

Cyclometallated fragments as building blocks for self-assembly reactions

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Abstract

Organometallic complexes have not hitherto been employed as building blocks in supramolecular chemistry, but they offer a number of interesting possibilities. Palladium(II) acetate reacts with derivatives of 1,3-bis-(benzimidazol-2-yl)-benzene (**1**) to give Pd(**1**-H)(OAc) which self-assembles to a molecular tricorn, but which may also undergo a second cyclometallation to give [Pd₂(**1**-2H)(OAc)₂]. This species may be cleaved by acid to give [Pd₂(**1**-2H)X₂] (X = Br, TsO); the latter species react with hydroxyacetate to give [Pd₂(**1**-2H)(HOCH₂CO₂)₂]₂. The crystal structure of this compound shows two Pd₂(**1**-2H) fragments clipped together by four bridging hydroxyacetate ligands. © 1997 Elsevier Science S.A.

Keywords: Cyclopalladation; Palladium; Self-assembly

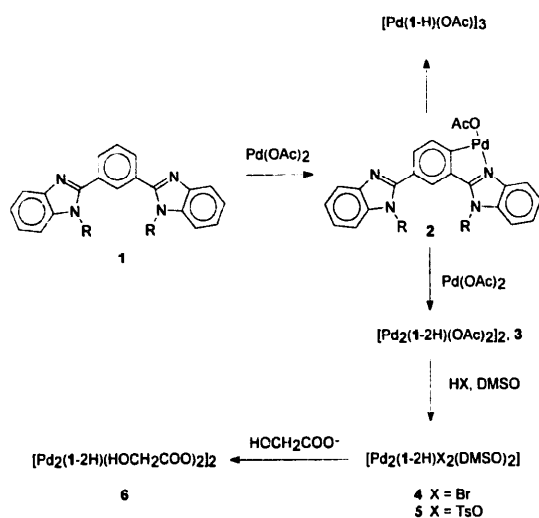
1. Introduction

The synthesis of molecular systems of increasing size and complexity has attracted considerable attention in recent years, and has resulted in the emergence of the new subject of supramolecular chemistry [1,2]. Interest has focused on self-assembly reactions [3,4] in which small, readily available molecular components are combined to form the supermolecule; the control of the assembly process is exercised by specific intermolecular attractions between components, or, frequently, by complexation around metal ions, the stereochemical control of the assembly arising from the coordination preferences of the ions. Such a strategy offers many advantages: coordination chemists have developed a great variety of metal-binding ligands, and the varying coordination preferences of different metal ions may be used to modify the structure obtained [5]; use of labile metal ions allows the system to search the potential energy surface efficiently and results in the formation of the thermodynamically stable product—errors in the assembly process are thereby corrected automatically. There are, however, two disadvantages: firstly, the metal ion is structurally a rather simple unit which seeks merely to

complete its coordination sphere, and secondly, the lability of the metal ion can result in rapid decomplexation of the metal and fragmentation of the supermolecule. A solution to the second problem is to transform the metal ion used for the self-assembly to an inert oxidation state once the assembly is complete, and we have previously reported a self-assembly around cobalt(II) followed by oxidation to the inert cobalt(III) which then undergoes assembly by hydrogen bonding [6].

Most work in this field has used classical coordination chemistry to effect the self-assembly, with heterocyclic nitrogen ligands dominating the field. The metal–carbon bond has been little studied, although Huck et al. [7,8] has recently reported the use of cyclopalladated species to build up dendrimers. The metal–carbon bond can often show considerable kinetic stability, especially with metals such as palladium. This offers the possibility of using palladated fragments of the general form LPd where L is a suitable ligand which occupies some but not all of the metal coordination sites, as rather stable, structured building blocks for further self-assembly reactions using the remaining free coordination sites of the palladium. Some years ago, we reported the synthesis of a molecular tricorn [Pd(**1a**-H)(OAc)₃] which is formed by a cyclometallation reaction of ligand **1a** with palladium acetate (Scheme 1) [9].

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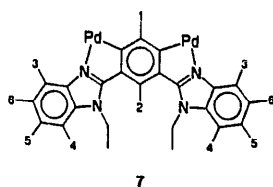


Scheme 1. The substitution of the benzimidazoles is indicated in the text by the suffices **a** (R = Me) and **b** (R = Et).

The proposed mechanism involved cyclometallation to give the monomer [Pd(1a-H)(OAc)] (2a) which possesses a vacant coordination site on the palladium atom, and a pendant benzimidazole and can, therefore, self-assemble to the trimer. In this communication, we show that the monomer may be trapped by a second cyclopalladation reaction which leads to a dimetallated product which may be used as a building block as discussed above.

2. Results and discussion

The synthesis of the tricorn also gave a low (ca. 10%) yield of an insoluble yellow product which gave an elemental analysis corresponding to [Pd₂(1a-2H)(OAc)₂]₂, 3a, indicating a double cyclometallation. The infrared spectrum of this product showed absorptions at 1585 and 1412 cm⁻¹ indicating the presence of bridging carboxylates [10]. Compound 3b could be obtained in high yield (ca. 95%) by the addition of 2.85 equivalents of Pd(OAc)₂ to one equivalent of 2b in acetic acid and refluxing overnight. The use of the stoichiometric amount of Pd(OAc)₂ gave a product contaminated with an unidentified green side product. 3b was insoluble in all common solvents; only in 1-chloronaphthalene was slight dissolution observed. No reaction was observed with the nucleophiles Br⁻ or



Scheme 2.

TsO⁻, but the addition of the stoichiometric amount of HBr or TsOH in DMSO resulted in dissolution of 3b to give the complexes 4b and 5b which could be precipitated by addition of methanol, and were characterised by elemental analysis (Scheme 2).

The ¹H NMR spectra of 4b and 5b showed only 6 aromatic proton resonances, consistent with the formation of the symmetrically dicyclopalladated fragment 7. At room temperature, protons 2 and 4 and the methylene protons of the ethyl groups gave broad signals, which narrowed upon raising the temperature to give, respectively, a singlet, a doublet, and a quartet. We attribute this to hindered rotation of the ethyl substituent; no broadening was observed in the NMR spectrum of 5a prepared in a similar way. The quartet observed for the methylene protons implies the molecule to be planar. Reaction of 5b with two equivalents of potassium hydroxyacetate in DMSO followed by diffusion of methanol into the solution allowed isolation of 6b as yellow crystals in essentially quantitative yield. An X-ray crystal structure determination of the crystals showed them to be [Pd₂(1b-2H)(HOCH₂COO)₂]₂ · MeCn.¹ The structure may best be described as a cleft in which two fragments 7 form the sides, and four bridging hydroxyacetate anions form the binding and hold the planar units together. Fig. 1 shows two views of the structure.

The structure confirms the double cyclometallation at the positions proposed by Trofimenko [14,15] and is to our knowledge only the second crystal structure of a doubly cyclopalladated arene to be reported, the other example being an *ortho* cyclo-dipalladation of benzene [16]. The two palladium coordination sites are identical within experimental error and are essentially square planar. The Pd-C bond distances (average 1.942(8) Å) are slightly shorter than the standard values [17] of 1.981 Å, but close to those given by Selbin et al. [18]. The Pd-N distances (average 1.993(7) Å) are normal. The coordination sphere is completed by two oxygens of bridging carboxylates: the average Pd-O distance for the oxygens *trans* to the σ-bonded aryl group is 2.134(5) Å, significantly longer than the value for the oxygens *trans* to a nitrogen atom (2.056(5) Å). This difference has been observed previously, [18,19] and may be at-

¹ Crystal dimensions: 0.17 × 0.18 × 0.55 mm, monoclinic, I2/a, a = 14.835(3), b = 18.457(2), c = 23.247(6) Å, β = 106.18(1)°, V = 6113(2) Å³, ρ_{calcd} = 1.62 g cm⁻³, 2θ_{max} = 45°, Mo Kα, λ = 0.71069 Å, ω-2θ scan, room temperature, 4146 measured, 4027 unique reflections, 3064 used for refinement (|Fo| ≥ 4σ(Fo)) Lorentz polarisation and absorption corrections (μ = 1.207 mm⁻¹, A_{min,max} = 1.198, 1.254), direct methods (MULTAN 87 [11]), refinement on |F| using XTAL 3.2 [12], 369 variables, 40 atoms anisotropic, C and O of methanol isotropic with population parameter of 50%, hydrogens calculated, R = 0.039, wR = 0.033 (w = 1/σ²(Fo)), residual electron density min. -0.72, max. 1.01 e Å⁻³.

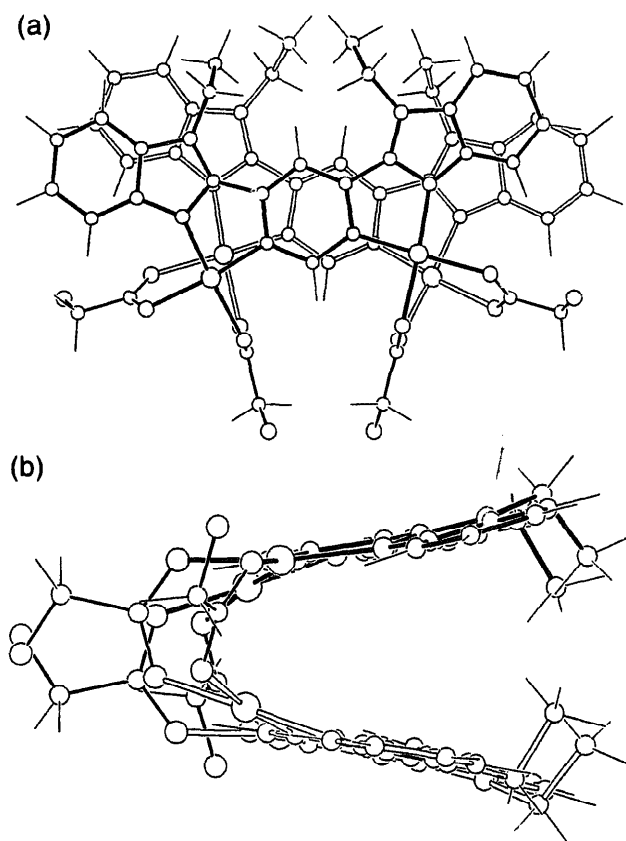


Fig. 1. ORTEP [13] view of $[\text{Pd}_2(\mathbf{1b-2H})(\text{HOCH}_2\text{COO})_2]_2$ (a) perpendicular to the ligand plane with the crystallographic twofold axis vertical, and (b) through the cleft, with the twofold axis horizontal. The two $\mathbf{1b-2H}$ units are distinguished by filled or open bonds.

tributed to the strong *trans* influence of the aryl group. The Pd–Pd distances of 2.886(1) Å are typical of carboxylate bridged systems, and are considered to be non-bonding. The components of the ligand, the phenyl ring and the two benzimidazoles, are planar within 0.02 Å, and the deviations from planarity of the whole ligand are due essentially to the torsions between the rings. The benzimidazole carrying the ethyl group lying closest to the twofold axis (the inner ethyl) is twisted by 8.4(2)° with respect to the phenyl ring, while the second benzimidazole is only twisted by 1.9(2)° with respect to the phenyl.

The angle between the two ligand planes is 20.8(1)° which is smaller than the 25° angle observed in the monocyclopalladated systems, [18,19] and the gap between the planes increases from 3.6 Å close to the binding to 5 Å at the extremities. There is, thus, no stacking interaction between the planes, and the methyl substituents of the ligands bend down to fill partially the cleft. The two ligand planes are not eclipsed, but are slightly displaced so that the methyl groups of the benzimidazole moieties are not superposed, but dovetail into each other (Fig. 1b) in a way reminiscent of a crocodile's teeth. The molecular symmetry is, thus, not C_{2v} but C_2 , and a crystallographic twofold axis relates

the two halves of the molecule. The molecule of methanol is hydrogen bonded to the external hydroxyacetates.

The ^1H NMR spectrum of $\mathbf{6b}$ showed significant differences from those of $\mathbf{4b}$ and $\mathbf{5b}$ which confirm the stability of the cleft in solution. The aromatic proton resonances were shifted upfield by an average of ca. 0.5 ppm resulting from the proximity of the shielding cones of the other ligand, and the methylene protons gave an ABX_3 spectrum according to the symmetry of $\mathbf{6b}$. The hydroxyacetates gave separate well-resolved signals corresponding, respectively, to ligands *trans* to C and N in fragment 7. These observations agree with the crystal structure, but the number of resonances observed implies a higher symmetry than C_2 . The crystal structure predicts two ethyl groups (inner and outer, distinguished by their distance from the C_2 axis), but only one is observed. The simplest explanation is that the methyl groups bend away from the cleft in solution to adopt an *exo*-conformation, with solvent entering the cleft, and the complex adopts a more symmetric eclipsed structure with C_{2v} symmetry. A dynamic explanation involving rapid interchange of inner and outer ethyls can be excluded since results for $\mathbf{4b}$ and $\mathbf{5b}$ show that ethyl rotation is slow at room temperature, and all signals for $\mathbf{6b}$ are sharp.

On the basis of the almost identical infrared spectra, we assume that $\mathbf{3}$ has the same cleft-like structure as $\mathbf{6b}$. This complex structure may be, thus, assembled or dismantled reversibly simply by deprotonation or protonation of the bridging carboxylates. Although monodentate carboxylate *trans* to carbon in $[\text{Pd}(\mathbf{1-H})\text{OAc}]_3$ was found to be extremely labile [20], the bidentate carboxylates in $\mathbf{6b}$ appear to be quite inert: heating solutions of $\mathbf{6b}$ to 90°C showed signs of proton exchange at the hydroxyl groups, but the different bridging ligands were not scrambled. Addition of a slight excess of hydroxyacetate to a solution of $\mathbf{6b}$ resulted in broadening of the signals due to coordinated hydroxyacetate, but the signals due to the aromatic ligand remained sharp. Thus, even though one ligand may be undergoing rapid exchange, the basic structure is not destroyed. This is another example of the observation that the assembly of polynuclear complexes via several labile metal–ligand bonds may lead to products which show kinetic stability much greater than that of the individual bonds used in the assembly [21].

3. Conclusion

In summary, the results confirm that the monomer $\mathbf{2}$ is in equilibrium with the tricorn $[\text{Pd}(\mathbf{1-H})\text{OAc}]_3$ since the latter species cannot undergo a second cyclopalladation because the pendant benzimidazole arm of $\mathbf{2}$ is no longer free. The dicyclopalladated species $\mathbf{3}$ may be

obtained in high yield, and can then readily undergo metathesis by acid labilisation of the carboxylate bridges. The tetranuclear species may then be reassembled with free hydroxyacetate ligand. The resulting species shows remarkable stability. The cyclopalladated species $[\text{Pd}_2(\text{1-2H})]^{2+}$ with four vacant coordination sites offers a potentially useful building block for self-assembly reactions, especially since the ligand **1** may be derivatised at points remote from the sites of complexation to allow interaction with other molecules which could be attracted into the cleft formed by the two $[\text{Pd}_2(\text{1-2H})]^{2+}$ units clipped together by carboxylates.

4. Experimental

$[\text{Pd}(\text{1-H})(\text{OAc})]_3$ (**2a** and **2b**) were prepared as described previously [9]. Complex **3b** was obtained by slow addition of 8.5 mg (37.9 μmol) of $\text{Pd}(\text{AcO})_2$ to a solution of 20 mg (12.6 μmol) of $[\text{Pd}(\text{1-H})\text{AcO}]_3$ in 3.5 ml acetic acid under reflux; after 24 h the yellow product was filtered (yield: 25 mg, 95%). IR (KBr): 1575(vs), 1412(s) cm^{-1} (COO). **3b**, $\text{C}_{56}\text{H}_{52}\text{N}_8\text{O}_8\text{Pd}_4$. Calcd. C, 48.36; H, 3.77; N, 8.06; Pd, 30.4. Found C, 48.36; H, 3.76; N, 8.07; Pd, 30.42.

10 mg (7.2 μmol) of **3b** in 2 ml DMSO and 33 μl HBr (0.886 M in DMSO, 29.2 μmol) were mixed in an ultrasonic bath for 5 min. Slow diffusion of ether gave 12.8 mg of **4b** (quantitative). ^1H NMR (DMSO- d_6 , 200 MHz, 20°C) δ = 1.50 (t, 6H, J = 7 Hz); 2.55 (s, 12H); 4.76 (q, 4H, J = 7 Hz); 7.20 (d, 2H, J = 8 Hz); 7.32 (d, 2H, J = 8 Hz); 7.51 (s, 1H); 7.75 (d, 2H, J = 8 Hz); 7.95 (s, 2H); 8.56 (s, 1H). **4b**, $\text{C}_{28}\text{H}_{32}\text{N}_4\text{O}_2\text{Br}_2\text{Pd}_2\text{S}_2$. Calcd. C, 37.64; H, 3.59; N, 6.27; Pd, 23.84. Found C, 37.84; H, 3.63; N, 6.30; Pd, 23.72.

Addition of 20 mg (14.4 μmol) of **3b** to a solution of 5.5 mg $\text{TsOH} \cdot \text{H}_2\text{O}$ (28.8 μmol) in DMSO (3 ml), followed by diffusion of ether yielded **5b** as a yellow powder (32.3 mg, 95%). ^1H NMR (DMSO- d_6 , 200 MHz, 20°C) δ = 1.54 (t, 6H, J = 6 Hz); 2.26 (s, 6H); 2.55 (15.6H, s); 4.78 (q, 4H, J = 6 Hz); 7.09 (d, 4H, J = 7 Hz); 7.4 (m, 5H); 7.48 (d, 4H); 7.63 (s, 1H); 7.85 (m, 4H). **5b**, $\text{C}_{42}\text{H}_{46}\text{N}_4\text{O}_8\text{Pd}_2\text{S}_4 \cdot 0.6(\text{CH}_3)_2\text{SO}$. Calcd. Pd, 19.0. Found 18.8.

Complex **6b** was obtained by addition of 17 mg (149 μmol) of HOCH_2COOK to a solution of **5b** (50 mg, 45 μmol) in DMSO (2.5 ml). Slow diffusion of methanol gave crystals of **6b** \cdot MeOH suitable for X-ray diffrac-

tion (32.4 mg, 97%). ^1H NMR (DMSO- d_6 , 200 MHz, 20°C) δ = 1.22 (t, 12H, J = 7 Hz); 4.05 (d, 2H, J = 6.3 Hz); 4.18 (d, 2H, J = 6.3 Hz); 4.27 (m, 4H); 4.39 (m, 4H); 5.01 (t, 4H, J = 6.3 Hz); 5.24 (t, 4H, J = 6.3 Hz); 6.73 (s, 2H); 6.78 (t, 4H, J = 9 Hz); 6.98 (m, 6H); 7.15 (d, 4H, J = 9 Hz); 7.36 (d, 4H, J = 9 Hz). ^{13}C NMR (DMSO- d_6 , 75.4 MHz, 20°C) δ = 182.05, 180.44 (carboxylates); 155.97, 153.29, 138.22, 132.38, 129.16 (quaternary C); 138.82, 123.09, 122.56, 115.80, 115.60, 109.47 (tertiary C); 62.55, 62.20, 39.93 (secondary C); 14.45 (primary C).

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