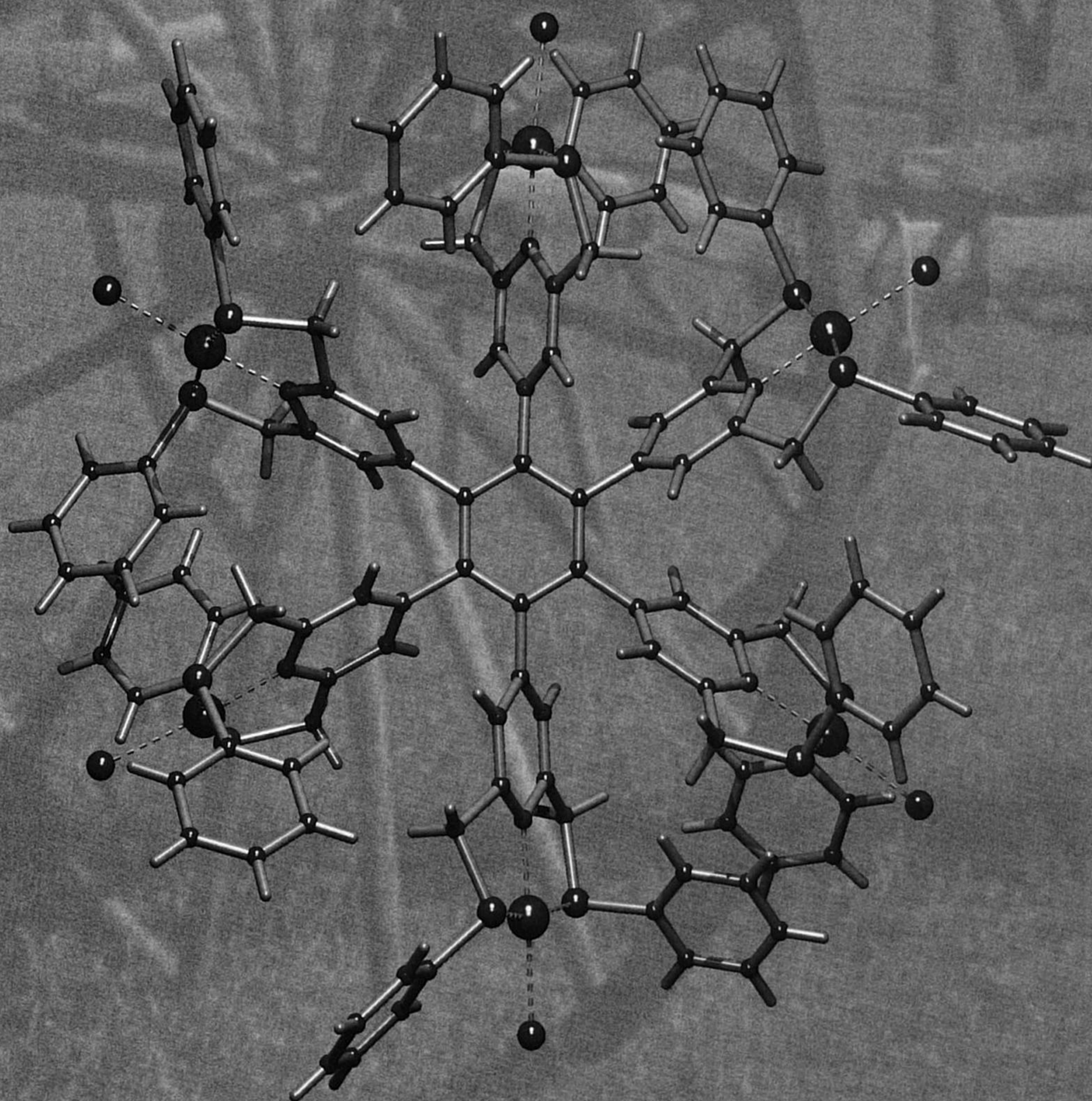


This cartwheel hexaorganopalladium catalyst has a rigid arrangement of catalytic sites. Its nanosize dimension (Pd-Pd distance 15.340(2) Å, diametrically) is of interest for its separation from product solutions by nanofiltration.



More details are given on the following pages.

# Design of Novel Hexametallic Cartwheel Molecules from Persubstituted Benzene Compounds\*\*

Harm P. Dijkstra, Pablo Steenwinkel, David M. Grove, Martin Lutz, Anthony L. Spek, and Gerard van Koten\*

In the field of homogeneous catalysis there is currently much interest in the application of tailored/engineered organic materials as soluble support materials for anchored catalytically active metal complexes.<sup>[1]</sup> Such organic materials often have a periphery bearing multidentate ligands or ligand precursors and are usually designed so that the resulting multimetallic systems can easily be removed after catalysis from the product-containing solution for reuse. A classic example of such a system is a dodecanickel carbosilane dendrimer<sup>[2]</sup> that, having twelve independent catalytic sites and a molecular weight of 7032 Dalton, has shown itself to be suitable for separation by nanomembrane filtration techniques.<sup>[3]</sup>

We propose that a high degree of rigidity in the central core is probably advisable for optimal retention of nano-sized molecules by nanomembrane filters. It is clear that metalated carbosilane dendrimers are rather flexible materials and we believe that better spatial organization and rigidity in a membrane-separable material might be achieved through derivatization of an arene nucleus.

Herein we present such an alternative approach to multimetallic materials using persubstituted benzene compounds  $C_6[3,5-(CH_2Y)_2C_6H_3]_6$  ( $Y = NMe_2$ ,  $P(O)Ph_2$ ,  $PPh_2$ ,  $SPh$ ), which are available in high yield from the dodecabromide  $C_6[3,5-(CH_2Br)_2C_6H_3]_6$ . An X-ray crystal structure determination of the hexametallic  $Pd^{II}$  species  $[C_6\{3,5-(CH_2SPh)_2\}_6C_6H_2-4-(PdCl)]$  (**7**) emphasizes the interesting spatial arrangements that these six-spoked cartwheel-type molecules afford.

A crucial aspect in the preparation of multimetallic materials is the sequence in which the metals and appropriate organic functionalities are introduced into the system. To minimize the risk of destroying organometallic units, one of the best approaches is to prepare the organic core, as far as possible, prior to the metalation procedures, that is, the metal

centers are introduced in the last step to give the multimetallic species.<sup>[2, 4]</sup> An alternative strategy to multimetallic materials is to anchor an appropriately functionalized monometalated ligand to a substrate.<sup>[5]</sup>

In the current investigation, the former synthetic strategy is applied to the synthesis of the hexasubstituted benzenes  $C_6[3,5-(CH_2Y)_2C_6H_3]_6$  (**3**:  $Y = NMe_2$ ; **4**:  $Y = P(O)Ph_2$ ; **5**:  $Y = PPh_2$ ; **6**:  $Y = SPh$ ) and in a final step (cyclo)metalation affords multimetallic species in which each of the six peripheral ligand systems is coordinated in a tridentate monoanionic  $Y,C,Y'$  fashion to a metal center (Scheme 1). The starting compound for the hexasubstituted benzenes **3–6** is **2**. We have developed a simplified synthetic procedure for multi-gram amounts of this compound starting from 3,5-dimethylaniline (**1**).<sup>[6a]</sup> The synthetic route to the desired compounds  $[C_6\{3,5-(CH_2Y)_2C_6H_3\}_6]$  (**3–6**)<sup>[7]</sup> from the dodecabromide **2** is a fairly general one. It is therefore also suitable for the synthesis of the known dodecathioether ( $Y = CH_2S(4-MeC_6H_4)$ ) prepared by Duchêne and Vögtle,<sup>[6b]</sup> and in general for compounds with twelve  $CH_2SR$ ,  $CH_2NR_2$ , or  $CH_2PR_2$  groups.

The desired dodecamine **3**, which is obtained by direct nucleophilic amination of **2** with  $HNMe_2$ , can be purified by crystallization of the corresponding  $HBf_4$  salt  $[C_6\{3,5-(CH_2N(H)Me_2)_2C_6H_3\}_6](BF_4)_{12}$  from  $H_2O/MeOH$  (1/2) and subsequent neutralization with aqueous  $NaOH$ .

A modification of a two-step procedure recently reported by us for the synthesis of the tetraphosphane 1,2,4,5- $(CH_2PPh_2)_4C_6H_2$  was used for the synthesis of the dodecaphosphane **5**.<sup>[8]</sup> In the first step, reaction of **2** with  $Ph_2POEt$  in xylenes (Arbuzov reaction conditions) affords the dodecaphosphane oxide **4**, in 87% yield. In the second step **4** is reduced with  $HSiCl_3$  to the corresponding dodecaphosphane **5**, which can be obtained in good yield as a white air-sensitive solid.

The reaction of **2** with thiophenol under basic conditions (DMF in the presence of  $K_2CO_3$ ) gives the corresponding dodecasulfide **6**, which is obtained in 83% yield as analytically pure off-white crystals.

To show the potential of **3–6** to function as multiligand precursors for transition metal ions we have examined the direct electrophilic palladation of dodecasulfide **6** with excess  $[Pd(NCMe)_4](BF_4)_2$  in refluxing  $MeCN$  (Scheme 1, reaction e). This reaction yields the ionic complex  $[C_6\{3,5-(CH_2SPh)_2C_6H_2[Pd(NCMe)]\}_6](BF_4)_6$  (**8**), in 90% yield as a pale-yellow solid. Complex **8** is readily converted, by addition of excess  $Bu_4NCl$  in  $MeCN$ , into the neutral hexapalladium(II) complex  $[C_6\{3,5-(CH_2SPh)_2C_6H_2(PdCl)\}_6]$  (**7**), which was isolated in quantitative yield as a yellow solid.<sup>[9]</sup>

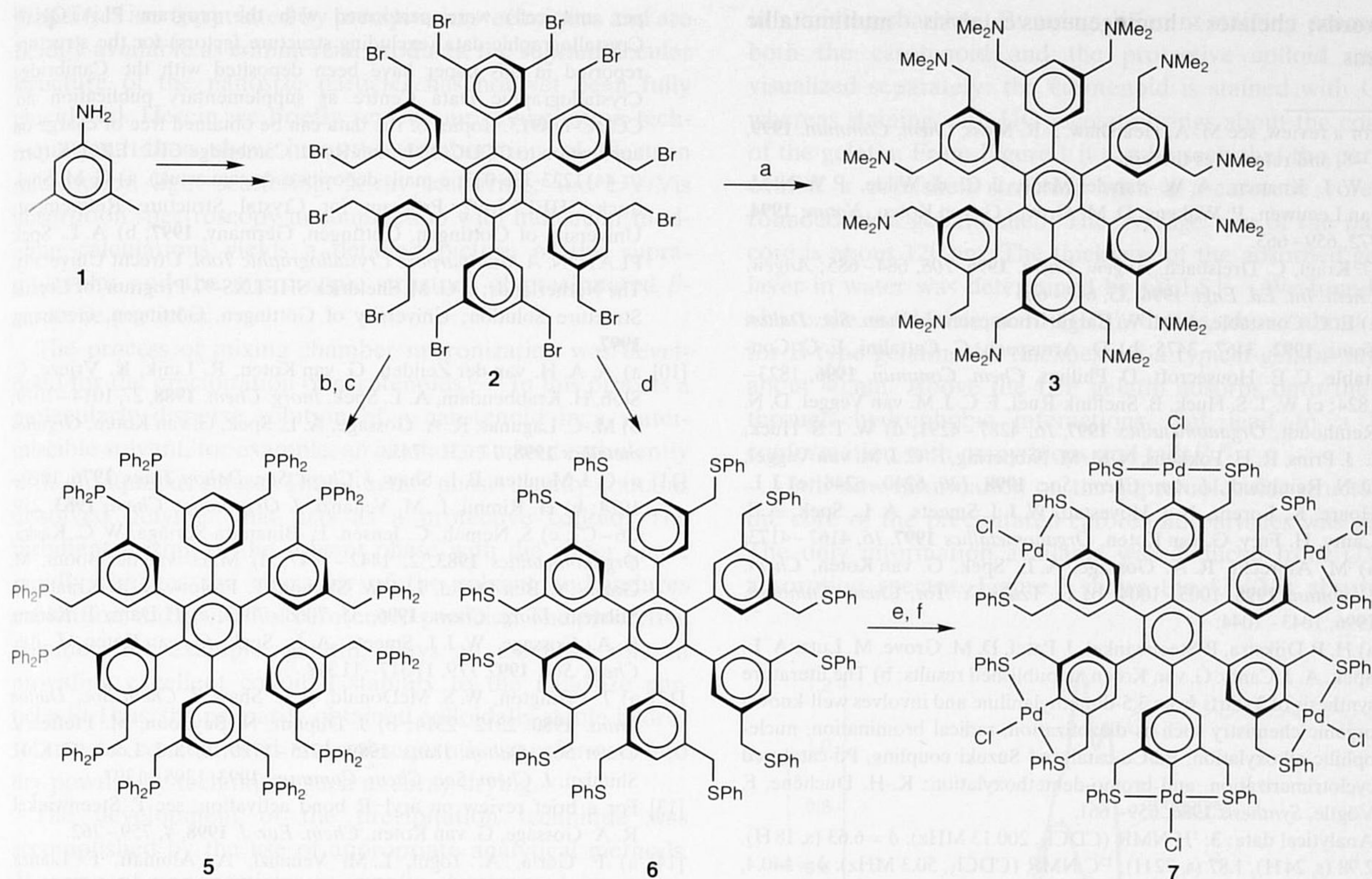
The molecular geometry of **7** shows a central benzene ring substituted with six diorganosulfide moieties each of which is cyclopalladated at the position between the  $CH_2SPh$  group (Figure 1). This affords square planar  $Pd^{II}$  centers with ligand environment that comprises tridentate  $S,C,S'$  coordination by the organic moiety with a chloro ligand *trans* to the metal-bonded aromatic carbon atom. An interesting aspect of the molecular structure of **7** is that there are three molecules in the unit cell; in each molecule all six  $Pd^{II}$  coordination centers adopt the same relative orientation with respect to the

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Scheme 1. Synthetic route to the new hexasubstituted benzenes **3–6**, and the hexapalladium(II) complex **7**, starting from 3,5-dimethylaniline (**1**). Conditions: a) HNMe<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, RT, 18 h; b) Ph<sub>2</sub>POEt, xylenes, 140 °C, 3 h; c) HSiCl<sub>3</sub>, 1,2-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>, 140 °C, 1 h; d) PhSH, K<sub>2</sub>CO<sub>3</sub>, DMF, 50 °C, 15 h; e) [Pd(NCMe)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub>, MeCN, reflux, 5 h; f) Bu<sub>4</sub>NCl, MeCN, RT, 30 min.

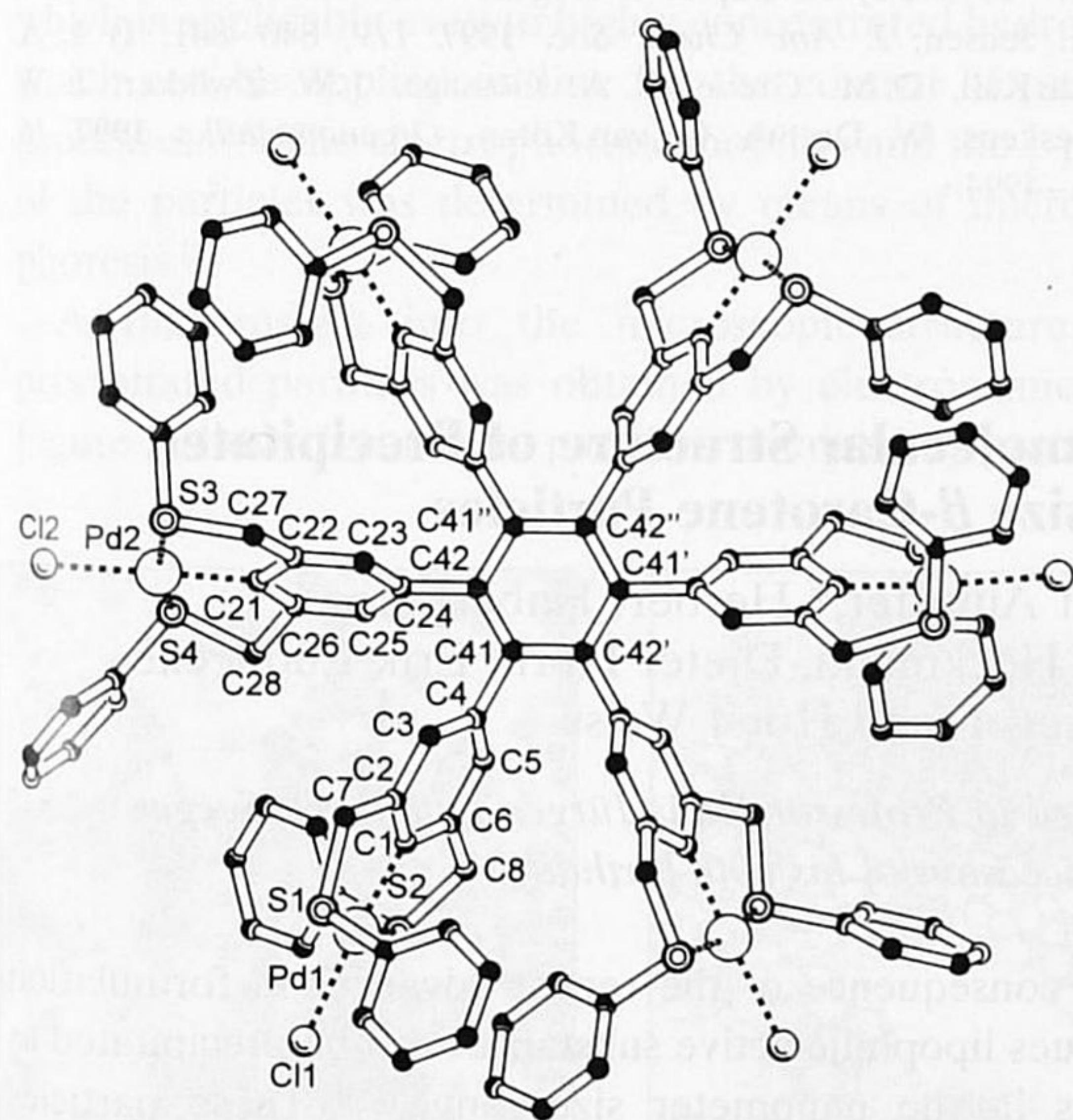


Figure 1. Molecular structure of **7**. Hydrogen atoms and solvent molecules are omitted for clarity. Only one conformation of the disordered SPh groups is shown. Selected bond lengths [Å], angles [°], and torsion angles [°]: Pd1–C1 1.978(12), Pd1–S2 2.283(3), Pd1–S1 2.300(4), Pd1–Cl1 2.403(4), Pd2–C21 1.964(11), Pd2–S4 2.277(4), Pd2–S3 2.285(4), Pd2–Cl2 2.367(4); C1–Pd1–S2 85.5(4), C1–Pd1–S1 84.5(4), S2–Pd1–S1 169.96(14), C1–Pd1–Cl1 175.9(4), S2–Pd1–Cl1 91.61(13), S1–Pd1–Cl1 98.42(15), C21–Pd2–S4 84.5(4), C21–Pd2–S3 85.8(4), S4–Pd2–S3 167.69(12), C21–Pd2–Cl2 176.5(5), S4–Pd2–Cl2 7.66(18), S3–Pd2–Cl2 92.41(18); C25–C24–C42–C41 –67(2), C23–C24–C42–C41 113.5(15), C5–C4–C41–C42' –63.5(16), C3–C4–C41–C42' 120.6(14). (Symmetry operations: single prime centers:  $-x+y, -x+1, z$ ; double prime centers:  $-y+1, x-y+1, z$ ).

central C6 ring (twist angle 63.5–67°) resulting in a chiral propellerlike structure with a  $C_3$  symmetry.

The spatial arrangement of the metal atoms in **7** leads to adjacent radial Pd–Pd separations of 7.339(2) and 8.006(2) Å and a diametrically opposed Pd–Pd separation of 15.340(2) Å. Although this molecule has a fairly low molecular weight of 2846 Dalton its six-spoked cartwheel structure gives it true nano-particle size dimensions and thus appropriate properties for retainment by nano (membrane) filtration materials.<sup>[3]</sup>

The facile synthesis of the cyclometalated complexes **7** and **8**, together with earlier work on metal systems with tridentate  $N,C,N'$ ,<sup>[10]</sup>  $P,C,P'$ ,<sup>[11]</sup> and  $S,C,S'$ <sup>[12]</sup> ligand coordination<sup>[13]</sup> indicates that compounds **3–6** are suitable ligand precursors for the preparation of multimetallic systems. These studies are currently in progress but from the present results it is already clear that the versatility of our approach should provide access to a vast range of multimetallic species characterized by a central rigid, and rather inert, aromatic hydrocarbon skeleton.

In recent years related mononuclear metal complexes with tridentate  $N,C,N'$ - and  $P,C,P'$ -bonded ligand systems have shown activity in a number of catalytic processes.<sup>[14]</sup> The extension and development of new multimetallic systems, such as those described in this paper, to provide other nano-sized soluble catalytic cartwheels, seems to be an area with great potential.

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## Supramolecular Structure of Precipitated Nanosize $\beta$ -Carotene Particles

Helmut Auweter,\* Herbert Haberkorn, Walter Heckmann, Dieter Horn, Erik Lüddecke, Jens Rieger, and Horst Weiss

*Dedicated to Professor Hans-Jürgen Quadbeck-Seeger on the occasion of his 60th birthday*

As a consequence of the recent advances in formulation techniques lipophilic active substances can be precipitated as particles in the nanometer size range.<sup>[1–4]</sup> These particles exhibit superior properties with respect to bioavailability, dispersibility in water, and color than previous larger particles. Although several carotenoids that display these desirable

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