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Silver and Gold Complexes with a New 1,10-Phenanthroline Analogue N-Heterocyclic Carbene: A Combined Structural, Theoretical, and Photophysical Study

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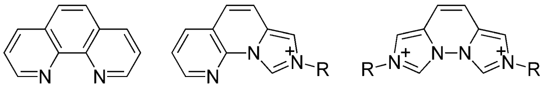
Transition-metal complexes with 1,10-phenanthroline (phen) ligands frequently reveal interesting photo- and electroluminescence properties, and thus are well suited for optoelectronic applications (organic light-emitting diodes (OLEDs) and sensors).[1,2] On the other hand, N-heterocyclic carbenes (NHCs) are strongly σ-donating ligands that form very stable complexes with favorable photophysical properties.[3] Furthermore, they show advantages as ligands in various catalytically active transition-metal complexes.[4] Therefore, the combination of both, the unique coordination geometry of phen-type ligands and the electronic properties of NHCs is a worthwhile synthetic goal.

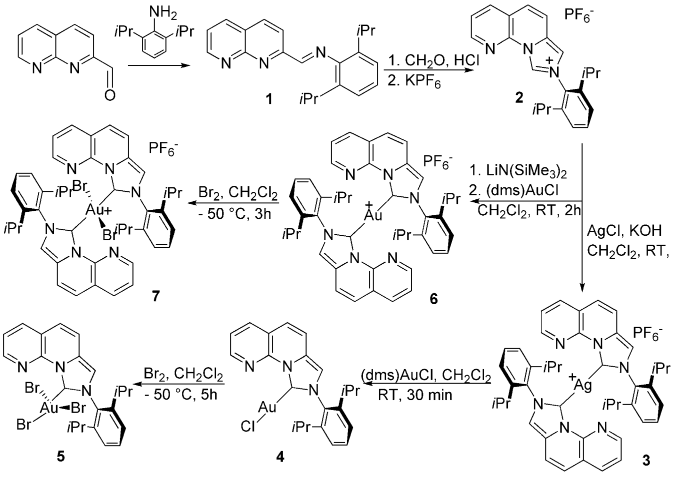
The substitution of one or two pyridine moieties by azolium moieties gave the ligand precursors **A** or **B**, respectively (Scheme 1). We chose structure **A** because of its smaller bite angle compared with **B** and the presence of two different donor atoms combining the properties of both an imine and a carbene function. The ligand precursor **B** and the coordination chemistry of the respective biscarbene has been reported just recently.[5]



Scheme 1. 1,10-Phenanthroline and the precursors of its NHC analogues.

Because the synthesis of gold complexes is straightforward, we chosen them as model substrates for probing the ligand properties of the carbene ligand derived from structure **A**.[6,7,8] The most common oxidation states of gold are +1 and +3 with linear or square-planar coordination geometries, respectively. Au^I complexes can in some cases extend their coordination number to four or might be further aggregated by aurophilic interactions,[9] whereas Au^{III} is known to form square-pyramidal complexes as has been demonstrated recently in complexes with dialkylamino-substituted NHC ligands.[10,11] The coordination number six is rarely found (e.g., in a thiocrown ether Au^{II} complex,[12] or in $Au(SO_3F)_3$[13] and AuF_3[14]), but to the best of our knowledge, has never been reported for an organometallic Au^{III} complex.

The NHC–Au^I compounds were conveniently synthesized by the reaction of [$(Me_2S)AuCl$] with the NHC–Ag complex **3** or the free carbene. Subsequent oxidation with Br_2 gives the respective NHC–Au^{III} complexes (Scheme 2).[15] In the absence of light, all complexes are perfectly stable both in solution and as solids, whereas the Au^{III} complexes are sensi-



Scheme 2. Synthesis of silver and gold complexes with a phen-analogue NHC ligand (dms = dimethyl sulfide).

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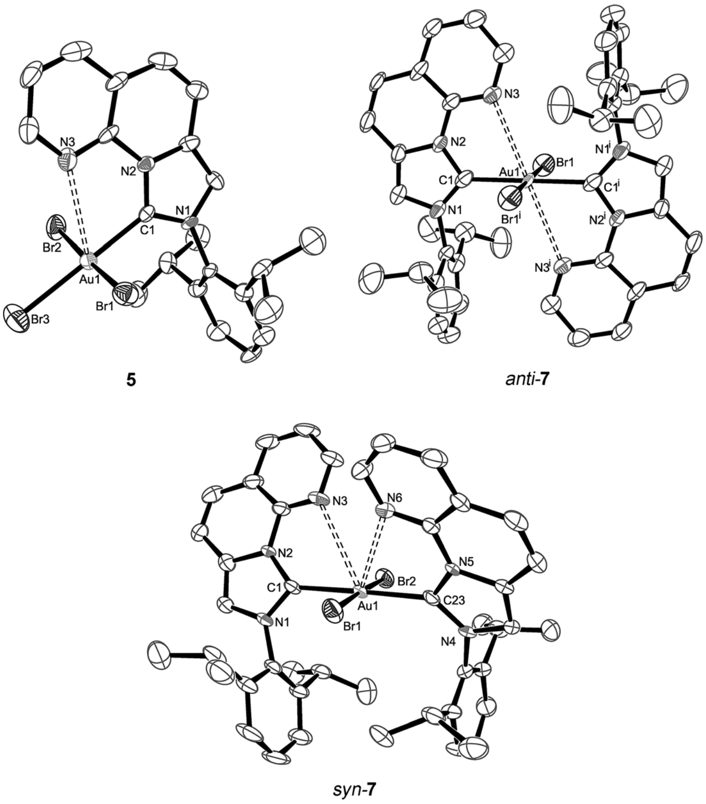
tive towards light and are easily reduced to the Au^{I} congener (vide infra). Just recently, we have proved the capability of a picolyl-substituted NHC to act as a chelating ligand by removing one bromide ligand in the $[(NHC)AuBr_3]$ complex as AgBr.[16] Analogously, we added one equivalent of $AgBF_4$ to a solution of **5** to facilitate the coordination of the nitrogen atom of the imine moiety to the gold atom, but extensive ligand-scrambling reactions and a reduction to Au^{I} and elemental gold occurred, and no κ-N derivative could be isolated. Instead, upon recrystallization of the residue from CH_2Cl_2/Et_2O, different crystals could be isolated, two of them were identified by X-ray diffraction analyses as [(NHC)AuBr] (**4**-Br) and the *trans–anti* isomer of **7** as its tetrafluoroborate salt $[(NHC)_2AuBr_2]BF_4$, *anti*-**7**-BF_4.

X-ray structures of all complexes and of the imidazolium salt were determined. All metal–carbon bond lengths are within the expected ranges with values in the narrow range of 1.94–2.09 Å. Due to the geometry of the ligand, all metal atoms feature weak M···N contacts, which are significantly lower than the sum of the van der Waals radii ($r(M) + r(N) = 3.27$ (Ag), 3.21 Å (Au)).[17] The homoleptic silver and gold complexes **3** and **6** crystallize isostructurally with Au–N distances of 2.72–3.05 Å (**3**) and 2.87–3.11 Å (**6**). Very similar are the Au–N distances (≈3.05 Å) of the heteroleptic [(NHC)AuX] (X = Cl (**4**), Br (**4**-Br), Figures S1–S5 in the Supporting Information). For comparison, the Au–N distance in the linear NHC-Au^{I}-N fragment with pyridine-type N-ligands account for about 2.1 Å.[16] Particularly interesting are the molecular structures of the Au^{III} complexes: compound **5** shows a square-pyramidal coordination geometry with the Au^{III} atom coordinated by the carbon atom of the carbene and the halide ligands in the equatorial position and the nitrogen atom N3 in the axial position [Au1–N3 2.910(6) Å, Figure 1]. A square-pyramidal coordination environment of a Au^{III} atom is well documented for diimine-type ligands like phen and 2,2′-bipyridine in their $[(N\cap N)AuCl_3]$ complexes[18] and also for amine functionalized $[(NHC)AuX_3]$ complexes with significantly shorter axial Au–N bond lengths (2.58–2.84 Å).[10] In the complex *anti*-**7**-BF_4, the Au^{III} exhibits a highly distorted octahedral environment defined by two carbene carbon atoms, two bromides, and two nitrogen atoms of the NHC ligand with an Au–N bond length of 2.933 Å (Figure S6 in the Supporting Information). The complex cation is C_i-symmetric with the gold atom lying on the inversion center. The orientation of the chelating carbene ligands of the cations in crystals of *syn*-**7** resemble the geometry of the NHC ligands in complex **6** and arise from the addition of two bromide ligands to the gold atom still maintaining the conformation of the complex. The geometry of the coordination sphere of the gold atom is a trigonal prism with the triangular consisting of the carbene carbon and nitrogen atoms and the bromide. The gold atom is lying in the center of one of the side planes (Figure S7 in the Supporting Information). All attempts to isolate the *trans*-isomer by recrystallization of compound **7** failed and repeatedly gave the *syn*-**7** isomer. Further structural parameters can be found in the Supporting Information.



5

anti-**7**

syn-**7**

Figure 1. Molecular structures of $[(NHC)AuBr_3]$, **5** (left), the cation in $[(NHC)_2AuBr_2]BF_4$, *anti*-**7**-BF_4 (right), and the cation in $[(NHC)_2AuBr_2]PF_6$, *syn*-**7**. Selected bond lengths [Å]: for **5**: Au1–C1 2.02(1), Au1–Br1 2.416(1), Au1–Br2 2.428(1), Au1–Br3 2.435(1), Au1–N3 2.91(1); for *anti*-**7**-BF_4: Au1–C1 2.06(1), Au1–Br1 2.427(1), Au1–N3 2.93(1); for *syn*-**7**: Au1–C1 2.07(1), Au1–C23 2.08(1), Au1–N3 2.96(1), Au1–N6 2.932(7), Au1–Br1 2.604(1), Au1–Br2 2.629(1).

Because there are only a few observations supporting the possibility of a hexa-coordinated Au^{III} cation,[13,14,19,20] we investigated the nature of the Au···N interactions in *anti*-**7** and *syn*-**7** more detailed by using DFT calculations. The solid-state structures can be reproduced well within the expected limits. Deviations between solid-state and (computed) gas-phase conditions are expected in the distances of Lewis-donor to Lewis-acceptor sites. Such structural parameters tend to be shorter in a polar environment (solid state) than in an unpolar environment (dilute gas or vacuum).[21–23] In agreement with this known trend, we found longer Au···N bond lengths of 3.028 Å for *anti*-**7** and 3.077 Å for *syn*-**7** in the calculation, compared with shorter bond lengths of 2.93(1) Å for *anti*-**7**-BF_4 and 2.96(1) or 2.93(1) Å for *syn*-**7** in the solid state. Thus, the Au···N contact resembles classic donor–acceptor interactions. Our next question is whether Au and N share any electrons. The calculated shared electron numbers (SEN)[24] for the Au–N atom pairs of 0.01 for both the *anti* and the *syn* conformer can be interpreted in such a way that the interaction between Au and N in both cases is not influenced by a stabilizing fragment orbital interaction. This is in agreement with the ligand-field-theory-based view of Au^{III} as a fourfold, square-planar acceptor site. A population analysis based on occupation numbers (PABOON)[24] resulted in a positive partial charge for Au of 0.83 and in negative partial charges for N3/N3' of the *syn*- and N3/N6 of the *anti*-conformer of −0.16, respectively. All remaining nitrogen atoms in both conformers have positive partial charges. Thus, there is an intramolecular electrostatic attractive component (possibly weak) between these negatively charged nitrogen atoms and the positively charged gold atom. In such cases, weak nonorbital-based attractive intramolecular interactions are found to be enhanced by dispersion-type interactions.[23] DFT-calculations cannot reproduce dispersion-type ("van der Waals") interactions, but empirical corrections (e.g., D3) are available.[25,26] However, we found no significant structural change upon application of the dispersion correction, nor any significant changes in the isomerization energy [$syn \rightarrow anti$: $-0.9\,\text{kcal}\,\text{mol}^{-1}$ (DFT), −1.3 (DFT–D3)]. We conclude that the experimentally observed sub van der Waals contacts between Au and N in *anti*-**7**-BF_4 and *syn*-**7** are not significantly orbital based, but may be stabilized by negative partial charges found exclusively on the two N atoms with the closest contacts to the positively charged Au atom, and we note that this intramolecular electrostatic stabilization contribution is not enhanced significantly by van der Waals interactions.

The electronic absorption and emission spectra of the imidazolium salt **2** featured typical signals for rigid annulated aromatic systems (Figure S8 in the Supporting Information).[27] For all gold compounds, comparable luminescence behavior with both a structured high-energy (HE) and a low-energy (LE) band (the latter dominating at 77 K) were observed (Figure 2). The silver complex is emissive only at 77 K exhibiting the LE band (Figures S10–12, S16 in the Supporting Information). Due to the similarity to the emission of **2** and their emission decay times (Figure S9, S13–15 in the Supporting Information), we assign the HE and LE bands to an intraligand fluorescence (^{1}IL) and phosphorescence (^{3}IL), respectively. The S_1–T_1 energy gap is large (e.g., $7300\,\text{cm}^{-1}$ for **6**) and is in agreement with published values of other gold complexes containing ligands with an extended π system.[28] The Au^{III} complexes underwent photoreductive elimination of Br_2 upon irradiation with polychromatic light giving the Au^{I} congener ($\lambda > 335$ nm, Figure S17–S20 in the Supporting Information). As a further deactivation path of the excited state exists, the photoreactivity is also accompanied by a significant drop of the emission-quantum yields. All photophysical data are summarized in Table S1 in the Supporting Information.

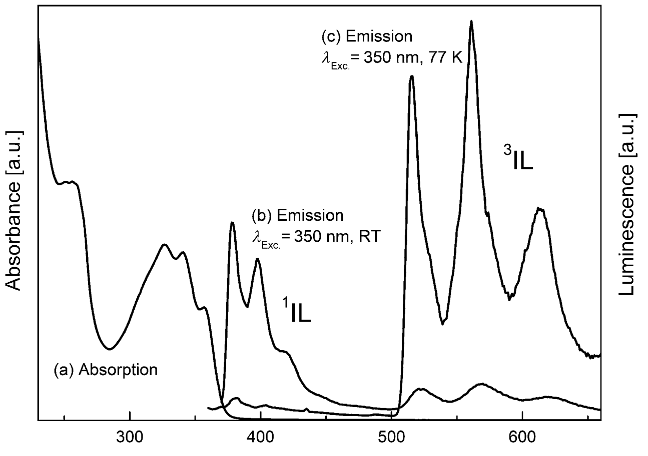


Figure 2. Electronic spectra of $[(NHC)_2Au]PF_6$, **6**: a) absorption spectrum, b) emission spectrum at RT in CH_2Cl_2 ($c = 4\times10^{-5}\,\text{mol}\,\text{L}^{-1}$, degassed, $\lambda_{exc} = 350$ nm), and c) emission spectrum at 77 K in MeTHF glass ($c \approx 10^{-5}\,\text{mol}\,\text{L}^{-1}$, $\lambda_{exc} = 350$ nm).

In this work, we presented a phenanthroline analogue NHC ligand and studied its coordination properties by the synthesis of neutral and ionic Au^{I} and Au^{III} complexes that exhibit unusual coordination environments with six donor atoms around the gold atom in two of the Au^{III} compounds. All complexes revealed luminescence that originated from intraligand excited states. Application of this new NHC as bidentate ligand for further transition-metal complexes (e.g., as catalysts or triplet emitters for OLEDs) may be envisaged. The synthesis and photophysical characterization of Pd, Pt, and Ir complexes are the subject of current investigations.

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Keywords: density functional calculations • gold • luminescence • silver • X-ray diffraction

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