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A Dinuclear Au(I) Complex with a Pyrene-di-N-heterocyclic Carbene Linker: Supramolecular and Catalytic Studies

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Supporting Information

ABSTRACT: A digold(I) complex with a pyrene-di-N-heterocyclic carbene ligand has been obtained and fully characterized. The host-guest properties of the complex were studied in chloroform with a series of polycylic aromatic hydrocarbons (PAHs), and the association constants were determined. The affinity increases with the size of the PAH, with a maximum binding constant of 105 M⁻¹ for the aggregation with coronene. The catalytic activity of the complex was tested in the hydroamination of phenylacetylene with three different amines. The studies showed that the addition of coronene to the reaction medium produces an enhancement of about 20-30% in the activity of the complex.

■ INTRODUCTION

Over the last two decades, the field of metallosupramolecular chemistry has experienced great development due to its wide range of applications in fields such as molecular recognition,¹ drug delivery,² light-emitting materials,³ and homogeneous catalysis.⁴ The basis for metallosupramolecular design is the availability of rigid bridging ligands, which in combination with metals form well-defined architectures with a variety of shapes and sizes.⁵ Most known metallosupramolecular molecules, or supramolecular coordination compounds (SCCs),⁶ are based on Werner-type polydentate ligands, and only recently have organometallic ligands (mostly based on poly-N-heterocyclic carbenes⁷) allowed the preparation of diverse types of SCCs including discrete molecules⁸ and polymers.⁹ In line with this field of research, our group has recently been interested in developing a library of rigid multidentate ligands bearing polyaromatic substituents, which have been used for the preparation of several metallosupramolecular assemblies. While our initial interest was to study how supramolecular interactions influenced the catalytic performance of our supra-organometallic complexes,¹⁰ we recently became interested in designing metal-driven self-assembly architectures for the recognition of organic substrates¹¹ and metal cations.¹²

SCCs are often called "molecular flasks"¹³ because they show well-defined nanoscopic cavities. These cavities are arguably responsible for their wide set of applications, mostly because they facilitate the selective encapsulation and recognition of organic substrates. We recently reported a series of Au(I) complexes bearing N-heterocyclic carbene (NHC) ligands fused to polycyclic aromatic hydrocarbons.¹⁴ In our work, we found that the catalytic performance of the complexes was significantly enhanced by the addition of a polycyclic aromatic hydrocarbon (PAH) such as pyrene. In order to study the



nature of the supramolecular interactions between our metal complexes and pyrene, we performed some preliminary hostguest chemistry studies, which allowed us to determine the association constants between our complexes and pyrene (K = 12 M^{-1} in CD₃CN). Prompted by this finding, in this new work we describe the preparation of a one-dimensional (1D) organometallic complex (not showing a cavity) that exhibits interactions with a variety of PAHs. For the preparation of this 1D organometallic receptor, we envisioned that our previously reported planar pyrene-connected di-NHC ligand¹⁵ (see Scheme 1) could act as an effective supramolecular antenna for interacting with aromatic guests. We decided to coordinate this ligand to Au(I) in order to obtain a linear structure that could minimize any undesired steric repulsions and therefore optimize the π -stacking interactions between the complex and the organic guests. The host-guest chemistry properties of this new complex are described herein.

RESULTS AND DISCUSSION

Pyrenebis(azolium) salt 1 was used as the NHC precursor for the synthesis of di-NHC-Au(I) complex 2. As depicted in Scheme 1, complex 2 was obtained by deprotonation of bis(azolium) salt 1 with potassium bis(trimethylsilyl)amide (KHMDS) and subsequent addition of [AuCl(SMe₂)]. After purification, complex 2 was obtained in 60% yield. The ¹H and ¹³C NMR spectra of **2** are in accordance with the pseudo- D_{2h} symmetry of the molecule. The ¹³C NMR spectrum reveals the

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Scheme 1. Synthesis of Complex 2



characteristic singlet assigned to the resonance of the two equivalent carbone carbons at 188.9 ppm.

Single crystals suitable for X-ray diffraction were obtained by slow diffusion of methanol into a solution of **2** in chloroform. The structure consists of a pyrenebis(imidazolylidene) ligand bridging two AuI units (Figure 1). The iodide and NHC



Figure 1. Molecular structure of **2.** Hydrogen atoms and solvent have been omitted for clarity. Thermal ellipsoids are shown at the 50% level of probability. Selected bond distances (Å) and angles (deg): Au1–C1 2.003(6), Au1–I1 2.5416(4), C1–Au1–I1 177.15(16), N1–C1–N2 107.5(5).

ligands are coordinated to the Au(I) centers in a quasi-linear geometry, as shown by the I–Au– $C_{\rm NHC}$ angle of 177.15°. The Au– $C_{\rm NHC}$ bond distance is 2.003 Å, and the through-space distance between the two Au centers is 13.15 Å, which is very similar to the M–M distance provided by the same ligand in our previously reported complexes of rhodium, iridium, ^{15a} ruthenium, ^{15c} and platinum.¹⁶

Given that the packing properties of complex 2 are highly influenced by π -stacking interactions (Figure 2), we decided to study the morphology of the bulk solid by scanning electron microscopy (SEM). Previous studies have shown that the rational design of supramolecular interactions may determine the morphology of the bulk material by the formation of highly



Figure 2. Detail of the crystal packing of **2** showing the π -stacking interactions along the *a* axis.

ordered nanostructures, such as spheres, nanoplates, fibers, or helical ribbons.¹⁷ As can be observed in Figure 3, SEM images of **2**, prepared by slow diffusion of MeOH into a saturated solution of the complex in chloroform, show laminar ribbons.



Figure 3. SEM images of **2**, prepared by slow diffusion of MeOH into a saturated solution of the complex in chloroform, at (a) lower and (b) higher magnifications.

We thought that the structural and electronic features of 2 should make it a good candidate for exploring its host-guest chemistry properties, despite the obvious fact that the complex does not exhibit any well-defined cavity for the encapsulation of organic guests. The recognition abilities of 2 were studied by ¹H NMR titration experiments in CDCl₃ by monitoring the variation of the chemical shifts of the signals of the complex upon addition of solutions containing the different polyaromatic guests. We first confirmed that the self-association of 2 in CDCl₃ was negligible by measuring a series of spectra of the complex in CDCl₃ at concentrations ranging from 0.2 to 20 mM. All of the titrations with guests were performed at a constant concentration of 2. In general, the addition of the solution of the guest induced important perturbations in the ¹H NMR spectra, indicating the formation of host-guest aggregates that showed fast kinetics on the NMR time scale. Figure 4 shows an example of the titration of 2 with coronene. As can be observed, the addition of incremental amounts of coronene induces an upfield shift of the signals due to the



Figure 4. Representative region of the ¹H NMR (400 MHz) spectra of the titration of **2** with coronene in CDCl_3 . The spectra were recorded at a constant concentration of **2** (0.4 mM).

proton of the host pyrene linker and the protons of the NCH₂ groups of the *n*-butyl wingtips. This observation is a clear indication that a π -stacking interaction between coronene and **2** occurs through the pyrene linker of the host. The analysis of the binding isotherm generated by this titration is consistent with a 1:1 host:guest stoichiometry, and an association constant of 105 \pm 1 M⁻¹ was determined by global nonlinear regression.¹⁸ A Job plot was also made in order to confirm the formation of the 1:1 host-guest complex (see the Supporting Information for details).

By means of a similar procedure, the association constants of **2** with a series of PAHs were also calculated. As can be observed from the data shown in Table 1, the binding affinities

Table 1. Association Constants K for the Complexation of 2 with PAHs^{*a*}

entry	guest	$K(M^{-1})$
1	phenanthrene	-
2	pyrene	4 ± 1
3	triphenylene	10 ± 1
4	perylene	17 ± 1
5	coronene	150 ± 1

^{*a*}The association constants were calculated by global nonlinear regression analysis¹⁸ using the HypNMR2008 program. Titrations were carried out using constant concentrations of 2 (0.3-0.4 mM) in CDCl₃ at 298 K. Errors refer to the nonlinear regression fits.

of the PAH guests increase in the order phenanthrene < pyrene < triphenylene < perylene < coronene (entries 1–5). This trend is in accordance with previous reports when receptors with large portals were used^{11b,c,19} and indicates that the host–guest interaction is dominated by the π surface area of the guests rather than by their degree of aromaticity.

Given the relatively high affinity of 2 to associate with coronene, we wanted to test whether this would have consequences for the catalytic performance of the complex. We recently showed how the addition of π -stacking additives increased the catalytic activity of a series of monometallic Au(I) complexes bearing NHC ligands decorated with polyaromatic functionalities in the hydroamination of terminal alkynes.¹⁴ Initially, the reactions were carried out at 90 °C in acetonitrile using a 0.5 mol % catalyst loading with the addition of AgBF₄ as a halide scavenger. The results given in Table 2 show that full conversion was achieved after 6 h of reaction, although the yields of the desired product were lower, thus indicating that the reaction was not fully selective. However, we were not able to identify any of the possible byproducts of the reaction. In any case, under the same reaction conditions, complex 2 outperformed the related pyrene-imidazolylidene-Au(I) complex that we recently described,¹⁴ although it shows lower activity than some other previous Au-NHC catalysts reported by us²⁰ and others.²¹ In order to test whether the addition of a π -stacking additive would modify the activity of the complex, we decided to perform a series of reactions at a lower catalyst loading (0.05 mol %), aiming to find significant differences at lower conversion values. As observed from the data shown in Table 2, this low catalyst loading still afforded moderate yields of the final products with turnovers ranging from 680 to 900 depending on the substrate used (entries 4, 6, and 8). The addition of a substoichiometric amount of coronene (10 mol % with respect to substrate) produces a clear enhancement of the activity of the catalyst, with turnovers rising to 900-1160

Table 2. Hydroamination of Phenylacetylene^a



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entry	cat. (mol %)	Ar	conv. (%) ^b	yield (%) ^b	TON
1	0.5	Ph	98	66	196
2	0.5	$4-MeC_6H_4$	93	65	186
3	0.5	2,4,6-Me ₃ C ₆ H ₂	99	86	198
4	0.05	Ph	34	26	680
5 ^d	0.05	Ph	58	50	1160
6	0.05	$4-MeC_6H_4$	41	33	820
7 ^d	0.05	$4-MeC_6H_4$	45	40	900
8	0.05	2,4,6-Me ₃ C ₆ H ₂	45	36	900
9^d	0.05	2,4,6-Me ₃ C ₆ H ₂	51	44	1110

"Reaction conditions: 0.5 mmol of phenylacetylene, 0.55 mmol of amine, 0.2 or 2 mol % $AgBF_4$ (depending on the catalyst loading), 1 mL of MeCN, 90 °C, 6 h. ^bConversions and yields were determined by GC using anisole (0.5 mmol) as an internal standard. ^cTurnovers calculated as a function of converted substrates. ^dUpon the addition of 0.05 mmol of coronene.

(entries 5, 7 and 9), thus 20–30% higher than the results provided by the same catalyst in the absence of coronene. This result is in clear agreement with our previous published findings,¹⁴ which we interpret to be a consequence of the formation of π -stacking aggregates of coronene and 2, which prevents the formation of nonactive dimers formed by the self-association of 2.

CONCLUSIONS

We prepared and characterized a dimetallic complex of Au(I) with a pyrenebis(imidazolylidene) ligand. The supramolecular properties of the complex were studied with regard to the association with several polycyclic aromatic hydrocarbons. Our studies demonstrate that despite not having a cavity that would allow the formation of inclusion host-guest aggregates, the dimetallic Au(I) complex is able to associate to large PAHs, achieving association constants as high as $105 M^{-1}$ in chloroform for the case of coronene. The catalytic activity of the complex was tested in the hydroamination of phenylacetylene, where we observed that the addition of coronene to the reaction medium produced an enhancement in the activity of the catalyst of about 20-30%. In line with our previous findings in this regard, this new work demonstrates how supramolecular interactions may be used to fine-tune the catalytic activity of catalysts bearing polyaromatic functionalities.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.8b00087.

Description of synthetic procedures and characterization details, catalytic experiments, spectra of the new complex, crystallographic data, and ¹H NMR spectra of host–guest titrations (PDF)

Accession Codes

CCDC 1811341 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge

Organometallics

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Notes

The authors declare no competing financial interest.

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DEDICATION

We dedicate this article to Professor Ernesto Carmona on the occasion of his 70th birthday. Professor Carmona has been one of the strongest contributors to the development of organometallic chemistry in Spain, a good friend, and a reference for many chemistry researchers.

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Organometallics

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