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N-Heterocyclic Carbene Ligands as Modulators of Luminescence in Three-Coordinate Gold(I) Complexes with Spectacular Quantum Yields

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Supporting Information

ABSTRACT: The first three-coordinate gold(I) N-heterocyclic carbene (NHC) complexes have been prepared with the *nido*-carborane diphosphine. The complexes are brightly luminescent and present very high quantum yield values. The carbene ligand is able to modulate the energy of the emissions and, depending upon the substituent, the luminescence changes from blue to green. Theoretical calculations corroborate that the emissions are phosphorescence and arise from charge transfer (LML′CT) transitions from *nido*-carborane ligand (L) to metal/ligand group "gold(I)−NHC ligand" (ML′).

The chemistry of the synthesis, characterization, and application of new N-heterocyclic carbene (NHC) transition metal complexes has undergone rapid development in the past few years.[1] In particular gold NHC complexes have attracted a great deal of interest because the numerous applications in catalysis, medicine, and materials chemistry.[2] An important property shown by these gold NHC species is their luminescence. Several complexes have been described in which the emissive nature of the compounds is due to the presence of metallophilic interactions, the π delocalized nature of the substituents in the imidazole ring, or the coordination to a chromophore ligand.[3]

The great coordination capacity of NHCs toward transition metals has allowed many complexes to be obtained which contain, in addition to the NHC ligand, different organic and inorganic functions coordinated to the metal, such as halogens, pseudohalogens, pyridines, or even labile molecules.[4] Surprisingly, there are few examples of (NHC) gold(I) phosphine complexes reported in the literature, although both ligands form very strong bonds to the gold center, and the first $[\mathrm{NHC{-}Au{-}PR_3}]^+$ adduct was reported by Grützmacher et al. in 2002. Until now only a few cationic NHC gold(I) phosphine complexes have been reported, all of which contain one phosphorus atom bonded directly to the metal center and in all cases the coordination around the metal center is of a linear nature.[5] The gold(I) center shows a clear preference for a linear geometry, and to the best of our knowledge all the NHC compounds reported have a linear environment around the metal, and only in some cases there is a distortion of the geometry when interactions with other metals are present.[6]

It is well-known that many of the three-coordinate phosphine gold(I) complexes show luminescent properties, and these are mainly attributed to a metal centered phosphorescence, in which the geometry changes in the excited state and arise from a Jahn−Teller distortion toward a T-shape.[7]

We have previously reported that complexes of the form $[\mathrm{AuCl(PR_3)}]$ react with different carborane diphosphines to afford the corresponding three-coordinate gold(I) complexes $[\mathrm{Au\{(PR)_2C_2B_9H_{10}\}(PR'_3)}]$,[8] and we believe that under the same reaction conditions it is possible to obtain analogous (NHC) gold diphosphine complexes. Herein, we report the synthesis, optical properties, and the structural and theoretical characterization of the first neutral three-coordinate NHC gold(I) complexes (Scheme 1). We have chosen several NHC ligands with differences in their electronic and steric properties in order to explore how this can affect the stability of the three-coordinate species (Chart 1). Furthermore, these factors together with or without the use of auxiliary chromophore groups as substituents will allow for the modulation of their

Scheme 1. Synthesis of the Three-Coordinate NHC Gold(I) Complexes

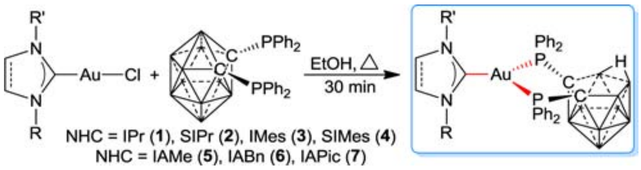
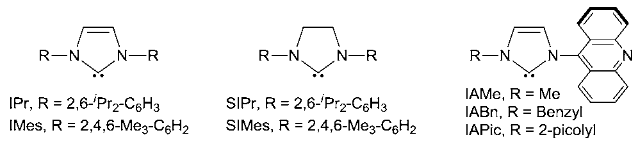


Chart 1. NHC Ligands Used



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luminescent properties. We have achieved that this selection of carbene ligands is key in both the energy of the emissions and in the high quantum yields observed for these complexes.

The reaction of the corresponding [AuCl(NHC)] complex with the carborane diphosphine $[(PPh_2)_2C_2B_{10}H_{10}]$ gives, after 30 min under reflux, complexes (**1**−**7**) in good yield and purity by filtration and after washing with ethanol.

Single crystals suitable for X-ray diffraction analysis were obtained for **1**, **4**, and **5**. The molecular structure of **1** is depicted in Figure 1. The geometry around the gold(I) center is distorted trigonal planar, with bond angles C1−Au1−P1 and C1−Au1−P2 of 130.40(6)° and 148.34(6)°, respectively. As we have observed for other three-coordinate gold(I) complexes containing carborane diphosphines, **1** has a small P1−Au1−P2 (81.223(19)°) bite angle, which is attributed to the great rigidity of the carborane.[8] The interplanar angle between the carbenic ring and the trigonal plane around the metal center is 48°, and this disposition of the carbene ligand in **1** could be the result of steric hindrance between the bis-isopropyl(phenyl) and phenyl groups. Although the Au1−C1 (2.051(2) Å) and Au1−P2 (2.3681(6) Å) bond distances found are in good agreement with Au−C and Au−P bond distances previously reported for NHC−M−PR_3 complexes,[5] the other Au1−P1 bond distance of 2.5311(5) Å is quite different.

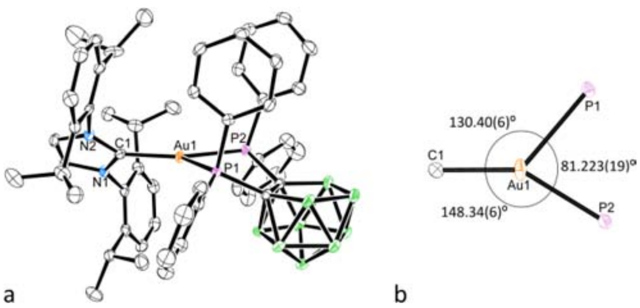


Figure 1. (a) Ortep diagram for **1** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. (b) View of the three-coordination around the gold(I) center.

Complex **4** shows an almost perpendicular disposition between the carbenic ring and the trigonal plane around the metal center (82°) in the solid state (see the Supporting Information (SI)), and this geometry could be favored by the planarity of the mesityl groups which lie in the middle of the phenyl groups. In this case, the smallest difference found for the Au−P bond distances (0.03 Å) compared to that found for **1** (0.16 Å) could suggest a better overlap of the involved bonding orbitals. In fact, this three-coordinate geometry is less distorted than that of **1**, since the C1−Au1−P1 and C1−Au1−P2 angles were 132.86(12)° and 140.31(12)°, respectively. The acridine derivative **5** has a three-coordinate geometry that is much more distorted since the C1−Au1−P1 and C1−Au1−P2 angles were 121.9(2)° and 155.6(2)°, respectively (see the SI). All these structures have a distorted trigonal planar geometry. The distortion mainly arises at the small bite angle of the diphosphine, which is very similar for the three complexes. According to the C−Au−P angles the order of the tendency to linearity can be established as **5** > **1** > **4** and must be attributed to the presence of an asymmetric substituted carbene ligand in complex **5** or to the bulkiness of the substituents in the carbene ligand in complexes **1** and **4**.

All complexes show a singlet around 50 ppm in the $^{31}P-\{^1H\}$ NMR spectra and were found more upfield than the analogous complex with only phosphines (around 63 ppm).[8b] The ^1H NMR spectra for complexes **1**−**7** show, in addition to the signals characteristic for the bis-isopropyl(phenyl), mesityl, and acridine derivatives, broad signals at around 0.5 and −2 ppm corresponding to the B−H bond and to the hydride of the *nido*-carborane, respectively. The best evidence of the stability of these complexes in solution has been found in the $^{13}C-\{^1H\}$ NMR spectra, in which the signal corresponding to the carbenic carbon appears as a triplet with a C−P coupling constant around 50 Hz. Substantial differences between these complexes are found in the $^{13}C-\{^1H\}$ NMR spectra that show triplets between 185 and 188 ppm for the unsaturated NHC ligands including acridine, IPr, and IMes substituents, while for the complexes with the saturated NHC ligands the corresponding signals are significantly deshielded appearing around 214 ppm.

Although all of the starting materials for the acridine derivatives ([AuCl(NHC)]) are emissive,[9] none of the three-coordinate gold(I) complexes **5**−**7** show luminescence. However, complexes **1**−**4** are strongly luminescent showing emissions in the blue-green region despite not having a chromophore group (see photophysical data in Table 1). The absorption spectra of complexes **1**−**4** are featureless showing a single absorption band at around 300−310 nm which is tentatively associated with IL transitions. Complexes **1**−**4** display a modulation of the luminescence upon excitation at 370 nm showing emission bands from 470 nm for SIMes (**4**) to 520 nm for SIPr (**2**) derivatives in the solid state (see Figure 2).

Table 1. Luminescence Data for Complexes 1−4

complex	medium (T [K])	emission[a] λ^{max} [nm]	τ_o [μs][d]	Φ_{em} [%][d]
1	solid (298, 77)	500, 500	16.2	34
	CH_2Cl_2 (298, 77)	520,[b] 490	10.9	
2	solid (298, 77)	520, 530	21.8	99
	CH_2Cl_2 (298, 77)	545, 495	11.6	
3	solid (298, 77)	490, 495	13.4	45
	CH_2Cl_2 (298, 77)	540,[b] 500	12.2	
4	solid (298, 77)	470, 480	15.8	65
	CH_2Cl_2 (298, 77)	570,[c] 490	11.4	

[a] Emission band upon excitation at 370 nm. [b] Emission band upon excitation at 330 nm. [c] Emission band upon excitation at 350 nm. [d] Lifetime and luminescence quantum yield, measured at room temperature.

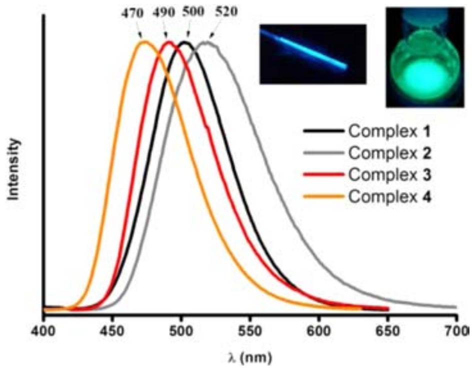


Figure 2. Normalized emission spectra of complexes **1**−**4** in the solid state upon excitation (370 nm) at 298 K.

No substantial changes were observed for the emissions at 77 K in the solid state except for a slight red shift arising from a thermal contraction that reduces the interatomic distances and, consequently, the band gap energy. Also, a moderate bathochromic shift was observed in degassed CH_2Cl_2 at rt, compared to the solid state, which is due to an increase of the polarity of the molecules in the excited state, which gives rise to a lowered relaxed state in a polar solvent. This effect suggests a photoinduced charge transfer as the origin of the observed luminescence.[10] The lifetimes found in both solid state and solution (10.9−21.8 μs) suggest that the electronic transitions involved in the blue-green emissions are of a phosphorescent nature, and this is in agreement with previous results found for other three-coordinate complexes.[11] Significantly, the four complexes show very high quantum yield values, reaching almost 100% for complex **2**. This quantum yield value is exceptional, and only two NHC complexes, of platinum and gold, have values around 90%.[1d,3g] Therefore, this characteristic together with the lifetimes in the microsecond range and the colors of the emissions in the blue-green region makes these species very attractive for future studies including practical applications as OLED emitters.

In order to confirm the origin of the emissions we have performed theoretical calculations. For this we first studied the electronic structures of the complexes **1** and **4** obtained through single-point DFT calculations using geometric parameters from XRD analysis (Figure 3). Later, we carried out TDDFT calculations of the excitation singlet→triplet, because the emission lifetimes in the microsecond range, together with the observed large Stokes shifts, suggest that the emissions are of triplet parentage. A visual inspection of the frontier orbitals of both complexes **1** and **4** shows that the highest occupied molecular orbital (HOMO) is mainly composed of the delocalized orbitals on the *nido*-carborane ligand (L) and in the gold−C(NHC) bond. The lowest occupied molecular orbital (LUMO) is predominantly located at the gold(I) center with further contributions from the C (NHC) and P atoms. This analysis shows also that in general the HOMOs are mainly located at the *nido*-carborane ligand with a strong contribution of the gold−C(NHC) bond, and the LUMOs are mainly located at the phosphine and NHC ligands, and the metal center (see the SI).

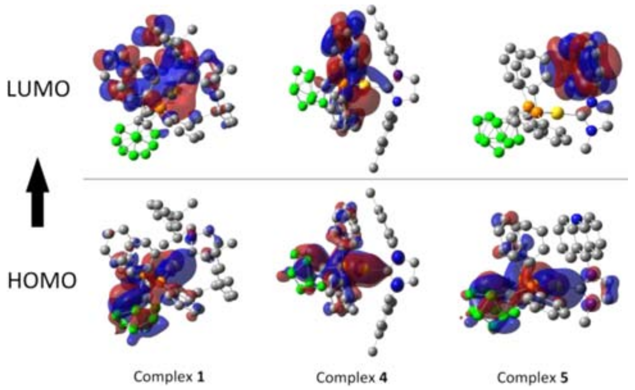


Figure 3. Contour plots of the frontier molecular orbitals for complexes **1**, **4**, and **5**.

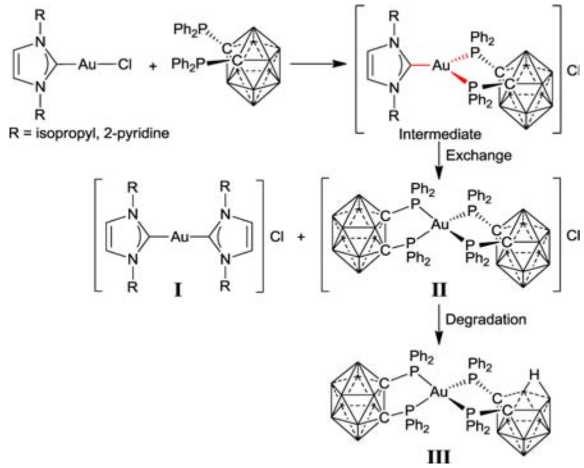
The TDDFT calculations show that the orbitals involved in the singlet→triplet transition are HOMO and LUMO with an energy of 2.8835 eV (429.98 nm) for complex **1** and HOMO and LUMO with energy of 2.9765 eV (417.54 nm) for complex **4**. The simplest analysis of this excitation shows that the HOMO involved is a π-bonding orbital between the *nido*-carborane ligand, pπ, and gold(I)-dπ. The LUMO is an antibonding combination of the dσ of gold(I) with its NHC ligand. The presence of the d_{xy} orbital in the HOMO, with higher energy than the corresponding d_{z^2} in a linear environment, explains the lowest energy needed to reach the triplet excited state.

Taking into account the TDDFT calculations together with the modulation of the luminescence observed by the use of different NHC ligands, we can propose the assignment of the origin of the phosphorescent emission as derived from the *nido*-carborane ligand to metal/ligand group "gold(I)−NHC ligand" (ML′) charge transfer (LML′CT) transition.

We can propose that the nonemissive behavior in the complexes **5**−**7** which have the highly electron-rich acridine group is probably because the LUMO of **5** is predominantly acridine-based with little contribution from the carbene ligand and with no contribution from metal. As we saw earlier, the orbitals involved in the singlet→triplet transition for complexes **1** and **4** are HOMO and LUMO, and the second one is predominantly metal-based with contributions from phosphine and carbene ligands, and these differences could be the reason for the quenching of the photoluminescence in complexes **5**−**7**.

In attempts to modify the optical properties of these novel complexes, we used NHC ligands with different steric and electronic properties to those of the NHC ligands in complexes **1**−**7**. Unexpectedly, the use of the isopropyl or 2-pyridine N-substituted carbenes gave a solid that was identified as the four-coordinate species $[Au\{(PPh_2)_2C_2B_9H_{10}\}\{(PPh_2)_2C_2B_{10}H_{10}\}]$ (**III**) (Scheme 2). The presence of an AA′BB′ system in the $^{31}P-\{^1H\}$ NMR spectrum in $CDCl_3$ at around 42 and 38 ppm confirms this hypothesis.[12] In order to better understand the formation mechanism of **III** we carried out the reaction in $CDCl_3$ to avoid the nucleophilic attack from EtOH. After addition of the NHC−Au−Cl derivative to the carborane diphosphine ligand, the signal corresponding to the free phosphine (7 ppm) disappears and a new singlet at around 42 ppm in the $^{31}P-\{^1H\}$ NMR spectrum characteristic of the cationic four-coordinate complex **II** appears,[13] while in the ^1H NMR spectrum the resonances attributed to the bis-carbene **I**

Scheme 2. Formation Mechanism of III



are present.[14] This fact confirms that the bulkiness of the NHC ligand is key in the formation and stabilization of the three-coordinate gold(I) complexes.

In conclusion, we have synthesized and characterized the first three-coordinate NHC gold(I) complexes, which are very stable in both solid state and solution. As we expected, most of these complexes are highly luminescent with emission energies from blue to green and the complexes present spectacular quantum yields. Surprisingly, the presence of a chromophore group, such as acridine, led to the quenching of photoluminescence. The use of less bulky NHC ligands with different electronic properties affording the homoleptic species **I** and **II**, and subsequent degradation to afford **III**, confirms that the bulkiness of the NHC ligands is essential for the formation of these three-coordinate gold(I) complexes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, synthesis, characterization, and crystallographic data (CIF) for **1**, **4**, and **5**. Excitation and emission spectra of complexes **1**−**4**, and details of the computational studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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