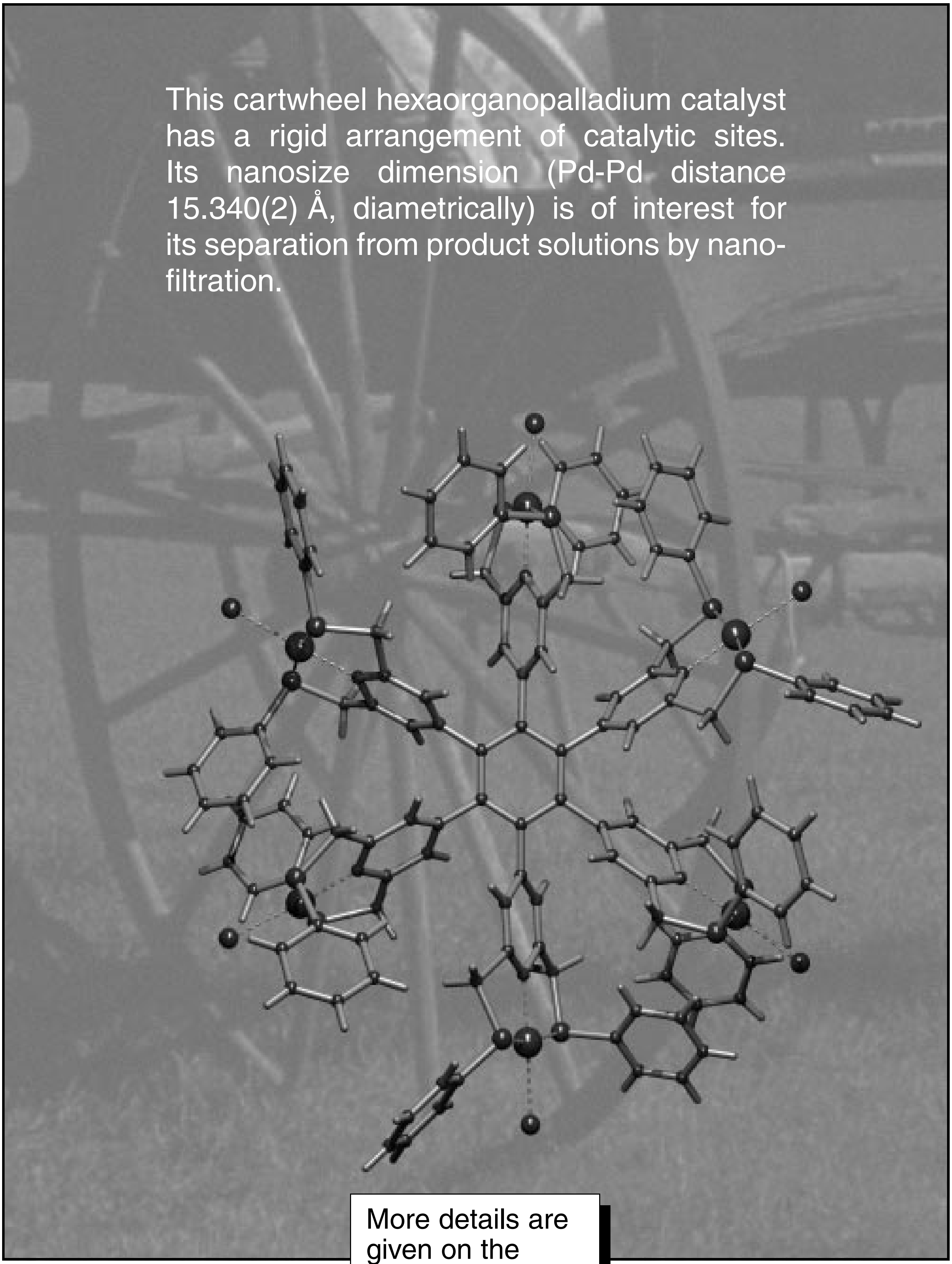

This cartwheel hexaorganopalladium catalyst has a rigid arrangement of catalytic sites. Its nanosize dimension (Pd-Pd distance 15.340(2) Å, diametrically) is of interest for its separation from product solutions by nanofiltration.

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.[1] 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[2] 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.[3]

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 $C_6[3,5\text{-}(CH_2Y)_2C_6H_3]_6$ ($Y = NMe_2$, $P(O)Ph_2$, PPh_2, SPh), which are available in high yield from the dodecabromide $C_6[3,5\text{-}(CH_2Br)_2C_6H_3]_6$. An X-ray crystal structure determination of the hexametallic Pd^{II} species $[C_6\{3,5\text{-}(CH_2SPh)_2\}_6C_6H_2\text{-}4\text{-}(PdCl)]$ (**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.[2, 4] An alternative strategy to multimetallic materials is to anchor an appropriately functionalized monometalated ligand to a substrate.[5]

In the current investigation, the former synthetic strategy is applied to the synthesis of the hexasubstituted benzenes $C_6[3,5\text{-}(CH_2Y)_2C_6H_3]_6$ (**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 multigram amounts of this compound starting from 3,5-dimethylaniline (**1**).[6a] The synthetic route to the desired compounds $[C_6\{3,5\text{-}(CH_2Y)_2C_6H_3\}_6]$ (**3**–**6**)[7] from the dodecabromide **2** is a fairly general one. It is therefore also suitable for the synthesis of the known dodecathioether ($Y = CH_2S(4\text{-}MeC_6H_4)$) prepared by Duchêne and Vögtle,[6b] 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 $[C_6\{3,5\text{-}(CH_2N(H)Me_2)_2C_6H_3\}_6](BF_4)_{12}$ 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**.[8] In the first step, reaction of **2** with Ph_2POEt in xylenes (Arbuzov reaction conditions) affords the dodeca(phosphane 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 $[C_6\{3,5\text{-}(CH_2SPh)_2C_6H_2[Pd(NCMe)]\}_6](BF_4)_6$ (**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 $[C_6\{3,5\text{-}(CH_2SPh)_2C_6H_2(PdCl)\}_6]$ (**7**), which was isolated in quantitative yield as a yellow solid.[9]

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 groups (Figure 1). This affords square planar Pd^{II} centers with a 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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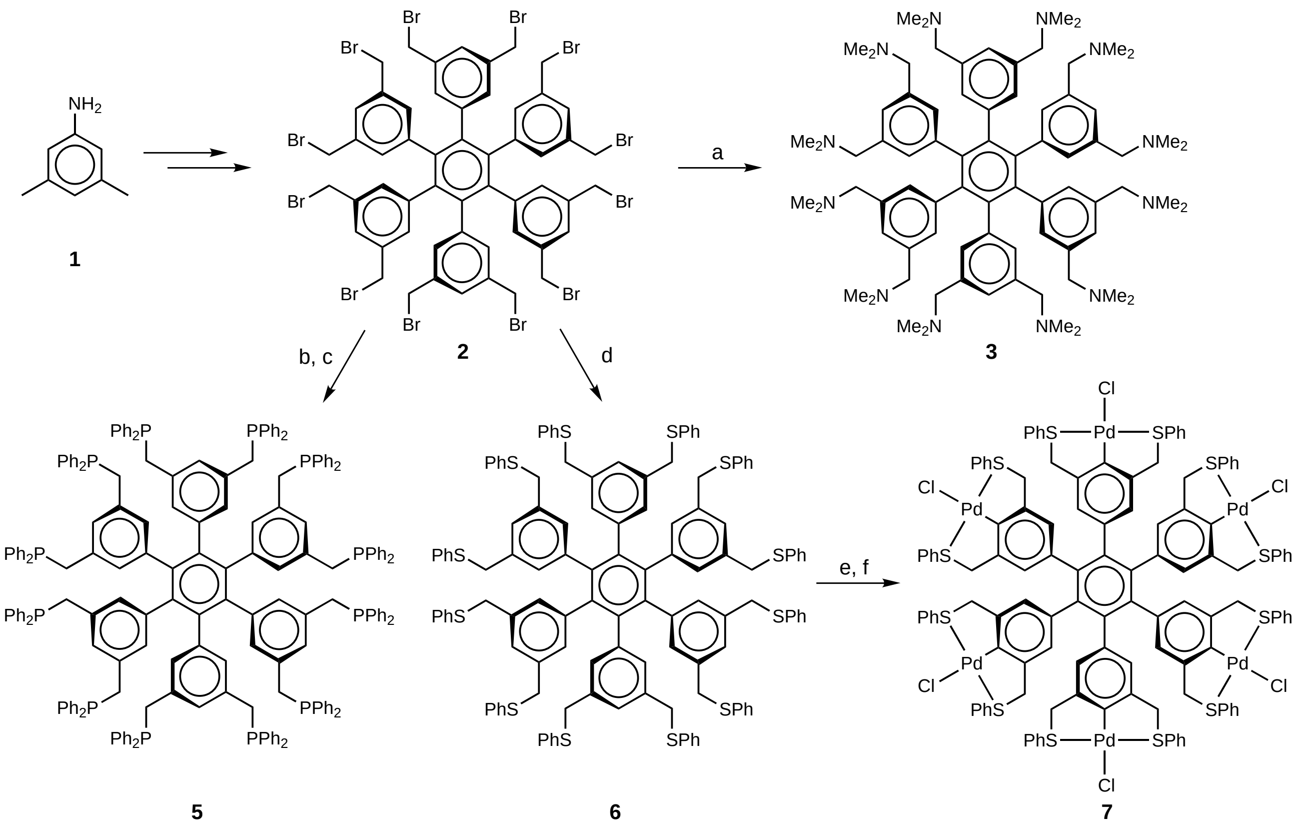

Scheme 1. Synthetic route to the new hexasubstituted benzenes **3**–**6**, and the hexapalladium(II) complex **7**, starting from 3,5-dimethylaniline (**1**). Conditions: a) HNMe$_2$, CH$_2$Cl$_2$, RT, 18 h; b) Ph$_2$POEt, xylenes, 140 °C, 3 h; c) HSiCl$_3$, 1,2-C$_6$H$_4$Cl$_2$, 140 °C, 1 h; d) PhSH, K$_2$CO$_3$, DMF, 50 °C, 15 h; e) [Pd(NCMe)$_4$](BF$_4$)$_2$, MeCN, reflux, 5 h; f) Bu$_4$NCl, MeCN, RT, 30 min.

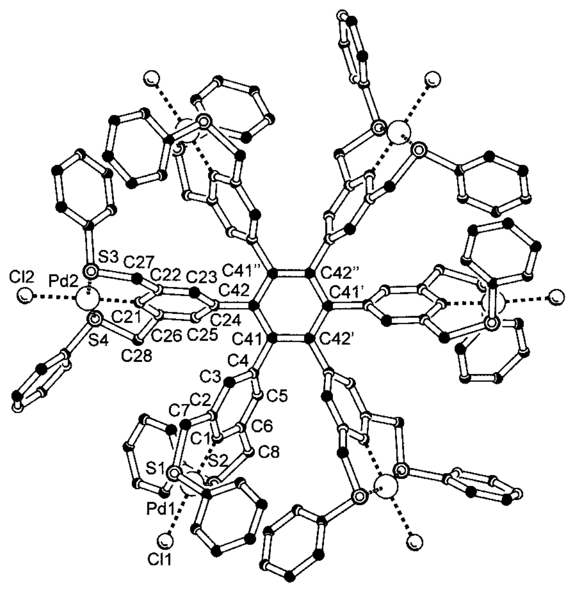

Figure 1. Molecular structure of **7**. Hydrogen atoms and solvent molecules are omitted for clarity. Only one conformation of the disordered SPh groups is shown. Selected bond lengths [Å], angles [°], and torsion angles [°]: Pd1–C1 1.978(12), Pd1–S2 2.283(3), Pd1–S1 2.300(4), Pd1–Cl1 2.403(4), Pd2–C21 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: $-x+y$, $-x+1$; 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.[3]

The facile synthesis of the cyclometalated complexes **7** and **8**, together with earlier work on metal systems with tridentate *N,C,N′*,[10] *P,C,P′*,[11] and *S,C,S′*[12] ligand coordination[13] 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.[14] 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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[9] Crystals of **7** were obtained by slow evaporation (in air) of a solution of **7** in a toluene/CH_2Cl_2 mixture. $C_{126}H_{96}Cl_6Pd_6S_{12}$ · solvent, $M_r = 2845.85$, trigonal, $R3$, $a = b = 27.195(3)$, $c = 15.728(4)$ Å, $V = 10074(3)$ Å^3, $Z = 3$, $\rho_{calcd} = 1.407$ g cm^{-3}, $T = 150(2)$ K, $(\sin\vartheta/\lambda)_{max} = 0.649$ Å^{-1}, yellow block $0.25 \times 0.38 \times 0.38$ mm^3, 9086 measured reflections, of which 8113 were unique ($R_{int} = 0.051$), R values ($I > 2\sigma(I)$): $R1 = 0.0756$, $wR2 = 0.1709$, all data: $R1 = 0.1201$, $wR2 = 0.1942$. $-0.52 < \Delta\rho < 1.06$ e Å^{-3}. Enraf-Nonius CAD4T diffractometer with rotating anode ($\lambda = 0.71073$ Å). Absorption correction based on psi scans ($\mu = 1.14$ mm^{-1}, 0.82–0.97 transmission). Structure solution with direct methods (SHELXS-97[8c]). Structure refinement with SHELXL-97[8a] against F^2. 415 parameters, 276 restraints. The SPh groups were heavily disordered and refined with isotropic parameters. All other non-hydrogen atoms were refined with anisotropic temperature parameters, hydrogen atoms were refined as rigid groups. Structure graphics, checking for higher symmetry, absorption correction, and treatment of disordered solvent (CALC SQUEEZE, 830 e$^-$ per unit cell) were performed with the program PLATON.[8b] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-114913. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). a) G. M. Sheldrick SHELXL-97. Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, **1997**; b) A. L. Spek PLATON. *A Multipurpose Crystallographic Tool*, Utrecht University, The Netherlands; c) G. M. Sheldrick SHELXS-97. Program for Crystal Structure Solution; University of Göttingen, Göttingen, Germany, **1997**.

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Supramolecular Structure of Precipitated Nanosize β-Carotene Particles

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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.[1–4] 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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