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Cyclometalated Palladium(II) Fragments as Building Blocks in the Construction of New Heteronuclear Metalomacrocycles

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The complexes $[\{(X)PdN(Cy){=}C(H)C_6H_2C(H){=}N(Cy)Pd(X)\}_2\{\mu\text{-}Ph_2PC_5H_4FeC_5H_4PPh_2\}_2]$ (X = Cl (**3**), X = Br (**4**)) have been prepared by reaction of $[(X)PdN(Cy){=}C(H)C_6H_2C(H){=}N(Cy)Pd(X)]_n$ (X = Cl (**1**), X = Br (**2**)) with 1,1′-bis(diphenylphosphino)ferrocene (dppf), and they were characterized by elemental analysis (C, H, N) and by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy in $CDCl_3$. The compounds are arranged as hexanuclear supramolecular cages containing two different metals, palladium and iron. The crystal structure of complex **4** was determined by X-ray diffraction studies.

Introduction

The use of metal complexes as versatile building blocks in supramolecular chemistry is a subject of increasing activity. In particular, attention has been focused on transition metal complexes containing suitably orientated ligands which may be substituted by a polyfunctional ligand capable of linking metal centers. This provides a means of forming macrocycles in a single reaction step.[1,2]

The square-planar geometry of platinum(II) and palladium(II) complexes proves them to be ideal building blocks. The syntheses of macrocycles derived from predesigned Pt(II) and Pd(II) complexes containing two blocked *cis*-coordination sites and polydentate nitrogen ligands are very abundant, especially those having internal cavities large enough to accommodate other molecules.[3−6] Recent examples include the use of predesigned organometallic components in the construction of macrocyclic compounds.[7−9] We have prepared complexes containing bidentate Schiff bases such as 1,4-$\{2,3,4\text{-}(MeO)_3C_6H_2C(H){=}N\}_2C_6H_4$, which upon reaction with tertiary diphosphines render complexes that show interesting supramolecular structures with 26- and 28-membered rings possessing four metal atoms.[10] We now report the self-assembly of two novel metalomacrocycles using as building blocks cyclopalladated fragments derived from related bidentate ligands. Due to the fact that the polyfunctional ligand used is 1,1′-bis(diphenylphosphino)ferrocene, the macrocycles synthesized are heteropolymetalic compounds, which have attracted great interest during the past decade, mainly due to their applications in several areas.[11−14]

Results and Discussion

The reaction of the cyclometalated complexes $[(X)PdN(Cy){=}C(H)C_6H_2C(H){=}N(Cy)Pd(X)]_n$[15] (X = Cl (**1**), X = Br (**2**)) with 2 equiv of 1,1′-bis(diphenylphosphino)ferrocene (dppf) in dichloromethane at room temperature for 24 h afforded complexes $[\{(X)PdN(Cy){=}C(H)C_6H_2C(H){=}N(Cy)Pd(X)\}_2\{\mu\text{-}Ph_2PC_5H_4FeC_5H_4PPh_2\}_2]$ (X = Cl (**3**), X = Br (**4**)) as orange solids in 81% (**3**) and 75% (**4**) yields, respectively.

The elemental analyses were consistent with the empirical formulas $C_{108}H_{108}N_4Pd_4Fe_2Cl_4P_4$ and $C_{108}H_{108}N_4Pd_4Fe_2Br_4P_4$, which evidence hexanuclear structures. The $^{31}P\{^1H\}$ spectra of **3** and **4** showed singlet resonances in each case (δ ca. 32), downfield shifted from

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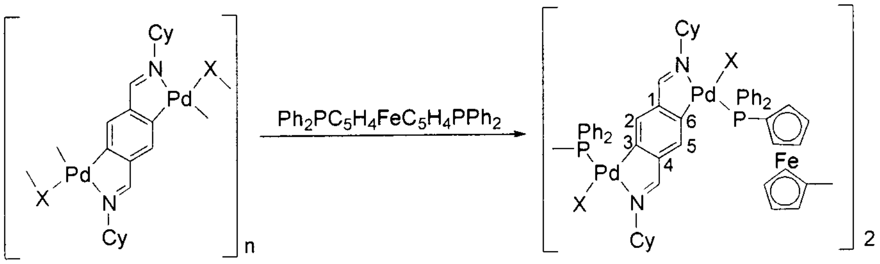
Scheme 1



1 X= Cl
2 X = Br

3 X= Cl
4 X = Br

their values in the free phosphine. This confirms coordination of both phosphorus atoms to the palladium atoms and suggests that the four phosphorus nuclei are equivalent and in a *trans* disposition to the nitrogen atom.[16,17] Interaction of the palladium atom with the C═N nitrogen atom was shown by the shift of the ν(C═N) stretching vibration to lower wavenumbers[18] and by the upfield shift of the HC═N proton resonance in the ^{1}H NMR spectra,[19] which appeared as a doublet due to coupling with the ^{31}P nucleus (δ 7.09, 4H, ^4J(PH) = 8.2 Hz (**3**); δ 7.07, 4H, ^4J(PH) = 8.4 Hz (**4**)). A doublet resonance was assigned to the two equivalent proton resonances H2 and H5 coupled to phosphorus (δ 6.03, 4H, ^4J(PH) = 5.8 Hz (**3**); δ 6.02, 4H, ^4J(PH) = 6.0 Hz (**4**)), which was shifted to lower frequency due to shielding by the phosphine phenyl rings.[10] As a result of double metalation, the HC═N protons are also shielded by the phosphine phenyl rings, as we have shown before in related compounds.[15] Electric conductivity measurements showed the compounds are nonelectrolytes.[20] The FAB mass spectra showed peaks at *m/z* 2265 (**3**) and 2443 (**4**), confirming the hexanuclear nature of these species.

The structural geometry of **4** has been definitely verified by an X-ray structure analysis (Experimental Details and Tables 1 and 2). A view of the molecular structure is shown in Figure 1. Single crystals of complex **4** suitable for X-ray analysis were grown by slow evaporation of a *n*-hexane/dichloromethane–chloroform solution at room temperature as orange prisms.

Table 1. Crystal Data and Structure Refinement Data for Compound 4

empirical formula	$C_{108}H_{108}N_4Pd_4Fe_2P_4Br_4\cdot CHCl_3\cdot 3CH_2Cl_2$
fw	2816.95
temp	173(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	*C*2/*c*
unit cell dimens	
	a 25.324(1) Å
	b 27.194(1) Å
	c 17.938(1) Å
	β 90.407(1)°
volume	12353.1(1) Å^3
Z	4
density (calcd)	1.515 Mg/m^3
abs coeff	2.383 mm^{-1}
F(000)	5616
cryst size	0.50 × 0.50 × 0.40 mm
θ range for data collection	1.10–28.31°
no. of reflns collected	42 391
no. of indep reflns	15 240 (R_{int} = 0.049)
abs corr	semiempirical
max and min transmn	0.449, 0.382
refinement method	full-matrix least-squares on F^2
goodness-of-fit on F^2	0.998
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0661$, $wR_2 = 0.1616$
R indices (all data)	$R_1 = 0.1063$, $wR_2 = 0.1862$
largest diff peak and hole	1.327 and −1.118 e/Å^3

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound 4

Pd(1)–C(1)	2.032(6)	Pd(2)–C(11)	2.004(6)
Pd(1)–P(1)	2.267(10)	Pd(2)–P(2)	2.260(2)
Pd(1)–N(1′)	2.120(5)	Pd(2)–N(2′)	2.127(6)
Pd(1)–Br(1)	2.4971(8)	Pd(2)–Br(2)	2.5137(9)
C(1)–Pd(1)–N(1′)	80.8(2)	C(11)–Pd(2)–N(2′)	80.5(2)
C(2)–C(1)–Pd(1)	133.5(4)	C(12)–C(11)–Pd(2)	132.2(5)
C(1)–Pd(1)–P(1)	95.85(16)	C(11)–Pd(2)–P(2)	92.56(18)
P(1)–Pd(1)–Br(1)	90.95(4)	P(2)–Pd(2)–Br(2)	95.32(5)
N(1′)–Pd(1)–Br(1)	92.40(15)	N(2′)–Pd(2)–Br(2)	93.51(15)

The structure of **4** comprises a molecule of [{(Br)PdN(Cy)═C(H)C$_6$H$_2$C(H)═N(Cy)Pd(Br)}$_2${μ-Ph$_2$PC$_5$H$_4$FeC$_5$H$_4$PPh$_2$}$_2$] (one-half molecule per asymmetric unit), one chloroform, and three dichloromethane solvent molecules. The complex can be regarded as a box-shaped supramolecular structure in which two dinuclear cyclometalated moieties are linked by the dppf bridging diphosphines acting as spacers (with a Pd(1)–Pd(2) distance of 7.6473(6) Å). A crystallographic 2-fold rotation axis passes through the centroids of the metalated phenyl rings. Each palladium atom is bonded, in a slightly distorted square-planar geometry, to four different donor atoms, the adjacent *ortho* carbon of the phenyl ring, one imine nitrogen atom, a bromine atom, and a phosphorus atom of the dppf ligand. The sum of angles about each palladium atom is 359.9° [Pd(1)] and 361.8° [Pd(2)], with the only noteworthy deviation being the somewhat reduced bond angles C(1)–Pd(1)–N(1′) of 80.8(2)° and C(11)–Pd(2)–N(2′) of 80.5(2)° consequent upon chelation. The geometry around Pd(1) is planar (rms deviations of mean Pd(1), C(1), N(1′), Br(1), P(1) plane 0.02 Å). However, coordination about Pd(2) is slightly twisted toward tetrahedral (rms deviations of mean Pd(2), C(11), N(2′), Br(2), P(2) plane 0.159 Å); N(2′) and P(2) are above the plane (deviations 0.218 and 0.180 Å, respectively), while C(11) and Br(2) are below the plane (deviations 0.231 and 0.157 Å, respectively).

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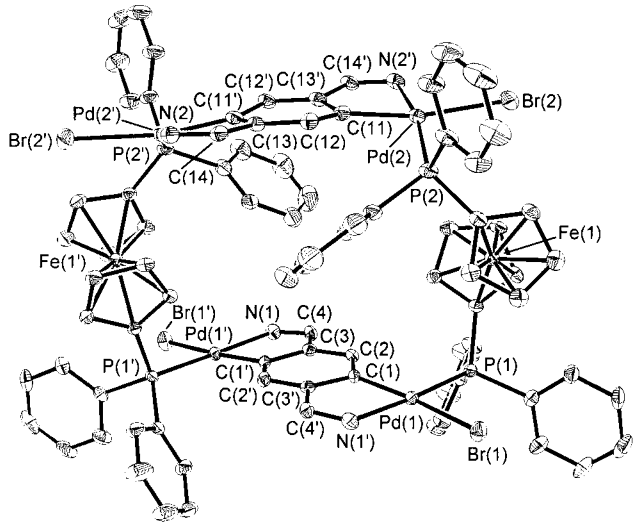

Figure 1. Structure of compound **4** showing the atom-numbering scheme. Hydrogen atoms and cyclohexyl rings were omitted for clarity.

We believe this is caused by the strain due to structural requirements imposed by the coordination to the dppf ligand.

The Pd−N bond lengths Pd(1)−N(1′), 2.120(5) Å, and Pd(2)−N(2′), 2.127(6) Å, are longer than the expected value of 2.01 Å calculated from the covalent radii of N(sp^2) and palladium (0.70 and 1.31 Å, respectively),[21] reflecting the strong *trans* influence of the phosphine ligand. The Pd−P and Pd−C bond lengths are shorter than the values predicted from their covalent radii, consistent with those found in related complexes.[22−24] The terminal palladium−bromine bonds [Pd(1)−Br(1), 2.4971(8) Å; Pd(2)−Br(2), 2.5137(9) Å] are somewhat longer than the sum of their covalent radii, revealing the strong *trans* influence of the C(phenyl) atom.[25,26] The two cyclometalated rings containing the Pd(1) atom and its symmetry equivalent Pd(1′) atom are planar (rms 0.0056 Å) and approximately coplanar (4.9°) with the aromatic phenyl ring of the Schiff base (rms 0.0184 Å). However, in the case of the Pd(2), Pd(2′) moiety the angle between the metalated aromatic ring (rms 0.0542 Å) and the cyclometalated rings (rms 0.0646 Å) is rather large, 10°, most probably due to structural requirements in the complex. The planes defined by the two metalacycles and the phenyl ring in each dinuclear moiety are parallel, and they are twisted, as evidenced by the angle of 36° between the Pd(1)−Pd(1′) and Pd(2)−Pd(2′) axes. As a consequence of the twisting about the 2-fold crystallographic axis, the molecule is chiral. The centrosymmetric natrure of the *C*2/*c* space group indicates that both enantiomers are present in the crystal. The C_5 rings of the ferrocenyl moiety are planar (mean deviations 0.023 and 0.035 Å) and parallel (the angle between the C_5 planes being 2.2°). The P(1) and P(2) atoms are slightly pushed away from the Fe atom with deviations from the mean C_5 planes of 0.218° and 0.069° for P(1) and P(2), respectively. The C_5H_4 fragments of the ferrocenyl group deviate from the staggered conformation by 7.1°. These data compare well with the values reported for other ferrocene derivatives.[27−29] In the solid state the "boxes" are packed with their open faces parallel to each other defining channels along the crystallographic axis. Nevertheless, the cavity of the channel is blocked by two of the phosphine phenyl rings. One interesting feature of this type of supramolecular species is the possibility of accommodating small molecules within the cavity defined by the box. In the case of complex **4** the shortest contacts with the solvent molecules correspond to one chloroform [H(2s)···Br(1), 2.86 Å; C(2s)···Br(1), 3.79(1) Å] and one dichloromethane [H(1s1)···Br(2), 2.68 Å; C(1s)···Br(2), 3.79(1) Å] solvent molecule, both located outside the cavity.

Recently we obtained single crystals of complex **3**. The molecular structure of **3** is analogous to the one described for complex **4**. However, in this case the structure showed a solvent chloroform molecule located inside the cavity of the complex. The chloroform molecule is not in the center of the cavity, with one of the chlorine atoms deviated 1.50 Å from the 2-fold crystallographic axis and 0.60 Å from the line connecting the two Fe atoms of the ferrocenyl fragments.

Conclusions

We have shown that when polymeric cyclometalated palladium(II) complexes such as **1** and **2** are treated with the diphosphine 1,1′-bis(diphenylphosphino)ferrocene, the resulting species self-assemble into hexanuclear supramolecular cages containing two different transition metals, palladium and iron. This behavior has not been observed in the reaction products when other tertiary diphosphines were used. Our interests are now focused on the construction of related structures employing this and other polyfunctional ligands capable of linking metal centers and forming metalomacrocycles in a single reaction step.

Experimental Details

Solvents were purified by standard methods.[30] Chemicals were reagent grade. The phosphine 1,1′-bis(diphenylphosphino)ferrocene was purchased from Aldrich-Chemie. Microanalyses were carried out at the Servicio de Análisis Elemental at the University of La Coruña using a Carlo Erba elemental analyzer, Model 1108. NMR spectra were obtained as $CDCl_3$ solutions and referenced to $SiMe_4$ (^1H, ^{13}C) or 85% H_3PO_4 (^{31}P-{^1H}) and were recorded on Bruker WM250 and AMX-300 spectrometers. All chemical shifts were reported downfield from standards. Compounds **1** and **2** have been synthesized by us before.[15]

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Synthesis of [{(X)PdN(Cy)=C(H)C_6H_2C(H)=N(Cy)Pd(X)}$_2${(μ-$Ph_2PC_5H_4FeC_5H_4PPh_2$}$_2$] (X = Cl (3), X = Br (4)). To a suspension of **1** (0.040 g, 0.069 mmol) or of **2** (0.040 g, 0.060 mmol) in dichloromethane (ca. 15 cm^3) was added $Ph_2PC_5H_4FeC_5H_4PPh_2$ (0.038 g, 0.069 mmol (**3**), 0.033 g, 0.060 mmol (**4**)). The resulting mixture was stirred at room temperature for 24 h, after which the solvent was eliminated under reduced pressure. The residue was recrystallized from dichloromethane−chloroform/*n*-hexane to give **3** or **4** as an orange solid.

3: Yield 81%. Anal. (%) Found: C, 57.3; H, 4.6; N, 2.4. Calcd for $C_{108}H_{108}N_4Pd_4Fe_2Cl_4P_4$: C, 57.3; H, 4.8; N, 2.5. IR: ν(C=N) 1620 m cm^{-1}, ν(Pd−Cl) 290 m cm^{-1}. ^{1}H NMR: δ 7.09 (d, 4H, ^4J(PH), 8.2 Hz), 6.03 (d, 4H, ^4J(PH), 5.8 Hz), 5.30 (br, 4H), 5.20 (br, 4H), 4.97 (br, 4H), 4.37 (br, 4H). ^{31}P{^{1}H}: δ 31.4 (s).

4: Yield 75%. Anal. (%) Found: C, 53.1; H, 4.4; N, 2.4. Calcd for $C_{108}H_{108}N_4Pd_4Fe_2Br_4P_4$: C, 53.1; H, 4.5; N, 2.3. IR: ν(C=N) 1621 m cm^{-1}. ^{1}H NMR: δ 7.07 (d, 4H, ^4JPH, 8.4 Hz), 6.02 (d, 4H, ^4JPH, 6.0 Hz), 5.40 (br, 4H), 5.20 (br, 8H), 4.49 (br, 4H). ^{31}P{^{1}H}: δ 32.0 (s).

Crystal data for 4: $C_{108}H_{108}N_4Pd_4Fe_2Br_4P_4\cdot CHCl_3\cdot 3CH_2Cl_2$, orange crystals, M_r = 2816.95, crystal dimensions 0.5 × 0.5 × 0.4 mm^3, a = 25.324(1), b = 27.194(1), c = 17.938(1) Å, β = 90.407(1)°, V = 12353.1(1) Å^3, μ(Mo Kα) = 2.383 mm^{-1}, Z = 4, T = 173(2) K, monoclinic, space group $C2/c$ (no. 15). Crystal structure determination: Three-dimensional, room-temperature X-ray data were collected in the range 1.10° < θ < 28.31° on a Siemens Smart CCD diffractometer by the ω scan method using graphite-monochromated Mo Kα radiation. Of the 42 391 reflections measured, all of which were corrected for Lorentz and polarization effects and for absorption by semiempirical methods based on symmetry-equivalent and repeated reflections [minimum and maximum transmission coefficients 0.382, 0.449], 10 307 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$ The structure was solved by direct methods and refined by full-matrix least-squares on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final R = 0.0661 (observed data, F) and wR_2 = 0.1862 (15 240 unique data, F^2), with allowance for thermal anisotropy of all non-hydrogen atoms. Hydrogen atoms were included in calculated positions and refined in riding mode. The cyclohexyl C(5) to C(9) atoms were found to be disordered, with each component having approximately 50% occupancies. The refinement was carried out taking into account both components. Minimum and maximum final electron density −1.118 and 1.327 e Å^{-3}. The structure solution and refinement were carried out using the program package SHELX-97.[31]

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Supporting Information Available: Crystallographic data (excluding structure factors) for structure **4** reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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