Communications



Homogeneous Catalysis

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Triphenylene-Based Tris (N-Heterocyclic Carbene) Ligand: Unexpected Catalytic Benefits



Triple play: A novel triphenylene-based tris (N-heterocyclic carbene) ligand with D_{3h} symmetry and a highly π -delocalized system has been prepared and coordinated to palladium and gold (see figure).

The catalytic activities of the new complexes have been compared with those of related benzimidazolylidene and a triptycene-based tris (N-heterocyclic carbene) complexes in three reactions.

Homogeneous Catalysis

Triphenylene-Based Tris(N-Heterocyclic Carbene) Ligand: Unexpected Catalytic Benefits**

Sergio Gonell, Macarena Poyatos, and Eduardo Peris*

Sophisticated ligands that do far more than fulfill their traditional spectator roles are attracting close attention because they can provide additional functions which can be useful in catalysis.^[1] In the search for new precursors to multifunctional materials, polytopic N-heterocyclic carbene ligands (NHCs) have emerged as very promising tools.^[2] Among them, those featuring rigid geometrically isolated carbene moieties, which prevent chelation have recently found great utility as building blocks for accessing improved multimetallic catalysts,^[3] and as novel macromolecules with structurally dynamic characteristics and useful electronic properties.^[4] While most of these carbenes refer to Janustype (facially opposed) bis(NHC)s,^[3a, d-f, 5] the only known rigid tris(NHC)s with geometrically isolated carbenes is restricted to the example reported by Williams and Bielawski in 2010 (1; Figure 1).^[6] This tris(NHC) holds potential in reticular chemistry and may serve for accessing an assortment of functional organic and metal-organic frameworks, but lacks an extended π -conjugated system (the π delocalization is disrupted by the presence of the triptycene core), which limits its utility in the formation of structurally dynamic



Figure 1. Triptycene-based tris-(NHC) described by Bielawski (R = nBu and nHex). The compound with R = H has been pre-

pared for this work.

materials.^[4a,b] With these precedents in mind, we sought to obtain a star-shaped tris-(NHC) in which the three carbenes are connected by a π -delocalized polyaromatic system derived from a triphenylene core. Polyaromaticbased ligands are also interesting tools in the design of efficient homogeneous catalysts because aromatic π stacking between ligands and substrates is known to

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improve catalytic effects, especially in some asymmetric inductions.^[7] We believe that a similar effect may have some consequences in other homogeneously catalyzed reactions involving aromatic substrates,^[7a] reactions in which the catalyst–substrate interactions may be facilitated by π stacking. Given the high affinity of NHCs for a broad range of metal fragments,^[2,8] this new D_{3h} -symmetry system should provide us with an excellent building block for the preparation of a wide variety of trimetallic complexes whose properties may be easily compared to those of their monometallic analogues.

The synthesis of the triphenylene-based trisazolium salt **2** starts from the multifold amination of hexabromotriphenylene^[9] and subsequent trisannulation with triethylorthoformate in the presence of HBF₄ (Scheme 1). The deprotonation of the trisazolium salt with potassium hexamethyldisilazane-(KHMDS) in tetrahydrofuran and subsequent addition of [{PdCl(allyl)}₂] and [AuCl(SMe₂)] yields the corresponding tris(NHC) complexes of Pd (**3**) and Au (**4**), respectively. All



Scheme 1. Synthesis of the D_{3h} -symmetric trisazolium salt **2** and its coordination to Pd and Au. IPrH·HCl=1,3-bis(2,6-diisopropylphenyl)-imidazolium chloride, THF=tetrahydrofuran.

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new species (hexamine triphenylene, **2**, **3** and **4**) were fully characterized by NMR spectroscopy, high-resolution mass spectrometry (HRMS), and elemental analysis. The NMR spectra of all three species are in agreement with their threefold symmetry. The complexes **3** and **4** display their representative carbene carbon resonances in the ¹³C NMR spectra at $\delta = 193.9$ and 182.5 ppm, respectively.

Because we wanted to compare the structural and catalytic properties of both 3 and 4 with trimetallic complexes derived from the triptycene-based triscarbene 1 (R = H), we also obtained the trimetallic complexes 5 and 6 (Figure 2).



Figure 2. The trimetallic complexes 5 and 6, and the monometallic complexes 7 and 8.

Also, for comparative purposes we obtained the related monometallic complexes with a benzimidazol-2-ylidene ligand (7 and 8). It is interesting to point out that these monometallic complexes can be regarded as being exactly one of the branches (in other words, one third) of the trimetallic complexes 3 and 4. Complexes 5–8 were obtained using a similar procedure as that described for 3 and 4, starting from the corresponding azolium salts. All these new complexes were characterized by NMR spectroscopy, as well as by HRMS and elemental

analysis.

The molecular structures of the two trimetallic gold(I) complexes 4 and 6 were unambiguously confirmed by means of X-ray analysis (Figure 3). Both complexes display threefold symmetry (quasi- D_{3h}), and differs in the relative conformation of the three benzimidazolylidene fragments, which are coplanar in 4. The molecular structure of 4 consists of one triphenylene trisimidazolylidene connecting three gold fragments. The linear coordination of each metal averages a C-Au-Cl angle of 178.0(5)° and is completed by a chloride ligand. The average Au-C_{carbene} bond length is 1.997(12) Å, and the average metal-to-metal distance is 13.48(4) Å. The molecular structure of **6** consists of a triptycene-connected trisimidazolylidene coordinated to three gold fragments. The linear arrangement about the metal is confirmed by the average C-Au-Cl angle (179.8(11)°). The average Au-C_{carbene} bond length is 2.07(4) Å, and therefore very similar to the related distance shown in **4**. The average separation between the Au centers is 13.64(59) Å, which is almost identical to that in **4**.

In recent years there has been an increasing interest in developing bimetallic complexes as homogeneous catalysts.^[10] In principle, polymetallic catalysts may introduce some catalytic improvements if the metals comprised in the molecule are able to cooperate. For this cooperation to occur, it is accepted that the metals need to be in close proximity (3.5-6.0 Å),^[10b] although in some macromolecular multimetallic structures some cooperative effects have been observed at longer distances in the so-called dendrimer effect.^[11] In our case, the trimetallic complexes described in this work are far from displaying the desired close proximity between the metals, but introduce several interesting features which may have consequences in their catalytic performance. First, the trimetallic complexes afford a high local concentration of the catalytic active sites within well-defined nanoscopic reaction volumes, and this would be true for all complexes of the triptycene- and triphenylene-derived tris-(NHC)s. Second, the presence of the polyaromatic connecting group in the triphenylene complexes 3 and 4 may facilitate catalyst–substrate interactions by π stacking. To evaluate the possible cooperative effects in the trimetallic species in homogeneous catalysis, we decided to test and compare all Pd^{II} and Au^I complexes described in this work in three benchmark reactions. All three types of complexes [triphenylene tris(NHC), triptycene tris(NHC), and benzimidazolylidene], constitute excellent elements for comparison because they afford similar individual stereolectronic properties,



Figure 3. Molecular structures of **4** (left) and **6** (right).^[14] Ellipsoids shown at 50% probability level. Hydrogen atoms and solvent are omitted for clarity. Selected bond lengths [Å] and angles [°]. For **4**: C1–Au1 1.997(12), Au1–Cl1 2.297(4); C2-Au1-Cl5 175.4(3). For **6**: C3–Au1 2.10(2), Au1–Cl2 2.263(8); C22-Au1-Cl3 179.7(11).

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therefore their different catalytic outcomes (if any) could be attributed to the inherent nature of the trimetallic species, or to π -stacking effects between the aromatic substrates and the ligands.

For the evaluation of the catalytic activity of the palladium complexes **3**, **5**, and **7**, we first studied the α -arylation of propiophenone with aryl bromides. As can be seen from the data shown in Table 1, **3** repeatedly affords the best catalytic performances, with yields over 99%. The complex **5**, also affords good to excellent yields, although lower than those shown by **3**.

Table 1: α -Arylation of propiophenone with aryl bromides.^[a]

Ar-Br						
Entry	Ar	Cat	Yield [%] ^[b]			
1	Ph	3	99			
2	Ph	5	97			
3	Ph	7	75			
4	4-MeC ₆ H ₄	3	99			
5	4-MeC ₆ H ₄	5	89			
6	4-MeC ₆ H ₄	7	60			
7	$4-FC_6H_4$	3	99			
8	$4-FC_6H_4$	5	86			
9	$4-FC_6H_4$	7	69			
10	4-MeOC ₆ H ₄	3	99			
11	4-MeOC ₆ H ₄	5	85			
12	4-MeOC ₆ H ₄	7	65			

[a] Reaction conditions: 1 mol% catalyst loading (based on metal),
0.5 mmol propiophenone, 0.55 mmol arylbromide, 0.65 mmol NaOtBu,
2 mL of toluene, T=120°C, 1 h. [b] Yields determined by GC using anisole (0.5 mmol) as internal standard.

The activity of the same three complexes was also tested in the Suzuki–Miyaura coupling between aryl boronic acids and arylbromides. The results are summarized in Table 2. Again, it is observed that **3** is the one to provide the best catalytic activities for all the substrates used. Contrary to what we observed in the α -arylation of propiophenone (Table 1), the activity of the monometallic complex **7** is higher than the one shown by **5**.

Because we wanted to prove that the catalytic benefits provided by the triphenylene-based tris(NHC) were not only restricted to a couple of reactions catalyzed by palladium, we also tested the catalytic activity of the gold complexes 4, 6, and 8 in the hydroamination of terminal alkynes, a reaction for which several Au/NHC complexes have proven to be very active.^[12] Table 3 summarizes the most relevant results. All the reactions catalyzed by the trimetallic complex 4 provided yields that exceeded 90%, a result that situates this catalyst among the most active Au^I catalysts, and thus compares well with previously reported examples based on stable cyclic (alkyl)(amino)carbenes (SCAAC).^[13] The catalytic activity of the monometallic complex $\mathbf{8}$ is higher than that shown by the trimetallic complex 6, except for the reactions carried out with o-methylaniline, for which the activities are similar (entries 11 and 12). The monitoring of the reaction between o-methylani-

Table 2: Suzuki–Miyaura reaction. ^[4]							
$Z - \langle -B(OH)_2 + Br - \langle -Y - YY \rangle Z - \langle -Y - Y \rangle - Y$							
Entry	Z	Y	Cat	Yield [%] ^[b]			
1	Н	н	3	90			
2	Н	Н	5	78			
3	Н	Н	7	81			
4 ^[c]	Н	Н	3	95			
5 ^[c]	Н	Н	5	66			
6 ^[c]	Н	Н	7	71			
7 ^[d]	Н	Н	3	83			
8 ^[d]	н	Н	5	67			
9 ^[d]	Н	Н	7	66			
10	Н	OMe	3	81			
11	н	OMe	5	62			
12	Н	OMe	7	69			
13	Me	Н	3	71			
14	Me	Н	5	55			
15	Me	Н	7	61			
16	Me	OMe	3	66			
17	Me	OMe	5	36			
18	Me	OMe	7	46			

[a] Reaction conditions: T = 80 °C, 0.5 mmol arylbromide, 0.6 mmol arylboronic acid, 1 mmol Cs₂CO₃, 2 mol % [Pd], 2 mL of 1,4-dioxane, 2 h. [b] Yields determined by GC using anisole (0.5 mmol) as an internal standard. [c] Used 0.5 mmol hexafluorobenzene. [d] Used 2 mmol hexafluorobenzene.

Table 3: Hydroamination of phenylacetylene.[a]

$$Ar-NH_2 + = Ph \longrightarrow$$

Entry	Ar	Catalyst	Yield [%] ^[b]
1	2,4,6-Me ₃ C ₆ H ₂	4	94
2	2,4,6-Me ₃ C ₆ H ₂	6	87
3	2,4,6-Me ₃ C ₆ H ₂	8	89
4	2,6- <i>i</i> Pr ₂ C ₆ H ₃	4	95
5	2,6- <i>i</i> Pr ₂ C ₆ H ₃	6	54
6	2,6- <i>i</i> Pr ₂ C ₆ H ₃	8	82
7	Ph	4	95
8	Ph	6	82
9	Ph	8	91
10	$2-MeC_6H_4$	4	99
11	$2-MeC_6H_4$	6	86
12	$2-MeC_6H_4$	8	85
13 ^[c]	2-MeC ₆ H ₄	4	96
14 ^[c]	$2-MeC_6H_4$	6	81
15 ^[c]	$2-MeC_6H_4$	8	83
16 ^[d]	2-MeC ₆ H ₄	4	87
17 ^[d]	$2-MeC_6H_4$	6	62
18 ^[d]	$2-MeC_6H_4$	8	85
19	$4-MeC_6H_4$	4	91
20	4-MeC ₆ H ₄	6	60
21	$4-MeC_6H_4$	8	70

[a] Reaction conditions: 0.5 mmol phenylacetylene, 0.55 mmol amine, 1% mol [Au], 2% mol AgBF₄, 1 mL of MeCN at 90°C, 6 h. [b] Yields determined by GC using anisole (0.5 mmol) as internal standard. [c] Used 0.5 mmol hexafluorobenzene. [d] Used 2 mmol hexafluorobenzene.

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line and phenylacetylene (see Figure S1 in the Supporting Information), reveals that **4** affords almost quantitative yields of the desired product after 3 hours, therefore implying that the catalytic differences between the three complexes under study may be even higher than the ones reflected in Table 3 (all data refer to yields after a 6 h reaction time).

From the results shown in the three benchmark reactions tested, it can be concluded that the triphenylene-based complexes 3 and 4 are the ones that afford the best catalytic results. To prove our initial hypothesis that the catalytic differences between these three complexes should be mainly attributed to the higher local concentration of the catalytic active species in the trimetallic complexes, or to the possibility of a π -stacking interaction between aromatic substrates and the polyaromatic core of the triphenylene-based compounds, we performed some experiments. First, we performed a stability test of all complexes, by leaving them in refluxing CD₃CN in the presence of an internal standard. The results show that the triptycene-based complexes 5 and 6 fully decompose after 3 hours, while the complexes derived of the triphenylene-based and benzimidazolylidene ligands display higher stabilities (decomposition below 50%). This simple result indicates that the lower activity of 5 and 6 may be attributed to their reduced stability, and therefore we cannot disregard that the trimetallic nature of the catalysts derived from the triptycene- and triphenylene-based ligands may benefit the catalytic outcomes of the reaction, compared to their monometallic counterparts.

We also performed some catalytic reactions in the presence of hexafluorobenzene (HFB). HFB is known to be an extremely good π -stacking agent, and therefore its addition to the reaction media may modify the catalytic properties of the catalysts while being inert to the reaction conditions. As can be seen from the results depicted in Tables 2 and 3, the addition of HFB to the reaction media has an influence in the catalytic activities of the complexes. HFB seems to only affect the activities of the trimetallic complexes, and it strongly depends on the amount of HBF added to the reaction medium. These observations lead us to conclude that there should be an influence derived from the π -stacking effect, although further studies are needed to determine its exact nature.

In summary, we have prepared a new type of rigid, planar tris(NHC) based on a triphenylene core, which we have coordinated to palladium and gold. We have focused our attention on the study of the catalytic activities of the trimetallic complexes derived from our new ligand, and experimentally proved that it provides a significant catalytic benefit compared with that of the trimetallic and monometallic complexes formally having the same stereoelectronic properties, a benefit which is reproduced in three different catalytic reactions using two different metals. We believe that the unique topological properties of our new triphenylene-based tris(NHC) may facilitate the interaction between aromatic substrates and the catalyst through π stacking, and that this effect may open a new conceptual approach for the design of improved homogeneous catalysts.

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