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Enantiospecific Assembly of a Homochiral, Hexanuclear Palladium Complex

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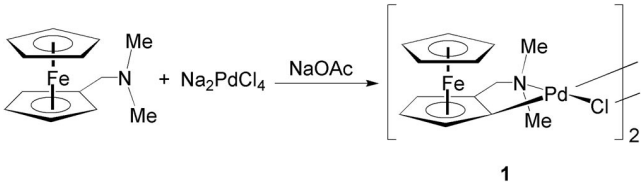
The linking of orthopalladated ferrocenylene units by parabanato(2–) ligands results in enantiospecific assembly of a hexanuclear complex in which (i) the steric bulk of the ferrocenylene moiety, (ii) the folded configuration dictated by the imidato(2–) bridging ligand, and (iii) the strong preference for a *trans* arrangement of the carbonyl oxygen and ferrocenyl carbon atoms, combine to ensure that only ferrocenylene-palladium units with the same chirality can be located at adjacent positions in the assembled complex. The resulting tris-parabanato(2–)-bridged, hexapalladium complex is thus homochiral (*R*,*R*,*R*,*R*,*R*,*R* or *S*,*S*,*S*,*S*,*S*,*S*), as demonstrated by ^{1}H NMR spectroscopy and by X-ray analysis of a racemic crystal which shows the complex to possess a tapering, twisted, trigonal-prismatic skeleton of palladium atoms with threefold crystallographic symmetry.

Introduction

Directed metallation of ferrocenyl ligands, for example the orthometallation of (dialkylamino)methylferrocenes (e.g. Scheme 1), can afford 1,2-disubstituted ferrocenylene complexes having planar chirality,[1,2] and these have found extensive application in organic synthesis as chiral reagents and catalysis.[3] High levels of enantioselectivity are generally observed in such reactions as a result of the steric bulk of the ferrocenyl group, which is held in close proximity to the palladium centre.



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Scheme 1. Orthopalladation of (dimethylamino)methylferrocene.

In this communication we report that the planar chirality of a ferrocenylene-palladacyclic unit, reinforced by antisymbiotic ligand effects, can be exploited in an entirely new way to direct the enantiospecific assembly of a high-nuclearity, homochiral transition-metal complex with imidato-type bridging ligands. There is very considerable interest at present in the synthesis of polyhedral, nanoscale structures from transition-metal-based subunits,[4] especially in the context of enantiospecific assembly,[4i] but the use of planar-chiral subunits has not, so far as we are aware, been previously investigated in this context.

Results and Discussion

Orthopalladation of (dimethylamino)methylferrocene with sodium tetrachloropalladate(2–) affords the chloro-bridged dimer $[Pd\{\eta^5\text{-}C_5H_3CH_2N(CH_3)_2Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ (**1**, Scheme 1).[5] Enumeration of the possible isomers of this complex reveals eight potential arrangements of the different components (Figure 1), but because *R*,*S*-*syn* and *S*,*R*-*syn* are identical (as are *S*,*R*-*anti* and *R*,*S*-*anti*) the number of chemically distinct dimers reduces to six. Moreover *R*,*R*-*syn* and *S*,*S*-*syn* are enantiomers, as are *R*,*R*-*anti* and *S*,*S*-*anti*, so that the number of isomers distinguishable – in principle – by NMR spectroscopy is reduced to four.

In practice, the ^{1}H NMR spectrum, of complex **1** (curiously, not reported in any detail before now) shows four resonances of almost equal intensity assignable to unsubstituted C_5H_5 rings, together with eight singlets arising from the two inequivalent *N*-methyl groups. This spectrum indicates that the assembly of **1** is completely non-stereospecific, with all possible isomers of **1** being formed in roughly equal proportions. This result is consistent with the extreme flexibility of the (normally coplanar) $[Pd_2Cl_2]$ unit,[6] which means there can be little, if any, difference in steric energy between *syn* and *anti* isomers. Moreover, the presence of two identical bridging atoms means that the electronic energies of the different isomers shown in Figure 1 must be essentially the same.

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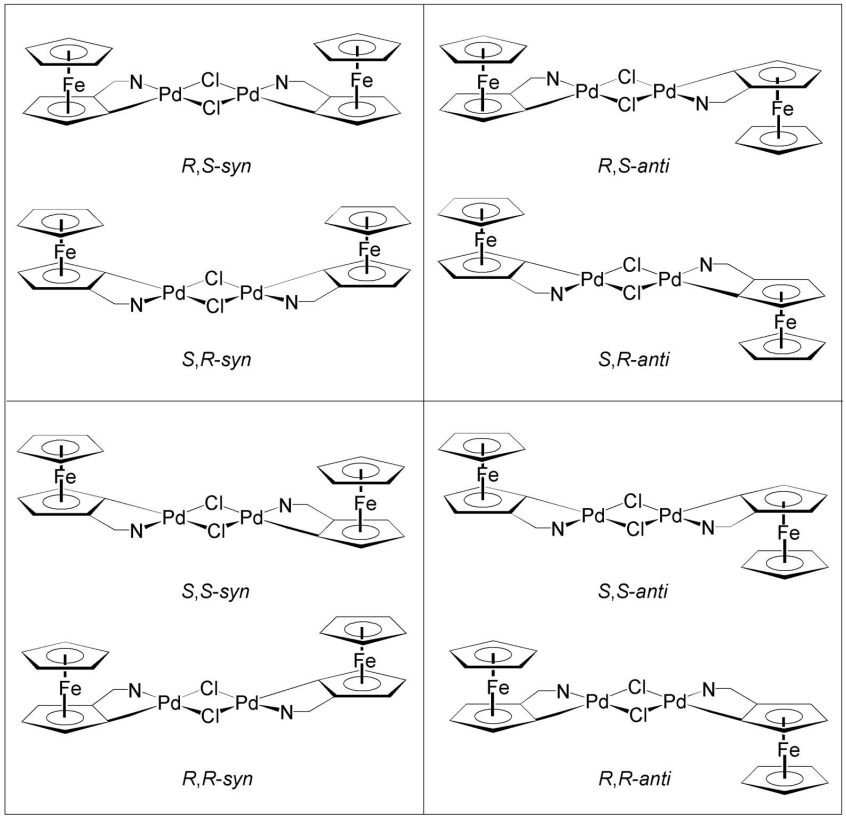
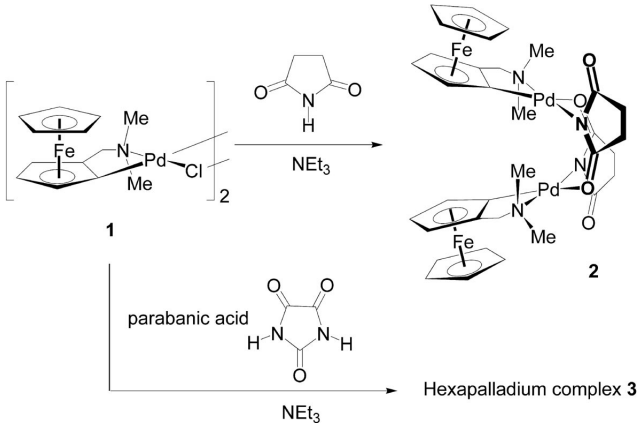


Figure 1. Potential arrangements of the components of compound **1**. Pairs of molecules in each of the upper boxes are related by twofold rotation axes and are thus degenerate. Pairs in the lower boxes are related by mirror planes and are hence enantiomeric. The four boxes thus indicate the isomers which are distinguishable, in principle, by NMR spectroscopy.

As a result, the construction of high-nuclearity molecular structures with fully defined geometry and chirality from orthopalladated systems of this type might be thought impossibly difficult, because for *n* chiral components in a molecule the number of potential isomers increases as 2^n. However, it has been shown in related (achiral) systems that μ-chlorido ligands at palladium(II) centres are readily replaced by ligands derived from phthalimide or succinimide, and that the resulting μ-imidato(1–) di-palladium complexes are *folded* at the bridging ligands, rather than being coplanar.[7] Bridging occurs through the imidato(1–) nitrogen atom and the oxygen of a carbonyl group, with the softest of the four ligands (the ferrocenyl carbon) invariably lying *trans* to the hardest ligand (the carbonyl oxygen), in keeping with Pearson's "antisymbiotic" rule for hard and soft ligands.[8]

It thus seemed possible that, in μ-imidato(1–) analogues of complex **1**, these relatively severe steric and electronic constraints might increase the stereoselectivity of complex formation, and so permit the assembly of chirally specified polynuclear systems. A first test of this proposal involved reaction of the red-brown complex **1** with succinimide, in the presence of triethylamine (Scheme 2), affording a 74% yield of a bright orange crystalline complex **2**, whose ^{1}H NMR spectrum was very much simpler than that of complex **1**, showing only a single resonance assignable to an unsubstituted C_5H_5 ring, and two equal-intensity *N*-methyl resonances (widely separated, by ca. 1.2 ppm). Addition of a chiral shift reagent produced a doubling of these signals and, consistent with this, the X-ray structure of **2** (Figure 2) showed that the crystals were racemic, comprising *R*,*R*-*syn* and *S*,*S*-*syn* isomers.



Scheme 2. Syntheses of the succinimidato(1–)-bridged dimer **2** and the parabanato(2–)-bridged hexapalladium complex **3**.

The tightly folded complex **2** has crystallographic twofold symmetry, and the X-ray structure shown in Figure 2 immediately accounts for the large difference in chemical

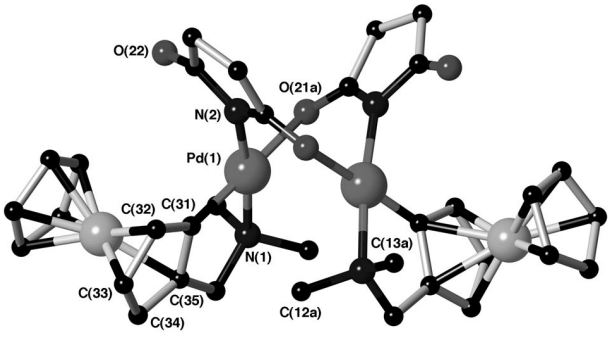


Figure 2. X-ray structure of the succinimidato(1–)-bridged dipalladium complex **2**. Hydrogen atoms omitted for clarity.

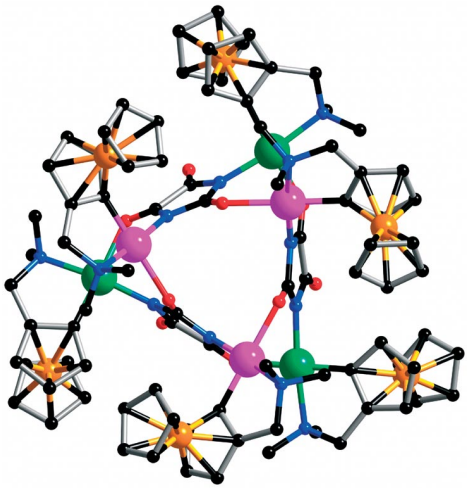


Figure 3. X-ray structure of the parabanato(2–)-bridged hexapalladium complex **3** (*S*,*S*,*S*,*S*,*S*,*S* enantiomer shown). Three of the six palladium atoms (those on the "upper" face of the tapering, twisted prism) are coloured magenta. The three on the "lower" face are shown in green. Hydrogen atoms omitted for clarity.

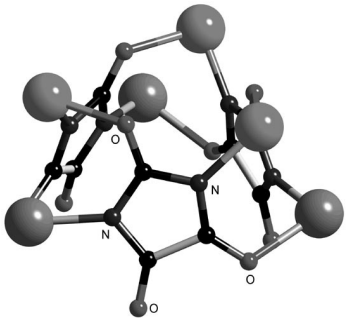


Figure 4. Molecular structure of **3** showing only the palladium atoms and the diagonally bridging parabanato(2–) ligands.

shift between the two inequivalent *N*-methyl groups. One such group (C12a) is found to be in almost van der Waals contact with the π-system of a ferrocenylene ligand (C31–C35) on the adjacent palladium, (distance C12a···Cp ring plane: 3.43 Å) and the resulting ring-current shielding of the methyl protons leads to a large shift of the corresponding ^{1}H NMR resonance to lower frequency.

The other methyl group (C13a) is more distant from the face of any cyclopentadienyl ring and is, if anything, closer to the *de*shielding zones of its adjacent ferrocenylene unit. As expected,[8] the ferrocenyl carbon (C31) is oriented *trans* to the carbonyl oxygen O(21a). The formation of dimer **2** as just a single pair of homochiral enantiomers (*R*,*R* or *S*,*S*) strongly supported the idea that assembly of high-nuclearity structures based on the (dimethylamino)methyl-ferrocenylene-palladium unit, linked by bis-imidato(1–)-type ligands, could proceed with high stereospecificity. Ligands of this type include the dianion of parabanic acid which is known to act as a binucleating ligand, for example in the di-iron complex $[\{CpFe(CO)_2\}_2C_3N_2O_3]$.[9] It thus seemed likely that reaction of **1** with parabanic acid would lead to formation of a polynuclear complex, quite possibly an octanuclear box-type structure analogous to that formed by the reaction of pyromellitic di-imide with the achiral complex $[Pd\{C_6H_4CH_2N(CH_3)_2\}(\mu\text{-}Cl)]_2$.[10]

Unexpectedly however, the reaction of parabanic acid with complex **1** (Scheme 2) gave an entirely novel type of complex which was shown by single-crystal X-ray analysis to comprise a homochiral *hexa*palladium system (**3**). As shown in Figure 3 and Figure 4, the palladium atoms define a tapering, twisted trigonal prism, with all six ferrocenylene-palladium stereocentres in each molecule having the same sense of planar chirality (*R*,*R*,*R*,*R*,*R*,*R* or *S*,*S*,*S*,*S*,*S*,*S*). The crystal is racemic, with each enantiomer also showing *helical* chirality,[10] as a result of the "diagonal" orientation (Pd–N···N–Pd) of the parabanato(2–) ligands (Figure 4).

The tapering, twisted prism has crystallographic threefold symmetry, but the upper and lower faces are inequivalent (the upper face is much the smaller of the two, with Pd···Pd distances averaging ca. 5.4 Å, compared with ca. 7.2 Å for the lower face) and this inequivalence is reflected in the ^{1}H NMR spectrum of **3**. Two resonances of equal intensity assigned to unsubstituted cyclopentadienyl rings are observed, corresponding to the ferrocenylene residues associated with the upper and lower faces of the prism (Figure 4), along with two equal-intensity pairs of *N*-methyl signals assigned to N–CH_3 groups directed above and below these faces. The ^{1}H NMR spectrum (see Supporting Information) shows no resonances assignable to any other isomer.

Conclusions

Enantiospecific assembly of planar-chiral transition-metal units into a hexanuclear, homochiral complex has been achieved by exploiting the steric bulk of the ferrocenylene residue, the tendency of imide-derived ligands to produce folded geometries at di-palladium(II) centres, and the antisymbiotic preferences of hard and soft ligands in square-planar complexes. A 1:1 mixture of *R* and *S* sub-

units thus assembles into a pair of enantiomeric, hexanuclear complexes (*R*,*R*,*R*,*R*,*R*,*R* or *S*,*S*,*S*,*S*,*S*,*S*) which together form a racemic crystal. This new approach to polynuclear transition-metal chemistry would seem to hold considerable general promise for the assembly of other nanoscale transition-metal systems with fully specified chirality.[4h,4i]

Experimental Section

Hexapalladium Complex 3: A solution of complex **1** (0.387 g, 0.505 mmol), parabanic acid (0.0577 g, 0.506 mmol), and triethylamine (1.01 g, 10.0 mmol) in dichloromethane (30 mL) was stirred under dry nitrogen for 16 h. The orange solution was extracted with water (3 × 100 mL), dried with magnesium sulfate, filtered, diluted with hexane (75 mL) and evaporated to ca. 10 mL. The resulting precipitate was filtered off, washed with hexane, dried under vacuum, and recrystallised from chloroform to give complex **3** (0.192 g, 43% yield). $C_{87}H_{96}Fe_6N_{12}O_9Pd_6$ (2427.27): calcd. C 43.05, H 3.99, N 6.92; found C 42.75, H 4.03, N 6.68. IR (paraffin mull): $\tilde{\nu}$ = 3079 (ν C–H_{arene}), 1739, 1636 (ν C=O), 1583 (ν C=C_{arene}) cm^{-1}. ^1H NMR (250 MHz, CD_2Cl_2): δ = 4.30 s (15 H, C_5H_5), 4.18 s (15 H, C_5H_5), 3.98 m (12 H, C_5H_3), 3.69 s (9 H, N-CH_3), 3.64 m (3 H, C_5H_3) 3.53 m (3 H, C_5H_3), 3.47 s (9 H, N-CH_3), 3.26 m (12 H, N-CH_2), 2.42 s (9 H, N-CH_3), 2.09 s (9 H, N-CH_3) ppm. Single crystals of **3** were grown from dichloromethane/methanol.

Crystal Data for Complex 2: $C_{34}H_{40}Fe_2N_4O_4Pd_2$, M = 893.20, monoclinic, space group $C2/c$, a = 19.348(2), b = 9.8853(9), c = 17.8652(15) Å, β = 90.695(7)°, V = 3416.7(6) $Å^3$, Z = 4, D_c = 1.736 $g\,cm^{-3}$, F_{000} = 1792, Mo-K_α radiation, λ = 0.71073 Å, T = 294(2) K, θ_{max} = 27.50°, μ = 1.911 cm^{-1}. 4485 reflections collected, 3916 unique. R_1 = 0.0275, wR_2 = 0.0728, R indices based on 3437 reflections with $I > 2\sigma(I)$ (refinement on F^2).

Crystal Data for Complex 3: $C_{87}H_{96}Fe_6N_{12}O_9Pd_6$, M = 2427.26, cubic, space group $I\text{-}43d$, a = 36.4453(2) Å, V = 48408.9(5) $Å^3$, Z = 16, D_c = 1.332 $g\,cm^{-3}$, F_{000} = 19296, Mo-K_α radiation, λ = 0.71073 Å, T = 159(2) K, θ_{max} = 27.68°, μ = 1.609 cm^{-1}. 593981 reflections collected, 9435 unique. R_1 = 0.0662, wR_2 = 0.1838, R indices based on 9045 reflections with $I > 2\sigma(I)$ (refinement on F^2). Residual electron density arising from the presence of disordered and unresolved solvent molecules was modelled using the SQUEEZE routine available in PLATON.[11]

Supporting Information (see also the footnote on the first page of this article): Analytical techniques and instrumentation. Synthesis and characterisation data for **2**. ^1H NMR spectra for **1**, **2** and **3** and ^{13}C NMR spectra for **2** and **3**.

CCDC-702011 (for **2**) and -702012 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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