# **ORGANOMETALLICS**

# Design and Synthesis of Polytopic Metalloligands Based on Fluoroaryl Gold(I) Organometallic Compounds

Montserrat Ferrer,<sup>\*,†</sup> Albert Gutiérrez,<sup>†</sup> Mounia Mounir,<sup>†</sup> Laura Rodríguez,<sup>†</sup> Oriol Rossell,<sup>†</sup> Mercè Font-Bardia,<sup>‡,§</sup> Pilar Gómez-Sal,<sup>§</sup> Avelino Martín,<sup>⊥</sup> and Xavier Solans<sup>‡</sup>

<sup>†</sup>Departament de Química Inorgànica, Universitat de Barcelona, c/Martí i Franquès 1-11, 08028 Barcelona, Spain

<sup>†</sup>Departament de Cristal·lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, c/Martí i Franquès s/n, 08028 Barcelona, Spain

<sup>§</sup>Unitat de Difracció de RX, Centre Científic i Tecnològic de la Universitat de Barcelona (CCiTUB), c/Solé i Sabarís 1-3, 08028 Barcelona, Spain

<sup>⊥</sup>Departamento de Química Inorgánica, Campus Universitario-Edificio de Farmacia, Universidad de Alcalá, 28871 Alcalá de Henares, Spain

Supporting Information

**ABSTRACT:** New neutral and anionic fluoroaryl gold(I) complexes featuring terminal pyridine rings were prepared following different strategies. The homoleptic anionic compounds NBu<sub>4</sub>- $[Au(C_5F_4N)_2]$  (1) and NBu<sub>4</sub> $[Au(C_6F_4py)_2]$  (2) were obtained by reacting [AuCl(tht)] (tht = tetrahydrothiophene) with the organolithium derivatives of BrC<sub>5</sub>F<sub>4</sub>N and BrC<sub>6</sub>F<sub>4</sub>py, respectively. This route required the previous synthesis of the new fluorinated compound BrC<sub>6</sub>F<sub>4</sub>py, which was produced by a Stille



cross-coupling between (4-pyridyl)trimethylstannane and 1,4-dibromotetrafluorobenzene. The neutral phosphane compounds  $[Au(C_6F_4N)(PPh_3)]$  (3) and  $[Au(C_6F_4py)(PPh_3)]$  (4) were obtained by treatment of  $[AuCl(PPh_3)]$  with the organolithium reagents  $LiC_6F_4N$  and  $LiC_6F_4py$ , respectively. However, this synthetic strategy failed for organogold compounds containing a polyphosphane ligand. Consequently, an alternative synthetic procedure, based on displacement reactions of the weakly coordinated tht ligand from  $[Au(C_6F_4py)(tht)]$  by the appropriate polyphosphane, was undertaken. Thus, the following complexes were isolated and characterized:  $[(AuC_6F_4py)_2(\mu_2-diphosphane)]$  [diphosphane = bis(diphenylphosphanyl)methane (dppm) (9), 2,2-bis(diphenylphosphanyl)propane (dppip) (10), 1,2-bis(diphenylphosphanyl)ethane (dppe) (11), trans-1,2-bis-(diphenylphosphanyl)ethylene (dppet) (12), 1,2-bis(diphenylphosphanyl)acetylene (dppa) (13), 1,3-bis(diphenylphosphanyl)propane (dppp) (14), 1,4-bis(diphenylphosphanyl)butane (dppb) (15), 4,4'-bis(diphenylphosphanyl)-1,1'-biphenyl (dppdph) (16)],  $[(AuC_6F_4py)_3(\mu_3-triphosphane)]$  [triphosphane = 1,1,1-tris(diphenylphosphanylmethyl)ethane (triphos) (17), 1,3,5tris(diphenylphosphanyl)benzene (triphosph) (18)], and [(AuC<sub>6</sub>F<sub>4</sub>py)<sub>4</sub>( $\mu_4$ -tetraphosphane)] [tetraphosphane = tetra-(diphenylphosphanyl)methane (tetraphos) (19), 1,2,3,5-tetra(diphenylphosphanyl)benzene (tetraphosph) (20)]. Coordination reaction assays of compounds 1, 2, 3, and 4 with  $[M(diphosphane)(H_2O)_2](OTf)_2$  (M = Pd, Pt) were performed in order to test their potential as building blocks in the self-assembly of discrete species. The crystal structures of compounds BrC<sub>6</sub>F<sub>4</sub>py, **1**, **4**, **17**, and 19 were determined. Extensive noncovalent interations, particularly fluorine interactions such as  $C-F\cdots\pi_F$ ,  $C-F\cdotsH$ , and  $F \cdot \cdot \cdot F$ , have been found to influence the molecular packing of these species.

# INTRODUCTION

The design and synthesis of supramolecular self-organized systems with specific properties and functions in order to obtain advanced materials has increased in recent years. In particular, noteworthy advances have occurred in the field of engineering crystalline materials built from selected molecular components.<sup>1–3</sup> Molecular subunits are particularly effective when they incorporate multiple sites in particular orientations that favor the self-assembly of the building blocks to yield the predesigned supramolecular species.

While most metal—organic systems have been synthesized directly from metal ions and organic ligands, the "complex as

ligand" or "metalloligand" strategy, i.e., the use of metal complexes with "free" donor groups for further metal bonding as synthetic precursors, has also been developed.<sup>6-11</sup> Such ligands are the basis for the preparation of multinuclear complexes and coordination arrays of various dimensionalities. Conceptually, in an expanded ligand the spacer groups introduced are replaced by metal-containing moieties.

The use of metallic complexes as building block precursors has proved to be a very useful strategy for the design and syntheses of

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Scheme 1



materials with specific structures and functions in areas such as catalysis<sup>1,12</sup> or molecular recognition and sensing.<sup>2,13</sup>

Our focus in this area is on the complementary use of directional spacers and geometrically defined metals to prepare small polygons with functional value. In particular, we have been studying the self-assembly reactions between *cis*-blocked Pd<sup>II</sup> and Pt<sup>II</sup> square-planar complexes and the tetrafluorophenylene pyridyl ligands 1,4-bis(4-pyridyl)tetrafluorobenzene<sup>14,15</sup> and 4,4'-bis(4-pyridyl)octafluorobiphenyl<sup>16</sup> with the aim of generating electron-poor cavities capable of interacting with electron-rich compounds.

With this in mind, we thought of extending our studies by using fluorinated organometallic compounds, and more specifically, we chose gold(I) compounds for several reasons; fluoroaryl gold(I) compounds are known to have both thermodynamic and kinetic stability, adopt linear two coordination, and have the possibility of forming supramolecular structures due to the establishment of short  $d^{10}-d^{10}$  aurophilic interactions, and, moreover, can display optical properties that could allow the study of their interactions with other species in molecular recognition processes.

Although a significant number of fluoroaryl gold(I) compounds have been described so far,<sup>17–19</sup> and their behavior as Lewis bases to generate unsupported Au···M interactions (M = acidic closed-shell metal atom) have been explored,<sup>19–22</sup> none of them have been specifically synthesized to contain terminal donor groups that are responsible for their basic properties.

In this paper we report the synthesis of a series of organometallic fluorinated gold(I) compounds containing terminal pyridine groups. These compounds have been designed to act as donor building blocks in self-assembly reactions. Preliminary assays of the donor capability of the synthesized compounds are also reported.

# RESULTS AND DISCUSSION

**Ditopic Anionic Metalloligands.** As mentioned in the Introduction, we wanted to synthesize gold(I) derivatives closely related to the linear fluorinated dipyridyl compounds indicated above, i.e., py-( $C_6F_4$ )<sub>n</sub>-py (n = 1, 2). Obviously, the simplest perfluoroarylgold(I) species containing terminal pyridine rings is the symmetrical organoaurate [Au( $C_5F_4N$ )<sub>2</sub>]<sup>-</sup>.

The compound  $NBu_4[Au(C_5F_4N)_2]$  (1) was obtained by reaction of  $LiC_5F_4N$  and [AuCl(tht)] following the procedure previously reported for analogous complexes (Scheme 1).<sup>23</sup>



**Figure 1.** Molecular structure of the anion of complex 1. Ellipsoids are set at the 50% probability level. Selected bond lengths (Å) and angles (deg): Au-C1 = 2.017(9), Au-C6 = 2.025(9); C1-Au-C6 = 177.4(4).

Analytical and spectroscopic data agree with the proposed structure. The IR spectrum shows absorptions at 1620, 1413, 1202, and 818 cm<sup>-1</sup> that correspond to the  $C_6F_4N$  and at 921 cm<sup>-1</sup> arising from the NBu<sub>4</sub><sup> $\pm$ </sup>. The <sup>19</sup>F NMR shows two multiplets that agree with the existence of two types of inequivalent fluorine atoms. The FAB(-) mass spectrum shows the parent peak at m/z = 497.1, which corresponds to the  $[Au(C_5F_4N)_2]^-$  species. In addition, the structure of 1 was confirmed by X-ray diffraction (Figure 1). A single crystal of the compound was obtained by slow diffusion of diethyl ether into a solution of 1 in dichloromethane. The lattice is built up by wellseparated NBu4<sup>+</sup> cations and aurate anions. The coordination at gold is quasi linear  $(C1-Au-C6 = 177.4(4)^{\circ})$ , and the Au-C distances are found to be 2.017(9) and 2.025(9) Å. These values are similar to those reported in the literature for related gold compounds.<sup>24–30</sup> The pyridine rings are tilted  $19^{\circ}$  with respect to each other. In general, the value of this angle has been reported to be less than 10° for bis-perfluorinated derivatives except in the case of the tetrabutylammonium derivative NBu<sub>4</sub>[Au( $C_6F_5$ )<sub>2</sub>]<sup>26</sup> and the closely related silver compound  $PNP[Ag(C_6F_4N)_2]^{31}$ where this angle is ca. 80°. Interestingly, the structure of the compound presents weak intermolecular  $C-F \cdots \pi_F$  interactions (3.32 Å) that result in a well-defined zigzag molecular arrangement (Supporting Information, Figure S1). Although these contacts have been found in many fluorinated organic compounds, 32-34 this is the first time that this kind of interaction is pointed out for the related fluoroaryl Au(I) compounds. A search of structural data from CSD have shown that the compounds  $[(pdma)_2][Au(C_6F_5)_2]^{24}$  [NEt<sub>4</sub>]<sub>2</sub>[S(AuC<sub>6</sub>F<sub>5</sub>)<sub>3</sub>],<sup>35</sup> and [Au<sub>2</sub>-(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>{ $\mu$ -2,2-Ph<sub>2</sub>As(5,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>C<sub>6</sub>H<sub>3</sub>)AsPh<sub>2</sub>}]<sup>36</sup> present  $C-F \cdots \pi_F$  interactions that have an influence on their crystal packing.

The donor capability of 1 was tested in reactions with acceptor complexes such as  $[M(dppp)(H_2O)_2](OTf)_2$  (M = Pd, Pt). However, no coordination of the pyridine to the metal centers was detected. The very poor donor ability of 1 is possibly due to the high electronegativity of the fluorine substituents on pyridine ligands. In order to overcome this drawback, we attempted to synthesize a longer symmetrical organometallic gold compound containing perfluoraryl groups directly attached to the gold(I) center and pyridine rings relatively far from the fluorine atoms, i.e., NBu<sub>4</sub>[Au(C<sub>5</sub>F<sub>4</sub>py)<sub>2</sub>] (2). To do this, the new organic compound BrC<sub>6</sub>F<sub>4</sub>py had to be synthesized. First, a Kumada coupling between the Grignard derivative of 1,4-dibromotetrafluorobenzene and 1 equiv of 4-bromopyridine was attempted, but this method produced the desired compound only in very



Scheme 3



low yields. As an alternative, the  $[PdCl_2(PPh_3)_2]/LiCl-pro$ moted Stille cross-coupling between 1 equiv of (4-pyridyl)trimethylstannane and 1,4-dibromotetrafluorobenzene (Scheme 2)gave us better results.

Although this kind of coupling had already been used by us to obtain the ditopic ligand 1,4-bis(4-pyridyl)tetrafluorobenzene,14 the synthesis of  ${\rm BrC}_6F_4py$  turned out to be more complicated mainly due to the formation of significant amounts of the homocoupling product whatever the molar ratio was. Thus, the purification of BrC<sub>6</sub>F<sub>4</sub>py proved to be very challenging, and we finally isolated the target compound in moderate yield (30%) after chromatographic workup and successive sublimations. The compound was characterized by elemental analyses and <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR and IR spectroscopies. The mass spectrum showed the peaks due to  $[M + H]^+$  (*m*/*z* = 307.1) and  $[M - Br]^+$  (*m*/*z* = 226.1) fragments. In addition, suitable crystals for single-crystal X-ray diffraction were obtained by slow diffusion of diethyl ether into a dichloromethane solution of the compound. The resolved structure (Supporting Information, Figure S2) shows a dihedral angle between the aromatic rings of  $58.4(2)^\circ$ , close to the  $50.47(5)^{\circ}$  found in the related pyC<sub>6</sub>F<sub>4</sub>py. The rest of the intramolecular bonds and angles are in the expected range. The crystal packing of BrC<sub>6</sub>F<sub>4</sub>py (Supporting Information, Figure S3) clearly shows the presence of  $N \cdots Br$  interactions with an intermolecular distance of 2.811(4) Å, which is considerably shorter than the sum of the van der Waals radii (3.40 Å). The N···Br–C angle is 180°, and the molecules are aligned in one-dimensional infinite head-to-tail chains as a result of these attractive forces. The adjacent chains run parallel to the crystallographic *c*-axis with an interchain distance of ca. 5 Å.

Once the synthesis of the  $BrC_6F_4py$  ligand was accomplished, the target compound 2 was obtained in a similar way to 1 (Scheme 3).

Characterization data agree with the proposed formulation. The <sup>1</sup>H NMR spectrum showed, together with the NBu<sub>4</sub><sup>+</sup> signals, those corresponding to  $\alpha$ - and  $\beta$ -protons of the terminal pyridine ring. The <sup>19</sup>F NMR showed two multiplets shifted



Figure 2. Molecular structure of compound 4. Ellipsoids are set at the 50% probability level. Selected bond lengths (Å) and angles (deg): Au-C9 = 2.046(4), Au-P = 2.2861(11), C3-C6 = 1.497(6); C9-Au-P = 174.7(2).

downfield with respect to the free  $BrC_6F_4py$ , which agrees with the existence of two types of fluorine atoms. The FAB(-) mass spectrum showed the parent peak at m/z = 649.1 that corresponds to the  $[Au(C_6F_4py)_2]^-$  species.

As indicated above, the perfluorinated compound 1 did not show basic properties and consequently could not be used as a donor fragment in self-assembly reactions. Compound 2, however, upon reaction with acceptors such as  $[M(dppp)(H_2O)_2](OTf)_2$ (M = Pd, Pt), led only to the formation of highly insoluble and untreatable solids that could not be characterized and that most probably correspond to coordination polymers. Changes in the reaction conditions (concentration, solvent, temperature, reaction time, etc.) did not modify the nature of the resulting products.

At this point, it seemed decisive to find the reason that selfassembled Pd(II) or Pt(II) squares and/or triangles are readily obtained from the analogous organic ditopic ligands, py-C<sub>6</sub>F<sub>4</sub>py<sup>14,15</sup> or py-C<sub>6</sub>F<sub>4</sub>-C<sub>6</sub>F<sub>4</sub>-py,<sup>16</sup> and why this kind of discrete species could not be obtained by using the anionic gold complex **2**. To test if it was the anionic character of the gold complex that precluded the success of the self-assembly processes, we decided to synthesize new heteroleptic neutral gold(I) compounds bearing the donor "C<sub>6</sub>F<sub>4</sub>py" group and the ligand PPh<sub>3</sub> since it is known that phosphanes stabilize gold complexes due to the back bonding  $(d-d)_{\pi}$  of the Au–P bond.

**Neutral Monotopic Metalloligands.** The compounds  $[Au(C_6F_4N)(PPh_3)]$  (3) and  $[Au(C_6F_4py)(PPh_3)]$  (4) were obtained by treatment of  $[AuCl(PPh_3)]$  with an excess of freshly prepared diethyl ether (compound 3) or thf (compound 4) solution of the appropriate organolithium reagent ( $LiC_6F_4N$  or  $LiC_6F_4py$ , respectively). The <sup>31</sup>P{<sup>1</sup>H} NMR spectra confirmed the formation of the compounds since a triplet due to the coupling between the phosphorus and the *ortho*-fluorine atoms to the gold center was observed ( ${}^4J(P-F) \approx 7 \text{ Hz}$ ). The FAB(+) mass spectra displayed the cationic molecular peaks  $[3 + H]^+$  and  $[4 + H]^+$  at m/z = 610.1 and 686.0, respectively. Moreover, the structure of compound 4 was confirmed by X-ray diffraction (Figure 2). Each Au(I) center has a linear ligand coordination

with geometric parameters inside the narrow range found in other triphenylphosphine *ortho*-substituted phenylgold(I) compounds.<sup>37–43</sup> The angle between the pyridine and the fluorinated ring is  $50.7(3)^\circ$ , a bit smaller than that indicated above for the brominated ligand BrC<sub>6</sub>F<sub>4</sub>py. Interestingly, the establishment of rather strong secondary C–H···F interactions (d(C–H) = 0.93 Å, d(H···F) = 2.33 Å, d(C···F) = 3.105(8) Å, C–H–F = 141°) between one phenyl group of the PPh<sub>3</sub> and a C<sub>6</sub>F<sub>4</sub> ring of a different molecule gives rise to association of the molecules in pairs (Figure 3) that associate among themselves by weaker nonclassical hydrogen bonds (Supporting Information, Figure S4). Fluorine interactions of this kind have been pointed out for other fluoroaryl gold(I) compounds.<sup>44–46</sup>

**Coordination Reaction Assays.** In agreement with the results reported above, the tetrafluoropyridine derivative 3 was not basic enough to coordinate to metal centers. However, the reaction of complex 4 with the acceptor metal complexes  $[M(diphosphane)(H_2O)_2](OTf)_2$  (M = Pd, Pt) (diphosphane = dppp, dppf) in 2:1 molar ratio afforded the corresponding trimetallic compounds  $[M(diphosphane)\{(pyC_6F_4)Au(PPh_3)\}_2](OTf)_2$  (5–8) as a result of the coordination of the pyridine group to either the palladium or the platinum atom (Scheme 4).

The analytical and spectroscopic properties are in accordance with the proposed formulation. The observed downfield shifts of the  $\alpha$ -pyridine protons of **4** in the <sup>1</sup>H NMR spectra together with the upfield shifts for the phosphorus atoms of the diphosphane in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra are in agreement with metal coordination. Moreover, species containing Pt(diphosphane) fragments have the particular advantage that the <sup>1</sup>J(Pt-P) are very sensitive to changes in the coordination sphere. These coupling constants in **5** and 7 are 3065 and 3410 Hz, respectively, ca. 800 Hz smaller than in the [Pt(diphosphane)(H<sub>2</sub>O)<sub>2</sub>](OTf)<sub>2</sub> precursors, thus clearly indicating the coordination of the pyridine rings. The mass spectra showed the peak due to [M - 2OTf]<sup>2+</sup> except for compound **8**, where the [**8** - 2OTf - PPh<sub>3</sub>]<sup>2+</sup> fragment was found instead.



Figure 3. Visualization of the association of 4 in dimers through  $C-H\cdots F$  interactions.

#### Scheme 4

These results confirmed that neutral organometallic gold compounds containing fluorinated  $C_6F_4py$  terminal units coordinate efficiently to acidic metal centers. Since the formation of the desired heterometallic metallomacrocycles of diverse dimensionalities implied the presence of more than one pyridine group in the metalloligand to generate cyclic structures, we undertook the synthesis of a series of gold(I)-containing di-, tri-, and tetraphosphanes closely related to **4**.

Neutral Polytopic Metalloligands. Attempts to prepare the corresponding diphosphane complexes  $[(AuC_6F_4py)_2(\mu_2$ diphosphane)] by the procedure described above for 4 were unsuccessful. The treatment of the appropriate chlorogold(I) phosphanes with a large excess of the organolithium reagent LiC<sub>6</sub>F<sub>4</sub>py did not allow the complete substitution of the terminal chlorine atoms by the desired  $C_6F_4py$  moiety, in spite of the excess. Most probably, the poor reproducibility together with the low yield in the formation of the lithium derivative of  $BrC_6F_4py$ precluded the completion of the reaction. An alternative synthetic procedure that allows a better control of the molar ratio between the reacting species is based on the use of the neutral derivatives [AuR(tht)] as precursors, since they allow the synthesis of gold(I) complexes through displacement reactions of the weakly coordinated ligand tht by other neutral or anionic ligands.47 The treatment of a dichloromethane solution of recently prepared  $[Au(C_6F_4py)(tht)]$  with a series of diphosphanes in a 2:1 molar ratio at room temperature gave the desired dinuclear gold derivatives in good yields,  $[(AuC_6F_4py)_2(\mu_2$ diphosphane)] (Scheme 5) [diphosphane = dppm (9), dppip (10), dppe (11), dppet (12), dppa (13), dppp (14), dppb (15), dppdph (16)]. Analogous reactions with tri- or tetraphosphanes in 3:1 and 4:1 molar ratios, respectively, allowed the isolation of the corresponding tri-gold [ $(AuC_6F_4py)_3(\mu_3\text{-triphosphane})$ ] [triphosphane = triphos (17), triphosph (18)] or tetranuclear gold  $[(AuC_6F_4py)_4(\mu_4-tetraphosphane)]$  [tetraphosphane = tetraphos (19), tetraphosph (20)] compounds (Scheme 5).

All the synthesized compounds gave satisfactory elemental analysis and were characterized by <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H}, and <sup>19</sup>F NMR spectroscopies, mass spectrometry (ESI or FAB), and IR spectroscopy. Moreover, the structures of complexes 17 and 19 were determined by X-ray crystallography. <sup>1</sup>H NMR spectra showed the expected signals for both  $\alpha$  and  $\beta$  pyridine protons as well as those attributable to the organic core of the polyphosphane ligands. <sup>31</sup>P{<sup>1</sup>H} NMR spectra displayed a resonance whose downfield shift from the free polyphosphane clearly indicates the coordination of the ligand to the gold center. In most of the compounds a broad signal is observed that splits into a triplet (<sup>4</sup>*J*(P–F)  $\approx$  8 Hz) for derivatives 14 (dppp), 15 (dppb), and 16



#### Scheme 5



(dppdph) in an analogous manner to that in compound 3.  $^{19}$ F NMR spectra showed two sets of signals that show complicated patterns corresponding to  $F_{ortho}$  and  $F_{meta}$  to the gold atom. The mass spectra (ESI or FAB) displayed peaks due to the protonation of one or more of the terminal pyridine groups.

The molecular structure of compound 17 (Figure 4) features the expected trinuclear compound where each gold center is coordinated to one  $C_6F_4py$  unit. A long Au····Au contact (3.331(1) Å) can be observed between Au1 and Au3 atoms, while Au2 was further away. This arrangement is generally adopted by compounds that contain the "Au<sub>3</sub>( $\mu_3$ -triphos)" unit.<sup>48–51</sup> The disorder in the C24–C29 and C31–C35 aromatic rings prevented the analysis of possible weak intermolecular interactions.

The molecular structure of compound **19** is shown in Figure 5. Complex **19** crystallized in the tetragonal  $I4_1/a$  space group; thus only a unique set of distances and angles corresponding to one of the four branches of the compound had to be determined. Although rather long, intramolecular Au···Au interactions (3.343(1) Å) are found between adjacent units. Other tetraphosphane gold(I) compounds show the gold atoms associated in pairs by aurophilic attractions in a similar way to those reported here.<sup>52,53</sup> This disposition is different from that found in the parent compound  $[(AuCl)_4(\mu_4$ -tetraphos)],<sup>54</sup> where a pair of gold centers show short contacts, while the other two lie far apart.

The molecules pack in such a way that fluorophilic contacts between the F(12)  $(d(F \cdots F) = 2.646(8) \text{ Å})$  of different units expand, giving rise to the 3D structure (Figure 6). Although traditionally attributed to packing forces, recent calculations<sup>55</sup>



**Figure 4.** Molecular structure of compound 17. Ellipsoids are set at the 50% probability level. Phenyl rings are omitted for clarity. Selected bond lengths (Å) and angles (deg): Au1–Au3 = 3.3310(10), Au1–P1 = 2.287(3), Au2–P2 = 2.300(3), Au3–P3 = 2.295(3), Au1–C114 = 2.06(1), Au2–C24 = 2.11(2), Au3–C314 = 2.08(1); P1–Au1–C114 = 174.3(4), P2–Au2–C24 = 178.3(5), P3–Au3–C314 = 176.1(4), P1–Au1–Au3 = 78.3(1), P3–Au3–Au1 = 78.3(1).

have demonstrated that these kinds of interactions are consistent with intermolecular stabilizing  $F \cdots F$  interactions and have been recently described for a related fluoroaryl gold(I) compound.<sup>56</sup>



**Figure 5.** Molecular structure of compound **19**. Ellipsoids are set at the 50% probability level. Selected bond lengths (Å) and angles (deg): Au1-Au1c = 3.343(1), Au1-P1 = 2.301(2), Au1-C15 = 2.076(6); P1-Au1-C15 = 173.3(2), C15-Au1-Au1c = 107.1(2), P1-Au1-Au1c = 78.3(1). Symmetry transformations used to generate equivalent atoms: #1 -y+1, x, -z; #2 y+0, -x+1, -z+0; #3 -x+1, -y+1, z+0.

#### CONCLUSION

In summary, a series of fluoroaryl compounds featuring one, two, three, and even four gold centers and terminal pyridine ligands have been prepared and structurally characterized to be used as building blocks in the assembly of supramolecular compounds through coordination bonds.

Since perfluorinated pyridine rings are poorly basic, the design and synthesis of the new fluorinated compound containing a pyridine ring has been performed, and a wide variety of derivatives have been prepared. Preliminary studies exploring the behavior of these Au(I) species as metalloligands have shown that neutral  $[Au(C_6F_4py)(PPh_3)]$  (4) allowed the synthesis of discrete species in high yields, while symmetrical anionic  $[Au(C_6F_4py)_2]^-$  (1) led to the formation of complex polymeric mixtures that could not be characterized.

Interestingly, the X-ray structures of the fluoroaryl gold(I) compounds 1, 4, and 19 are good examples of  $C-F\cdots\pi_F$ ,  $C-F\cdotsH$ , and  $F\cdotsF$  interactions, showing that these types of secondary bonds can be found in fluoroaryl gold(I) organometallics in the same way as has been described for a wide range of organic fluorinated compounds.<sup>33</sup> The establishment of these interactions increases the dimensionality of discrete supramolecular species, giving rise to more complex structures.

We are currently investigating the self-assembly reactions between the polytopic metalloligands reported here and acceptor coordination compounds in order to synthesize new heterometallomacrocycles whose potential properties deserve to be investigated.

# EXPERIMENTAL SECTION

All manipulations were performed under prepurified N<sub>2</sub> using standard Schlenk techniques. All solvents were distilled from appropriate drying



Figure 6. Molecular packing of 19 following the crystallographic *c*-axis. Visualization of fluorophilic contacts between F12 atoms of different molecules.

agents. Infrared spectra were recorded on an FT-IR 520 Nicolet spectrophotometer. <sup>31</sup>P NMR ( $\delta(85\% H_3PO_4) = 0.0 \text{ ppm}$ ), <sup>19</sup>F NMR ( $\delta(CFCl_3) = 0.0 \text{ ppm}$ ), <sup>13</sup>C NMR ( $\delta(TMS) = 0.0 \text{ ppm}$ ), and <sup>1</sup>H NMR ( $\delta(TMS) = 0.0 \text{ ppm}$ ) spectra were obtained on Bruker DXR 250, Varian Gemini 200, Varian-Unity 300, Varian-Inova 300, and Varian Mercury 400 spectrometers. (See numbering scheme for fluorine assignation.) Elemental analyses of C, H, and N were carried out at the Institut de Bio-Orgànica in Barcelona. FAB, ESI, and IE mass spectra were recorded on a Fisions VG Quattro, a LC/MSD-TOF (Agilent Technologies), and a ThermoFinnigan TRACE DSQ spectrometer, respectively. MALDI-TOF spectra were recorded on a Voyager DE-RP (Perspective Biosystems) time-of-flight (TOF) spectrometer.

Commercial reagents triphenylphosphine, dppet, dppa, dppp, triphos, 4-bromopyridine hydrochloride, 1,4-dibromotetrafluorobenzene, and trimethyltin chloride were used as received. Compounds dppm,<sup>57</sup> dppip,<sup>57</sup> dppdp,<sup>58,59</sup> triphosph,<sup>60</sup> tetraphos,<sup>54</sup> tetraphosph,<sup>60</sup> (4-pyridyl)trimethylstannane,<sup>61</sup> [Au(C<sub>6</sub>F<sub>4</sub>py)(tht)],<sup>62</sup> [Pt(dppp)(H<sub>2</sub>O)<sub>2</sub>]-(OTf)<sub>2</sub>,<sup>63</sup> [Pd(dppp)(H<sub>2</sub>O)<sub>2</sub>](OTf)<sub>2</sub>,<sup>63</sup> [Pt(dppf)(H<sub>2</sub>O)<sub>2</sub>](OTf)<sub>2</sub>,<sup>63</sup> were prepared as described previously.

X-ray Structure Determinations. Crystal data for all the complexes are presented in Table 1. A suitable crystal was selected with the aid of a microscope, attached to a glass fiber, and in the case of  $BrC_6F_4py$ , 17, and 19 immediately placed in the low-temperature nitrogen stream (100 K  $BrC_6F_4py$  and 200 K 17 and 19) after being covered with a layer of a viscous perfluoropolyether (Fomblin Y). Crystals of 1 and 4 were mounted on a MAR345 diffractometer with an image plate detector, while a Bruker-Nonius Kappa CCD diffractometer equipped with an Oxford Cryostream 700 unit was used for compounds  $BrC_6F_4py$ , 17, and 19. Intensities were collected with graphite-monochromatized Mo Kα radiation.

The structures were solved, using the WINGX package,<sup>64</sup> by direct methods (SHELXL-97) and refined by least-squares against  $F^2$  (SHELXL-97).<sup>65</sup> Absorption correction procedures were carried out using the multiscan SORTAV program<sup>66</sup> for BrC<sub>6</sub>F<sub>4</sub>py, **17**, and **19** and the empirical SADABS program for **1** and **4**.

All H atoms were calculated and refined, using a riding model, with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom to which they are linked. All the non-hydrogen atoms

Гable 1. Crystal an	l Structure D	Determination	Data
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	$BrC_6F_4py$	1	4	17	19
empirical formula	$C_{11}H_4BrF_4N$	C <sub>26</sub> H <sub>36</sub> AuF <sub>8</sub> N <sub>3</sub>	C <sub>29</sub> H <sub>19</sub> AuF <sub>4</sub> NP	C <sub>74</sub> H <sub>51</sub> Au <sub>3</sub> F <sub>12</sub> N <sub>3</sub> P <sub>3</sub>	C <sub>97</sub> H <sub>64</sub> Au <sub>4</sub> F <sub>16</sub> N <sub>4</sub> P <sub>4</sub>
fw	153.03	739.54	685.39	1893.99	2501.27
temperature (K)	100(2)	293(2)	293(2)	200(2)	200(2)
wavelength (Å)	0.71073	0.71069	0.71073	0.71073	0.71073
cryst syst	orthorhombic	monoclinic	orthorhombic	monoclinic	tetragonal
space group	Pcnb	$P2_1/n$	Pbcn	C2/c	$I4_1/a$
unit cell dimens					
a (Å)	7.809(1)	9.7080(10)	13.4380(10)	35.584(2)	14.984(2)
b (Å)	10.747(2)	17.2870(10)	18.4960(10)	24.932(5)	14.984(2)
c (Å)	11.826(1)	17.7240(10)	20.214(10)	22.090(6)	46.536(10)
$\alpha$ (deg)	90	90	90	90	90
$\beta$ (deg)	90	93.5850(10)	90	119.13(1)	90
$\gamma$ (deg)	90	90	90	90	90
$V(Å^3)$	992.5(4)	2968.7(4)	5024(3)	15676(5)	10449(3)
Ζ	4	4	8	8	4
$D_{calc} (mg/m^3)$	2.048	1.655	1.812	1.605	1.590
absorp coeff $(mm^{-1})$	4.173	5.025	5.968	5.731	5.731
<i>F</i> (000)	592	1456	2640	7248	4776
cryst size (mm <sup>3</sup> )	$0.45\times0.35\times0.33$	0.2  imes 0.1  imes 0.1	0.2  imes 0.1  imes 0.1	$0.2\times0.1\times0.1$	$0.3\times0.2\times0.2$
$\theta$ range for data collection (deg)	3.13-27.49	1.65-24.96	1.87-29.01	5.00-26.93	3.07-27.61
index ranges	$-9 \le h \le 9$	$-11 \le h \le 10$	$0 \le h \le 18$	$-41 \le h \le 36$	$-19 \le h \le 19$
	$-13 \le k \le 13$	$0 \le k \le 20$	$0 \le k \le 25$	$-31 \le k \le 31$	$-19 \le k \le 18$
	$0 \le l \le 15$	$0 \le l \le 20$	$0 \le l \le 27$	$0 \le l \le 28$	$0 \le l \le 60$
reflns collected	8734	14 405	46 064	138 589	101 976
indep reflns	1105 [ $R(int) = 0.067$	4489 $[R(int) = 0.068]$	6605 [ $R(int) = 0.0494$ ]	16775 [R(int) = 0.039]	5629 [R(int) = 0.078]
completeness/ $\theta(\max, \deg)$	96.8%/27.50	86.1%/24.99	98.6%/29.01	98.7%/26.93	92.5%/27.61
refinement method	full-matrix least-squares	on F <sup>2</sup>			
data/restraints/params	1105/0/80	4489/24/345	6605/20/325	16775/0/921	5629/0/282
goodness-of-fit on $F^2$	1.090	0.820	1.232	1.140	0.938
final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1=0.036,wR_2=0.085$	$R_1=0.0423,wR_2=0.0894$	$R_1 = 0.0374,  wR_2 = 0.0839$	$R_1 = 0.066, wR_2 = 0.189$	$R_1 = 0.048, wR_2 = 0.099$
R indices (all data)	$R_1{=}\;0.059,wR_2{=}0.094$	$R_1=0.1070,wR_2=0.1011$	$R_1=0.0735,wR_2=0.1061$	$R_1 = 0.146, wR_2 = 0.217$	$R_1 = 0.089, wR_2 = 0.107$
largest diff peak/hole (e Å $^{-3}$ )	0.805/-1.122	0.792/-0.470	0.803/-0.583	2.488/-1.469	1.397/-1.241

were refined anisotropically except C(213) and C(222), which were isotropically refined in 17.

Molecules of 17 presented disorder in the C24–C29 and C31–C35 aromatic rings. Both cases were treated with the use of the SHELXL PART command together with the corresponding occupancy free variables in the refinement process. Both 17 and 19 crystallized with solvent molecules. All attempts to model these molecules failed, and the Platon Squeeze procedure was used to remove their contribution to the structure factors. However, the poor quality of crystals in the case of complex 17 precluded the complete removal of the solvent residues, and still a fairly large difference peak of 2.488 e Å<sup>-3</sup> could be found in the Fourier difference map.



**Numbering Scheme** 

Synthesis of BrC<sub>6</sub>F<sub>4</sub>py. 1,4-Dibromotetrafluorobenzene (475 mg, 1.54 mmol), [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (54 mg, 0.075 mmol), and LiCl

(326 mg, 7.50 mmol) were added to a toluene solution (60 mL) of (4-pyridyl)trimethylstannane (373 mg, 1.54 mmol). The reaction was refluxed for 72 h; after cooling, the mixture was treated with 50 mL of H<sub>2</sub>O. The organic phase was removed, and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 40 mL). The combined organic layers were dried (MgSO<sub>4</sub>) and concentrated to dryness under reduced pressure. The resulting crude residue was purified by column chromatography on silica gel using first CH<sub>2</sub>Cl<sub>2</sub> and subsequently CH<sub>2</sub>Cl<sub>2</sub>/MeOH (98:2) as eluents. The obtained cream solid was further purified by two subsequent sublimations (40 and 60 °C), giving 185 mg of a white product (yield: 40%). <sup>1</sup>H NMR (298 K, acetone-*d*<sub>6</sub>): 8.79 (m, 2H, H<sub>α-pyr</sub>), 7.57 (m, 2H, H<sub>β-pyr</sub>). <sup>13</sup>C NMR (298 K, CDCl<sub>3</sub>): 150.7 (C<sub>α-pyr</sub>), 147.2 (d, *J*(C-F) = 105 Hz, C-F<sub>X</sub>), 143.2 (d, *J*(C-F) = 105 Hz, C-F<sub>A</sub>), 135.5 (C<sub>γ-pyr</sub>), 124.9 (C<sub>β-pyr</sub>), 117.1 (m, C<sub>q</sub>-py), 101.0 (m, C<sub>q</sub>-Br). <sup>19</sup>F NMR (298 K, CDCl<sub>3</sub>): -134.7 (m, 2F, F<sub>X</sub>), -144.1 (m, 2F, F<sub>A</sub>). IE *m*/*z*: 306.0 ([BrC<sub>6</sub>F<sub>4</sub>py + H]<sup>+</sup>, calc 306.0), 226.1 ([BrC<sub>6</sub>F<sub>4</sub>py - Br]<sup>+</sup>, calc 226.0). IR (KBr, cm<sup>-1</sup>): 1598, 1467, 973, 803. Anal. Calc: C, 43.17; H, 1.32; N, 4.58. Found: C, 43.29; H, 1.30; N, 4.66.

Synthesis of  $(NBu_4)[Au(C_5F_4N)_2]$  (1). <sup>n</sup>BuLi (1.6 mL, 2.60 mmol) was added dropwise to a precooled (-78 °C) solution of 4-bromotetrafluoropyridine (0.3 mL, 2.50 mmol) in diethyl ether (15 mL). After 1 h of stirring a suspension of [AuCl(tht)] (267 mg, 0.83 mmol) in diethyl ether (15 mL) was added, and the stirring was

maintained until solubilization of the gold complex (ca. 30 min). Then, solid NBu<sub>4</sub>Br was added (268 mg, 0.83 mmol) and the solution was allowed to warm slowly to room temperature. A white precipitate was obtained, filtered under vacuum, and washed with diethyl ether. Yield: 65% (400 mg). <sup>1</sup>H NMR (298 K, acetone-*d*<sub>6</sub>): 3.45 (m, 8H, NCH<sub>2</sub>), 1.83 (m, 8H, NCH<sub>2</sub>CH<sub>2</sub>), 1.43 (m, 8H, NCH<sub>2</sub>CH<sub>2</sub>), 0.97 (t, 12H, J(H−H) = 7.3 Hz, CH<sub>3</sub>). <sup>19</sup>F NMR (298 K, CH<sub>2</sub>Cl<sub>2</sub>, inset D<sub>2</sub>O with CF<sub>3</sub>COOH): −101.9 (m, 4F, F<sub>X</sub>), −124.9 (m, 4F, F<sub>A</sub>). FAB(−) *m/z*: 497.1 ([Au(C<sub>5</sub>F<sub>4</sub>N)<sub>2</sub>]<sup>−</sup>, calc 497.0). IR (KBr, cm<sup>−1</sup>): 2968, 1474, 921 (NBu<sub>4</sub>), 1620, 1413, 1202, 818 (C<sub>5</sub>F<sub>4</sub>N). Anal. Calc: C, 42.22; H, 4.91; N, 5.68. Found: C, 42.33; H, 4.87; N, 5.72.

Synthesis of (NBu<sub>4</sub>)[Au(C<sub>6</sub>F<sub>4</sub>py)<sub>2</sub>] (2). <sup>n</sup>BuLi (0.8 mL, 1.30 mmol) was added dropwise to a precooled (-78 °C) solution of (4-bromotetrafluorophenyl)pyridine (400 mg, 1.30 mmol) in tetrahydrofuran (20 mL). After 1 h of stirring, [AuCl(tht)] (139 mg, 0.43 mmol) was added, and the mixture was left to react at -40 °C for 1 h. Then, solid NBu<sub>4</sub>Br was added (140 mg, 0.43 mmol), and the suspension was allowed to warm slowly to room temperature and then concentrated to dryness. The resulting solid was extracted with tetrahydrofuran (10 mL), and diethyl ether was added to precipitate a white solid, which was filtered and dried under vacuum. Yield: 60% (230 mg). <sup>1</sup>H NMR (298 K, CD<sub>2</sub>Cl<sub>2</sub>): 8.67 (d, J(H-H) = 4.7 Hz, 4H,  $H_{\alpha-pyr}$ ), 7.47  $(d, J(H-H) = 4.7 \text{ Hz}, 4H, H_{\beta-\text{pyr}}), 3.18 \text{ (m, 8H, NCH}_2), 1.67 \text{ (m, 8H, NCH}_2)$  $NCH_2CH_2$ ), 1.46 (m, 8H,  $NCH_2CH_2CH_2$ ), 1.02 (t, 12H, J(H-H) =7.3 Hz, CH<sub>3</sub>). <sup>19</sup>F NMR (298 K, CD<sub>2</sub>Cl<sub>2</sub>, inset D<sub>2</sub>O with CF<sub>3</sub>COOH): -118.1 (m, 4F, F<sub>X</sub>), -148.1 (m, 4F, F<sub>A</sub>). FAB(-) m/z: 649.1  $([Au(C_6F_4py)_2]^-$ , calc 649.0). IR (KBr, cm<sup>-1</sup>): 2966, 1472, 946 (NBu<sub>4</sub>), 1443, 826 (C<sub>6</sub>F<sub>4</sub>). Anal. Calc: C, 51.18; H, 4.97; N, 4.71. Found: C, 51.37; H, 4.99; N, 4.68.

**Synthesis of** [Au(C<sub>5</sub>F<sub>4</sub>N)(PPh<sub>3</sub>)] (3). <sup>n</sup>BuLi (0.18 mL, 0.30 mmol) was added dropwise to a precooled (-78 °C) solution of 4-bromotetrafluoropyridine (0.036 mL, 0.30 mmol) in diethyl ether (25 mL). After 1 h of stirring a suspension of [AuCl(PPh<sub>3</sub>)] (150 mg, 0.30 mmol) in diethyl ether (15 mL) was added, and the mixture was maintained on stirring 1 h. The solution was allowed to warm slowly to room temperature and then filtered and concentrated to dryness. The obtained white solid was recrystallized with dichloromethane/hexane, giving 118 mg of the corresponding product (yield: 65%). <sup>1</sup>H NMR (298 K, CDCl<sub>3</sub>): 7.60–7.50 (m, 15H, Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (298 K, CDCl<sub>3</sub>): arest D<sub>2</sub>O with CF<sub>3</sub>COOH): -99.7 (m, 2F, F<sub>X</sub>), -124.5 (m, 2F, F<sub>A</sub>). FAB(+) *m/z*: 610.1 ( $[3 + H]^+$ , calc 610.1), 459.1 ([AuPPh<sub>3</sub>]<sup>+</sup>, calc 459.1), 262.1 (PPh<sub>3</sub>, calc 262.1). IR (KBr, cm<sup>-1</sup>): 1620, 1446, 1201, 920, 827 (C<sub>5</sub>F<sub>4</sub>N), 1100, 745, 690, 539 (PPh<sub>3</sub>). Anal. Calc: *C*, 45.39; H, 2.48; N, 2.30. Found: C, 45.50; H, 2.42; N, 2.40.

Synthesis of [Au(C<sub>6</sub>F<sub>4</sub>py)(PPh<sub>3</sub>)] (4). <sup>n</sup>BuLi (0.20 mL, 0.32 mmol) was added dropwise to a precooled (-78 °C) solution of 4-(4bromotetrafluorophenyl)pyridine (100 mg, 0.32 mmol) in tetrahydrofuran (50 mL). After 1 h of stirring, solid [AuCl(PPh<sub>3</sub>)] (158 mg, 0.32 mmol) was added, and the mixture was stirred for another hour. Then, the solution was allowed to warm slowly to room temperature. The mixture was hydrolyzed with a few drops of water, dried with MgSO<sub>4</sub>, and concentrated to dryness. The obtained solid was recrystallized with dichloromethane/hexane, giving 110 mg of a yellow solid (yield: 50%). <sup>1</sup>H NMR (298 K, CDCl<sub>3</sub>): 8.70 (d, J(H-H) = 5.4 Hz, 2H,  $H_{\alpha-pvr}$ ), 7.66–7.49 (m, 20H, Ph), 7.45 (d, J(H-H) = 5.4 Hz, 2H,  $H_{\beta-pyr}$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (298 K, CDCl<sub>3</sub>): 37.9 (t,  ${}^{4}J(P-F) = 7.8$  Hz). <sup>19</sup>F NMR (298 K,  $CH_2Cl_2\text{, inset }D_2O$  with  $CF_3COOH)\text{:}$  –119.7 (m, 2F,  $F_X\text{),}$ -147.6 (m, 2F, F<sub>A</sub>). FAB(+) m/z: 686.0 ([4 + H]<sup>+</sup>, calc 686.1). IR (KBr, cm<sup>-1</sup>): 1429, 943, 826 (C<sub>6</sub>F<sub>4</sub>), 1101, 690 (PPh<sub>3</sub>). Anal. Calc: C, 50.82; H, 2.79; N, 2.04. Found: C, 50.67; H, 2.73; N, 2.10.

Synthesis of  $[Pt(dppp){(pyC_6F_4)Au(PPh_3)}_2](OTf)_2$  (5). Solid  $[Pt(dppp)(H_2O)_2](OTf)_2$  (16 mg, 0.02 mmol) was added to a dichloromethane (5 mL) solution of  $[Au(C_6F_4py)(PPh_3)]$  (27 mg, 0.04 mmol). After 3 h of stirring at room temperature, the mixture was concentrated to ca. 2 mL, and diethyl ether was added in order to complete the precipitation of the product. A white solid was obtained in 79% yield (31 mg). <sup>1</sup>H NMR (298 K, CDCl<sub>3</sub>): 9.12 (d, J(H-H) = 5.2 Hz, 4H,  $H_{\alpha$ -pyr}), 7.62–7.36 (m, 50H, Ph), 7.22 (d, J(H-H) = 5.2 Hz, 4H,  $H_{\beta$ -pyr}), 3.32 (br, 4H, PCH<sub>2</sub>), 2.24 (m, 2H, PCH<sub>2</sub>CH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (298 K, CDCl<sub>3</sub>): 41.9 (t, <sup>4</sup>J(P-F) = 7.8 Hz, PPh<sub>3</sub>), -15.8 (s, <sup>1</sup>J(P-Pt) = 3066 Hz, dppp). <sup>19</sup>F NMR (298 K, CDCl<sub>3</sub>, inset D<sub>2</sub>O with CF<sub>3</sub>COOH): -81.1 (s, 6F, OTf), -118.7 (m, 4F, F<sub>X</sub>), -146.8 (m, 4F, F<sub>A</sub>). FAB(+) m/z: 989.5 ([5 - 2OTf]<sup>2+</sup>, calc 988.6), 756.1 ([Pt(dppp)(OTf)]<sup>+</sup>, calc 756.1), 686.1 ([Au(C<sub>6</sub>F<sub>4</sub>py)(PPh<sub>3</sub>) + H]<sup>+</sup>, calc 686.1). IR (KBr, cm<sup>-1</sup>): 1480, 946 (C<sub>6</sub>F<sub>4</sub>), 1436, 1423, 1101, 695 (dppp, PPh<sub>3</sub>), 1280, 1250, 1155, 1030, 640, 513 (OTf). Anal. Calc: C, 45.90; H, 2.83; N, 1.23. Found: C, 45.79; H, 2.79; N, 1.30.

**Synthesis of [Pd(dppp){(pyC<sub>6</sub>F<sub>4</sub>)Au(PPh<sub>3</sub>)}<sub>2</sub>](OTf)<sub>2</sub>] (6).** Details of the synthesis of [Pt(dppp){pyC<sub>6</sub>F<sub>4</sub>)Au(PPh<sub>3</sub>)}<sub>2</sub>](OTf)<sub>2</sub>] were also applied to the preparation of 6, but in this case, hexane was used to precipitate instead of diethyl ether. Yield: 80% (35 mg). <sup>1</sup>H NMR (298 K, CDCl<sub>3</sub>): 9.08 (d, J(H-H) = 5.5 Hz, 4H,  $H_{\alpha$ -pyr}), 7.67–7.36 (m, 50H, Ph), 7.18 (d, J(H-H) = 5.2 Hz, 4H,  $H_{\beta$ -pyr}), 3.23 (br, 4H, PCH<sub>2</sub>), 2.26 (m, 2H, PCH<sub>2</sub>CH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (298 K, CDCl<sub>3</sub>): 42.0 (t, <sup>4</sup>J(P-F) = 8.8 Hz, PPh<sub>3</sub>), 5.7 (s, dppp). <sup>19</sup>F NMR (298 K, CDCl<sub>3</sub>, inset D<sub>2</sub>O with CF<sub>3</sub>COOH): -81.0 (s, 6F, OTf), -118.8 (m, 4F, F<sub>X</sub>), -146.9 (m, 4F, F<sub>A</sub>). FAB(+) m/z: 944.2 ([6 – 2OTf]<sup>2+</sup>, calc 944.6), 686.1 ([Au(C<sub>6</sub>F<sub>4</sub>py)(PPh<sub>3</sub>) + H]<sup>+</sup>, calc 686.1), 667.8 ([Pd(dppp)(OTf)]<sup>+</sup>, calc 668.0), 518.1 ([Pd(dppp) - H]<sup>+</sup>, calc 518.0). IR (KBr, cm<sup>-1</sup>): 1480, 946 (C<sub>6</sub>F<sub>4</sub>), 1435, 1424, 1101, 695 (dppp, PPh<sub>3</sub>), 1283, 1253, 1155, 1030, 635, 516 (OTf). Anal. Calc: C, 47.76; H, 2.95; N, 1.28. Found: C, 47.59; H, 2.99; N, 1.31.

Synthesis of [Pt(dppf){(pyC<sub>6</sub>F<sub>4</sub>)Au(PPh<sub>3</sub>)}<sub>2</sub>](OTf)<sub>2</sub> (7). Solid  $[Pt(dppf)(H_2O)_2](OTf)_2$  (11 mg, 0.01 mmol) was added to a dichloromethane (5 mL) solution of  $[Au(C_6F_4py)(PPh_3)]$  (14 mg, 0.02 mmol). The solution was stirred under reflux for 24 h. Then, the mixture was filtered and concentrated to ca. 2 mL, and diethyl ether was added in order to complete the precipitation of the product. A yellow solid was obtained in 81% yield (20 mg). <sup>1</sup>H NMR (298 K, CDCl<sub>3</sub>): 9.01 (d, J(H-H) = 3.8 Hz, 4H,  $H_{\alpha-pyr}$ ), 7.88–7.46 (m, 50H, Ph), 7.17 (d,  $J(H-H) = 5.8 \text{ Hz}, 4H, H_{\beta-\text{pyr}}), 4.82 \text{ (br, 4H, } H_{\alpha-\text{ferr}}), 4.56 \text{ (br, 4H, } H_{\beta-\text{ferr}}).^{31}P\{^{1}H\} \text{ NMR} (298 \text{ K}, \text{CDCl}_3): 41.9 \text{ (t, }^{4}J(P-F) = 7.8 \text{ Hz}, \text{PPh}_3),$ 3.5 (s,  ${}^{1}J(P-Pt) = 3410$  Hz, dppf).  ${}^{19}F$  NMR (298 K, CDCl<sub>3</sub>, inset D<sub>2</sub>O with CF<sub>3</sub>COOH): -80.5 (s, 6F, OTf), -118.0 (m, 4F, F<sub>X</sub>), -146.1 (m, 4F,  $F_A$ ). ESI(+) m/z: 1060.0 ([7 - 20Tf]<sup>2+</sup>, calc 1059.6), 898.0 ([Pt(dppf)(OTf)]<sup>+</sup>, calc 898.0), 749.0 ([Pt(dppf)]<sup>+</sup>, calc 749.0), 687.0  $([Au(C_6F_4py)(PPh_3) + H]^+, calc 686.1)$ . IR (KBr, cm<sup>-1</sup>): 1480, 946 (C<sub>6</sub>F<sub>4</sub>), 1435, 1424, 1097, 695 (dppf, PPh<sub>3</sub>), 1281, 1247, 1153, 1030, 636, 495 (OTf). Anal. Calc: C, 46.68; H, 2.75; N, 1.16. Found: C, 46.55; H, 2.80; N, 1.11.

**Synthesis of [Pd(dppf){(pyC<sub>6</sub>F<sub>4</sub>)Au(PPh<sub>3</sub>)}<sub>2</sub>](OTf)<sub>2</sub> (8).** Details of the synthesis of 5 were also applied to the preparation of this compound. Yield: 78% (36 mg). <sup>1</sup>H NMR (298 K, CDCl<sub>3</sub>): 8.98 (d, J(H-H) = 6.0 Hz, 4H,  $H_{\alpha-pyr}$ ), 7.90–7.46 (m, 50H, Ph), 7.13 (d, J(H-H) = 6.0 Hz, 4H,  $H_{\beta-pyr}$ ), 4.86 (br, 4H,  $H_{\alpha-ferr}$ ), 4.59 (br, 4H,  $H_{\beta-ferr}$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (298 K, CDCl<sub>3</sub>): 42.0 (t, <sup>4</sup>J(P-F) = 7.8 Hz, PPh<sub>3</sub>), 32.2 (s, dppf). <sup>19</sup>F NMR (298 K, CDCl<sub>3</sub>, inset D<sub>2</sub>O with CF<sub>3</sub>COOH): -81.5 (s, 6F, OTf), -118.8 (m, 4F, F<sub>X</sub>), -146.8 (m, 4F, F<sub>A</sub>). MALDI(+) m/z: 884.8 ([8 – 2OTf-PPh<sub>3</sub>]<sup>2+</sup>, calc 884.5), 809.8 ([Pd(dppf)(OTf)]<sup>+</sup>, calc: 810.0), 686.0 ([Au(C<sub>6</sub>F<sub>4</sub>py)(PPh<sub>3</sub>) + H]<sup>+</sup>, calc 686.1), 659.9 ([Pd(dppf) - H]<sup>+</sup>, calc 660.). IR (KBr, cm<sup>-1</sup>): 1483, 946 (C<sub>6</sub>F<sub>4</sub>), 1436, 1424, 1098, 695 (dppf, PPh<sub>3</sub>), 1280, 1248, 1152, 1029, 635, 495 (OTf). Anal. Calc: C, 48.46; H, 2.85; N, 1.20; S, 2.75. Found: C, 48.31; H, 2.82; N, 1.21; S, 2.82.

Synthesis of  $[(AuC_6F_4py)_2(\mu_2-dppm)]$  (9). A dichloromethane solution (10 mL) of dppm (58 mg, 0.15 mmol) was added to a dichloromethane solution (10 mL) of  $[Au(C_6F_4py)(tht)]$  (150 mg,

0.30 mmol) at room temperature. After 1 h of stirring, the reaction mixture was filtered through Celite, concentrated to 5 mL under vacuum, and precipitated with hexane (20 mL). During all the manipulations the solution was protected from light in order to avoid decomposition. A white solid was obtained in 79% yield (145 mg). <sup>1</sup>H NMR (298 K, CDCl<sub>3</sub>): 8.52 (d, J(H-H) = 5.5 Hz, 4H,  $H_{\alpha$ -pyr), 7.75–7.35 (m, 20H, Ph), 7.20 (d, J(H-H) = 4.8 Hz, 4H,  $H_{\beta$ -pyr), 3.70 (t, 2H, J(H-P) = 10.8 Hz,  $P-CH_2-P$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (298 K, CDCl<sub>3</sub>): 33.7 (s). <sup>19</sup>F NMR (298 K, CDCl<sub>3</sub>): -117.0 (m, 4F, F<sub>X</sub>), -145.5 (m, 4F, F<sub>A</sub>). FAB(+) m/z: 1231.4 ([9 + H]<sup>+</sup>, calc 1231.1), 1004.5 ([9 -  $C_6F_4py$ ]<sup>+</sup>, calc 1005.0), 808.4 ([9 - AuC<sub>6</sub>F<sub>4</sub>py]<sup>+</sup>, calc 808.1). IR (KBr, cm<sup>-1</sup>): 1436, 1101, 690 (dppm). Anal. Calc: C, 45.87; H, 2.46; N, 2.28. Found: C, 45.77; H, 2.45; N, 2.23.

**Synthesis of** [(AuC<sub>6</sub>F<sub>4</sub>py)<sub>2</sub>( $\mu_2$ -dppip)] (10). Details of the synthesis of 9 were also applied to the preparation of this compound. A white solid was obtained in 65% yield (122 mg). <sup>1</sup>H NMR (298 K, CDCl<sub>3</sub>): 8.52 (d, *J*(H–H) = 4.2 Hz, 4H, H<sub>α-pyr</sub>), 8.05–7.36 (m, 20H, Ph), 7.20 (d, *J*(H–H) = 4.2 Hz, 4H, H<sub>β-pyr</sub>), 1.80 (t, 6H, *J*(H–P) = 14.7 Hz, P–C(CH<sub>3</sub>)<sub>2</sub>–P). <sup>31</sup>P{<sup>1</sup>H} NMR (298 K, CDCl<sub>3</sub>): 56.7 (br). <sup>19</sup>F NMR (298 K, CDCl<sub>3</sub>): -117.3 (m, 4F, F<sub>x</sub>), -145.5 (m, 4F, F<sub>A</sub>). ESI(+) *m*/*z*: 1259.1 ([10 + H]<sup>+</sup>, calc 1259.1); 630.3 ([10+2H]<sup>+</sup>, calc 630.1). IR (KBr, cm<sup>-1</sup>): 1436, 1100, 693 (dppip). Anal. Calc: C, 46.76; H, 2.72; N, 2.23. Found: C, 46.62; H, 2.74; N, 2.24.

**Synthesis of** [(AuC<sub>6</sub>F<sub>4</sub>py)<sub>2</sub>( $\mu_2$ -dppe)] (11). Details of the synthesis of 9 were also applied to the preparation of this compound. A white solid was obtained in 85% yield (158 mg). <sup>1</sup>H NMR (298 K, CDCl<sub>3</sub>): 8.70 (d, *J*(H−H) = 6.4 Hz, 4H, H<sub>α-pyr</sub>), 7.85–7.45 (m, 20H, Ph), 7.42 (d, 4H, H<sub>β-pyr</sub>), 2.86 (s, br, 2H, P−(CH<sub>2</sub>)<sub>2</sub>−P). <sup>31</sup>P{<sup>1</sup>H} NMR (298 K, CDCl<sub>3</sub>): 39.0 (s). <sup>19</sup>F NMR (298 K, CDCl<sub>3</sub>): −117.3 (m, 4F, F<sub>X</sub>), −144.8 (m, 4F, F<sub>A</sub>). FAB(+) *m/z*: 1244.9 ([11 + H]<sup>+</sup>, calc 1244.9); 1018.3 ([11 − C<sub>6</sub>F<sub>4</sub>py], calc 1018.0); 821.8 ([11 − AuC<sub>6</sub>F<sub>4</sub>py], calc 821.0). IR (KBr, cm<sup>-1</sup>): 1442, 1409, 1104 (dppe). Anal. Calc: C, 46.32; H, 2.59; N, 2.25. Found: C, 46.45; H, 2.61; N, 2.28.

**Synthesis of** [(AuC<sub>6</sub>F<sub>4</sub>py)<sub>2</sub>( $\mu_2$ -dppet)] (12). Details of the synthesis of 9 were also applied to the preparation of this compound. A white solid was obtained in 60% yield (111 mg). <sup>1</sup>H NMR (298 K, CDCl<sub>3</sub>): 8.71 (d, *J*(H−H) = 4.0 Hz, 4H, H<sub>α-pyr</sub>), 7.74−7.53 (m, 22H, Ph + P−CH=CH−P), 7.42 (d, *J*(H−H) = 4.0 Hz, 4H, H<sub>β-pyr</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (298 K, CDCl<sub>3</sub>): 39.4 (br). <sup>19</sup>F NMR (298 K, CDCl<sub>3</sub>): -117.3 (m, 4F, F<sub>X</sub>), -144.7 (m, 4F, F<sub>A</sub>). ESI(+) *m*/*z*: 1243.1 ([12 + H]<sup>+</sup>, calc 1243.1); 622.1 ([12 + 2H]<sup>2+</sup>, calc 622.1). IR (KBr, cm<sup>-1</sup>): 1436, 1100, 688 (dppet). Anal. Calc: C, 46.39; H, 2.43; N, 2.25. Found: C, 46.31; H, 2.44; N, 2.21.

**Synthesis of** [(AuC<sub>6</sub>F<sub>4</sub>py)<sub>2</sub>( $\mu_2$ -dppa)] (13). Details of the synthesis of 9 were also applied to the preparation of this compound. A white solid was obtained in 70% yield (130 mg). <sup>1</sup>H NMR (298 K, CDCl<sub>3</sub>): 8.72 (d, *J*(H–H) = 5.1 Hz, 4H, H<sub>α-pyr</sub>), 7.90–7.54 (m, 20H, Ph), 7.47 (d, *J*(H–H) = 4.8 Hz, 4H, H<sub>β-pyr</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (298 K, CDCl<sub>3</sub>): 19.4 (br). <sup>19</sup>F NMR (298 K, CDCl<sub>3</sub>): -116.8 (m, 4F, F<sub>X</sub>), -144.5 (m, 4F, F<sub>A</sub>). ESI(+) *m/z*: 1241.6 ([13 + H]<sup>+</sup>, calc 1241.1); 621.7 ([13 + 2H]<sup>2+</sup>, calc 621.1). IR (KBr, cm<sup>-1</sup>): 1436, 1099, 692 (dppa). Anal. Calc: C, 46.47; H, 2.27; N, 2.26. Found: C, 46.39; H, 2.24; N, 2.22.

**Synthesis of** [(AuC<sub>6</sub>F<sub>4</sub>py)<sub>2</sub>( $\mu_2$ -dppp)] (14). Details of the synthesis of 9 were also applied to the preparation of this compound. A white solid was obtained in 88% yield (165 mg). <sup>1</sup>H NMR (298 K, CDCl<sub>3</sub>): 8.73 (d, *J*(H−H) = 6.1 Hz, 4H, H<sub>α-pyr</sub>), 7.78−7.44 (m, 24H, Ph + H<sub>β-pyr</sub>), 3.06−2.97 (m, 4H, P−CH<sub>2</sub>−CH<sub>2</sub>−CH<sub>2</sub>−P), 2.12−1.98 (m, 2H, P−CH<sub>2</sub>−CH<sub>2</sub>−CH<sub>2</sub>−CH<sub>2</sub>−P). <sup>31</sup>P{<sup>1</sup>H} NMR (298 K, CDCl<sub>3</sub>): 34.6 (t, <sup>4</sup>*J*(P−F) = 7.5 Hz). <sup>19</sup>F NMR (298 K, CDCl<sub>3</sub>): −116.7 (m, 4F, F<sub>x</sub>), −145.0 (m, 4F, F<sub>A</sub>). FAB(+) *m/z*: 1258.3 ([14 + H]<sup>+</sup>, calc 1259.1). IR (KBr, cm<sup>-1</sup>): 1445, 1104, 691 (dppp). Anal. Calc: C, 46.76; H, 2.72; N, 2.23. Found: C, 46.89; H, 2.75; N, 2.28.

Synthesis of  $[(AuC_6F_4py)_2(\mu_2-dppb)]$  (15). Details of the synthesis of 9 were also applied to the preparation of this compound.

A white solid was obtained in 70% yield (130 mg). <sup>1</sup>H NMR (298 K, CDCl<sub>3</sub>): 8.71 (d, J(H–H) = 6.0 Hz, 4H, H<sub>G-pyr</sub>), 7.74–7.45 (m, 20H, Ph), 7.44 (d, J(H–H) = 5.4 Hz, 4H, H<sub> $\beta$ -pyr</sub>), 2.54 (m, 4H, P–CH<sub>2</sub>–(CH<sub>2</sub>)<sub>2</sub>–CH<sub>2</sub>–P), 1.97 (br, 4H, P–CH<sub>2</sub>–(CH<sub>2</sub>)<sub>2</sub>–CH<sub>2</sub>–P). <sup>31</sup>P{<sup>1</sup>H} NMR (298 K, CDCl<sub>3</sub>): 39.2 (t, <sup>4</sup>J(P–F) = 8.0 Hz). <sup>19</sup>F NMR (298 K, CDCl<sub>3</sub>): -116.9 (m, 4F, F<sub>X</sub>), -144.8 (m, 4F, F<sub>A</sub>). FAB(+) m/z: 1272.3 ([15 + H]<sup>+</sup>, calc 1273.1); 1046.2 ([15 – C<sub>6</sub>F<sub>4</sub>py]<sup>+</sup>, calc 1047.1) . IR (KBr, cm<sup>-1</sup>): 1435, 1098, 693 (dppb). Anal. Calc: C, 47.19; H, 2.85; N, 2.20. Found: C, 47.07; H, 2.84; N, 2.25.

**Synthesis of** [(AuC<sub>6</sub>F<sub>4</sub>py)<sub>2</sub>( $\mu_2$ -dppdph)] (16). Details of the synthesis of 9 were also applied to the preparation of this compound. A white solid was obtained in 58% yield (120 mg). <sup>1</sup>H NMR (298 K, CDCl<sub>3</sub>): 8.70 (d, *J*(H−H) = 5.1 Hz, 4H, H<sub>α-pyr</sub>), 7.72−7.47 (m, 28H, Ph + P−(C<sub>6</sub>H<sub>4</sub>)−P), 7.28 (br, 4H, H<sub>β-pyr</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (298 K, CDCl<sub>3</sub>): 42.9 (t, <sup>4</sup>*J*(P−F) = 8.0 Hz). <sup>19</sup>F NMR (298 K, CDCl<sub>3</sub>): −116.7 (m, 4F, F<sub>X</sub>), −144.8 (m, 4F, F<sub>A</sub>). ESI(+) *m*/*z*: 1369.5 ([16 + H]<sup>+</sup>, calc 1369.2); 685.8 ([16 + 2H]<sup>2+</sup>, calc 685.1). IR (KBr, cm<sup>-1</sup>): 1436, 1104, 692 (dppdph). Anal. Calc: C, 50.89; H, 2.65; N, 2.05. Found: C, 50.71; H, 2.69; N, 2.03.

**Synthesis of** [(AuC<sub>6</sub>F<sub>4</sub>py)<sub>3</sub>( $\mu_3$ -triphos)] (17). A dichloromethane solution (10 mL) of triphos (60 mg, 0.10 mmol) was added to a dichloromethane solution (15 mL) of [Au(C<sub>6</sub>F<sub>4</sub>py)(tht)] (153 mg, 0.30 mmol) at room temperature. After 1 h of stirring, the reaction mixture was filtered through Celite, concentrated to 5 mL under vacuum, and precipitated with hexane (20 mL). During all the manipulations the solution was protected from the light in order to avoid decomposition. A white solid was obtained in 84% yield (160 mg). <sup>1</sup>H NMR (298 K, CDCl<sub>3</sub>): 8.67 (d, *J*(H−H) = 6.0 Hz, 6H, H<sub>α-pyr</sub>), 7.75−7.29 (m, 36H, Ph + H<sub>β-pyr</sub>), 3.32 (d, *J*(H−P) = 10.8 Hz, 6H, CH<sub>2</sub>), 1.19 (s, 3H, CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (298 K, CDCl<sub>3</sub>): 21.4 (br). <sup>19</sup>F NMR (298 K, CDCl<sub>3</sub>): −117.8 (m, 6F, F<sub>X</sub>), −144.5 (m, 6F, F<sub>A</sub>). ESI(+) *m/z*: 1894.5 ([17 + H]<sup>+</sup>, calc 1894.2). IR (KBr, cm<sup>-1</sup>): 1442, 1409, 1097 (C<sub>6</sub>F<sub>4</sub>py). Anal. Calc: C, 46.93; H, 2.71; N, 2.22. Found: C, 46.99; H, 2.73; N, 2.23.

**Synthesis of [(AuC<sub>6</sub>F<sub>4</sub>py)<sub>3</sub>(\mu\_3-triphosph)] (18).** Details of the synthesis of 17 were also applied to the preparation of this compound. A white solid was obtained in 60% yield (114 mg). <sup>1</sup>H NMR (298 K, CD<sub>2</sub>Cl<sub>2</sub>): 8.65 (d, J(H–H) = 6.0 Hz, 6H, H<sub>α-pyr</sub>), 7.82 (t, J(H–P) = 12.0 Hz, 3H, P–C<sub>6</sub>H<sub>3</sub>–P), 7.54–7.41 (m, 30H, Ph), 7.37 (d, J(H–H) = 4.4 Hz, 6H, H<sub>β-pyr</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (298 K, CD<sub>2</sub>Cl<sub>2</sub>): 43.3. <sup>19</sup>F NMR (298 K, CD<sub>2</sub>Cl<sub>2</sub>): -117.2 (m, 6F, F<sub>X</sub>), -145.5 (m, 6 F, F<sub>A</sub>). ESI(+) m/z: 1900.2 ([18 + H]<sup>+</sup>, calc 1900.2); 950.6 ([18 + 2H]<sup>2+</sup>, calc 950.6). IR (KBr, cm<sup>-1</sup>): 1436, 1101, 691 (triphosph). Anal. Calc: C, 47.41; H, 2.39; N, 2.21. Found: C, 47.46; H, 2.41; N, 2.20.

Synthesis of  $[(AuC_6F_4py)_4(\mu_4\text{-tetraphos})]$  (19). A dichloromethane solution (10 mL) of tetraphos (80 mg, 0.10 mmol) was added to a dichloromethane solution (20 mL) of  $[Au(C_6F_4py)(\text{tht})]$  (204 mg, 0.40 mmol) at room temperature. After 45 min of stirring, the reaction mixture was filtered through Celite, concentrated to 5 mL under vacuum, and precipitated with hexane (20 mL). During all the manipulations the solution was protected from light in order to avoid decomposition. A white solid was obtained in 64% yield (160 mg). <sup>1</sup>H NMR (298 K, CDCl<sub>3</sub>): 8.68 (d, J(H-H) = 6.0 Hz, 88H,  $H_{\alpha\text{-pyr}}$ ), 7.99–6.65 (m, 48H, Ph +  $H_{\beta\text{-pyr}}$ ), 3.14 (s, br, 8H, CH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (298 K, CDCl<sub>3</sub>): 24.1. <sup>19</sup>F NMR (298 K, CDCl<sub>3</sub>): -114.9 (m, 8F, F<sub>X</sub>), -145.3 (m, 8F, F<sub>A</sub>). FAB(+) m/z: 2502.2 ([19 + H]<sup>+</sup>, calc 2501.2); 1251.5 ([19 + 2H]<sup>2+</sup>, calc 1251.1). IR (KBr, cm<sup>-1</sup>): 1446, 1408, 1099 (tetraphos). Anal. Calc: C, 46.58; H, 2.58; N, 2.24. Found: C, 46.60; H, 2.59; N, 2.23.

Synthesis of [(AuC<sub>6</sub>F<sub>4</sub>py)<sub>4</sub>( $\mu_4$ -tetraphosph)] (20). Details of the synthesis of 19 were also applied to the preparation of this compound. A white solid was obtained in 64% yield (161 mg). <sup>1</sup>H NMR (298 K, CDCl<sub>3</sub>): 8.60 (d, J(H-H) = 5.8 Hz, 8H,  $H_{\alpha$ -pyr}), 7.40–7.10 (m, 50H, Ph + P-C<sub>6</sub>H<sub>2</sub>-P + H<sub> $\beta$ -pyr</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR

 $\begin{array}{l} (298 \ K, \ CDCl_3): \ 36.9 \ (br). \ ^{19}F \ NMR \ (298 \ K, \ CDCl_3): -116.6 \ (m, \ 8F, \ F_X), \ -145.1 \ (m, \ 8F, \ F_A). \ ESI(+) \ m/z: \ 2507.7 \ ([\mathbf{20} + H]^+, \ calc \ 2507.2); \ 1254.6 \ ([\mathbf{20} + 2H]^{2+}, \ calc \ 1254.1); \ 836.7 \ ([\mathbf{20} + 3H]^{3+}, \ calc \ 836.4). \ IR \ (KBr, \ cm^{-1}): \ 1436, \ 1105, \ 690 \ (tetraphosph). \ Anal. \ Calc: \ C, \ 46.95; \ H, \ 2.33; \ N, \ 2.23. \ Found: \ C, \ 46.90; \ H, \ 2.31; \ N, \ 2.20. \end{array}$ 

# ASSOCIATED CONTENT

**Supporting Information.** CIF file giving X-ray crystallographic data for the structural characterization of compounds  $BrC_6F_4py$ , **1**, **4**, **17**, and **19**. X-ray structure of  $BrC_6F_4py$  and views of crystal packing of  $BrC_6F_4py$ , **1**, **4**, and **19**. This material is available free of charge via the Internet at http://pubs.acs.org.

#### AUTHOR INFORMATION

# **Corresponding Author**

\*E-mail: montse.ferrer@qi.ub.es.

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