Inorganic Chemistry

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Electronic Properties and Solid-State Packing of Isocyanofulvenes and Their Gold(I) Chloride Complexes

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5-dibenzo[a,d]cycloheptenylidene; f, 9-thioxanthenylidene; and g, 2,5-dimethyl-3,4-diphenylcyclopentadienylidene) were prepared along with their gold(I) chloride complexes (R2=CH-NC-AuCl, 5a-f). A comprehensive study of the properties of the precursors, free ligands, and gold(I) complexes is reported and complemented by DFT calculations. Solid-state structure of two complexes (5a and 5c) show extensive aurophilic interactions and $\pi - \pi$ stacking of the ligands. The metal centers are not involved in optical transitions. However, metal coordination leads to a consistent



bathochromic shift in the absorption spectra, which signifies the effective conjugation between the isocyano group and the π -systems of the ligands. Furthermore, an additional DFT study of carbonyl complexes of the type R_2 =CH-NC-M(CO)₅ (M = Cr, Mo, and W; $R_2 = CH - NC = 4a$) indicates very effective metal-to-ligand charge transfer when isocyanopentafulvenes are used as ligands.

INTRODUCTION

Isocyanides have long proven to be valuable compounds in a variety of different fields, such as organic, inorganic, and coordination chemistry. In organic chemistry, they have been widely used as building blocks in the Ugi¹ and Passerini² multicomponent reactions and a broad range of other insertion and condensation reactions,³ including polymerization to polyisocyanides that possess a helical main chain.⁴ Furthermore, as stable carbenes that are isoelectronic to CO, they can serve as strong ligands to transitions metals that behave as good σ -donors but are weaker π -acceptors than CO. This has led to the development of equally rich coordination chemistry for isocyanides.⁵ Isocyanide complexes serve as precursors for other transition metal complexes,⁶ as sensitizers in photocatalysis,7 and as catalysts for a broad range of chemical transformations.⁸ In recent years, new ligands with increased steric bulk⁹⁻¹¹ and chelating functional groups^{7,8t,g,j,n} have been developed to generate new molecular architectures and tune optical properties and catalytic activity. Notably, isocyanoarenes are also known to facilitate electronic communication between metal centers,¹² a property that has been expanded recently in the development of redox-active azulene-¹³⁻¹⁵ and ferrocene-derived¹⁶ isocyano ligands (Chart $1B).^{15}$

In our group, we have worked on the development of isocyanides bearing conjugated fulvenyl groups as a new type of redox-active ligand. Fulvenes¹⁷ can act as electron-donors (tria- and heptafulvenes) or electron-acceptors (pentafulvenes)

and have been investigated as promising lead structures for organic electronics¹⁸ and sensory applications.¹⁹ Pentafulvenes are also commonly encountered in organometallic coordination chemistry either as π -ligands directly coordinated to transition metals^{17a} or as ligand-precursors,²⁰ while complexes that contain an intact and non- π -coordinated fulvenyl moiety are more rare.²¹⁻²³ Notably, it has been shown that dibenzopentafulvene-derived ligands can act as acceptors in metal-to-ligand charge-transfer processes in rhenium carbonyl complexes (Chart 1A).²⁴

We recently reported a first series of fulvenyl-functionalized arylisocyanides and investigated the properties of their corresponding polyisocyanides.^{25–27} To explore the possibilies of the monomers in coordination chemistry, we also prepared and characterized the corresponding gold(I) chloride complexes (Chart 1C).²⁸ Isocyanides are among the most widely used ligands in gold(I) chemistry, which itself is a highly vibrant field of research due the potential use of gold(I) complexes as functional materials.²⁹ The solid-state structures of gold complexes are often governed by aurophilic

Received: August 14, 2020 Published: November 23, 2020





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Chart 1. Electroactive Isocyanides and Fulvenes As Ligands in Coordination Chemistry



interactions, i.e., close and non-covalent Au…Au contacts.²⁹ Owing to these contacts, the electronic properties of bulk solids can differ significantly from those of the molecularly dissolved compounds, manifesting in ways such as aggregationinduced emission.³⁰ Furthermore, gold compounds show highly diverse bulk packing due to the high directional flexibility and broad range of interatomic distances covered by the Au…Au contacts (2.75–3.50 Å). Hence, complexes can adopt polymorphic crystal structures with inherently different optical properties.³¹ Moreover, electronic properties can also change in response to external stimuli such as temperature,³² mechanical stress,^{31b,30a-c,32b,c,33} irradiation,³⁴ or the presence

Scheme 1. Ligand Synthesis^a

of solvent vapors.³⁵ Only recently, liquid crystalline isocyano–gold(I) complexes have also been reported (Chart 1B).¹⁵

We considered the combination of the redox-active fulvenyl chromophore and a strongly coordinating isocyano group a promising lead structure for the development of new organometallic functional materials and therefore further explored this topic after the report of our initial findings.²⁸ In the present paper, we report the use of isocyanofulvenes as ligands to gold(I) complexes (Chart 1D). In these systems, the isocyano group is directly attached to the exocyclic double bond of the fulvene moiety. Compared to Chart 1C, this ligand system provides a more direct conjugation pathway between the metal center and the fulvene. Our findings provide evidence for more effective conjugation between the metal center and the fulvenyl moiety and also showcase the possibilities of this new type of ligand for coordination chemistry.

RESULTS AND DISCUSSION

Syntheses. Different methods for the preparation of $\alpha_{,\beta}$ unsaturated isocyanides have been reported before.^{36–43} For the synthesis of the isocyanofulvenes in this survey, we used two different synthetic routes starting from suitable carbonyl compounds (1a–g; see the Supporting Information for details of the syntheses of 1b–d and 1g). These were converted to isocyano-fulvenes either directly via Horner–Wadsworth– Emmons olefination⁴⁴ (method B, Scheme 1B) or via a route requiring a vinylic nucleophilic substitution (S_NV;^{45–48} method A, Scheme 1A) on chlorofulvenes.

For the S_NV strategy, 9-(chloromethylene)-9H-fluorene (2a, 78%), 9-(chloromethylene)-2,7-dioctyloxy-9H-fluorene (2b, 67%), and 5-(chloromethylene)-5H-dibenzo[a,d]cycloheptene (2c, 89%), were prepared in good yields via a Wittig olefiniation of the corresponding ketones (1a-c). In the next step, *N*-formylamino groups were introduced (3) via S_NV -reactions with formamide in the presence of sodium *tert*-



 ${}^{a}R' = n$ -octyl; the base was either *n*BuLi or LiN(SiMe₃)₂.

butoxide. 2c, as a formally non-activated substrate, could not be converted to its formamide 3c. Substitutions on 2a and 2b were successful, however, and gave amides 3a and 3b in 71% and 81% yields, respectively.⁴⁹ The subsequent dehydration of 3a,b with phosphoryl chloride then gave the isocyanides 4a and 4b in 55% and 40% yields, respectively.

Despite these successes, the direct conversion via HWE reactions with commercially available isocyanomethylphosphonate proved more versatile. The reaction progress can be readily monitored by IR spectroscopy (Figure S1), and isocyanides 4a-g could be prepared in satisfying to excellent yields from the corresponding ketones 1a-g.

The compounds were characterized by ¹H and ¹³C NMR spectroscopy and high-resolution mass spectroscopy. Additionally, the isocyanides could be readily identified by the characteristic IR band of the R—N \equiv C stretching vibration at between $\tilde{v} = 2114$ (4c) and 2106 cm⁻¹ (4g). These values lie at the lower end of the range usually observed for isocyanides,³⁶ which indicates a weakening of the N \equiv C bond by conjugation to the π -system.

All isocyanides proved sensitive and changed color from colorless or yellow to greenish or black amorphous solids when handled in air. The isocyanides apparently oligomerize to undefined materials, with mass distributions corresponding to 5-10 monomer units according to analyses by gel permeation chromatography. Oligomerization is induced by ambient air and moisture but is likely also promoted by trace impurities, since only highly purified samples were stable under an inert atmosphere. 4d turned out to be particularly sensitive as it slowly changed color even when stored under an argon atmosphere at -35 °C.

Gold(I) chloro-complexes of the isocyanides were then prepared by stirring the ligands in a DCM solution with Me_2S^*AuCl as the metal source (Scheme 2). The complexes





were isolated and purified by precipitation through the addition of *n*-hexane, followed by washing with the same solvent. Unlike the free ligands, the complexes could be readily handled in air.

The formation of the complexes was confirmed by IR spectroscopy, which showed a shift of the distinct isocyano stretching bands by about 100 cm⁻¹ to ca. 2200 cm⁻¹ for all compounds (Figures S2 and S3). These values lie in the typical range for gold(I) complexes of isocyanides.⁵⁰ Further characterization by ¹H and ¹³C NMR spectroscopy showed distinct differences between the free ligands and the complexes. For instance, the ¹H NMR signal of the vinylic proton on the fulvene bond was consistently shifted to a lower field by about 0.1 ppm. ¹³C NMR spectra of the free ligands generally showed the signal of the isocyano-carbon from 166.7 (4e) to 174.9 ppm (4g). Interestingly, the methylidene carbon atoms (=

CH—NC) were observed as triplets from 101.3 (4c) to 111.6 (4e) ppm, with coupling constants of ${}^{1}J_{CN} = 10-12$ Hz due to coupling with the neighboring ${}^{14}N$ atom.⁵¹ In the complexes, only the broadened signals of methylidene-carbon atoms in **Sb**, **Sd**, and **Sf** could be observed by ${}^{13}C$ NMR spectroscopy between 108.3 (**Sb**) and 100.4 (**Sd**) ppm.

Solid-State Structures. In the course of this work, single crystals suitable for X-ray diffraction were obtained of ketone 1c, chlorofulvene 2b, amide 3a, isocyanide 4e, and gold(I) complexes 5a and 5c. Crystallographic data were also obtained for 5e and 5f (see the Supporting Information for details). However, due to inadvertent twinning and disordering, only a partial structure solutions were possible for these complexes. The molecular structures of the fluorene derivatives 1c. 2b. and 3a confirm the identity of these compounds. Furthermore, their bulk packing highlights the influence of their respective substituents. Due to the planarity of the fluorene frame, 1c (Figures S61 and S62) and 2b (Figures S63 and S64) adopt tightly π -stacked brick-layer-like structures. In **2b**, the packing is additionally stabilized by the interdigitation of the octyloxy chains within the plane of the fluorenyl frame. Contrarily, amide 3a adopts a herringbone packing that is stabilized by hydrogen bonds between the amide oxygen and the N-H groups in neighboring molecules (Figures S65 and S66).

The structure of **4e** is the first example of a crystal structure of an isocyanofulvene (Figures S67 and S68). Single crystals of **4e** could be obtained by the diffusion of *n*-hexane into a solution of the ligand in dichloromethane. The fulvene crystallizes in the form of colorless blocks in the orthorhombic space group *Pbca* with eight molecules in the unit cell. The dibenzo[*a,d*]cycloheptene skeleton adopts a concave and saddle-like structure, which is typical for this building block.^{28,25} The length of the N≡C bond (1.161(4) Å) lies in the range of other free isonitriles (1.152–1.166 Å).⁵² In the packing structure of **4e**, the non-planar molecules noticeably still exhibit an unusual type of loose π – π -stacking (Figure S68).

The complex 5a crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell (Figure 1A; see also Figures S69 and S70), while 5c crystallizes from THF/hexane solution in the tetragonal space group $P42_1c$ with eight molecules of 5c and two molecules of THF in the unit cell (Figure 1B; see also Figures S71-S73). Ligand 4c is significantly more electron-rich than 4a. Hence, structural differences in the coordination properties due to differences in σ -donation and π -back bonding were expected for complexes 5a and 5c. However, a comparison of the bonds along the isocyano-AuCl groups of 5a and 5c shows only marginal deviations (Table 1). The complexes show metal carbon bonds (5a, d(Au-C) = 1.925(6) Å; 5c, d(Au-C) = 1.930(7) Å) that lie within the typical range for electron-rich phenylisocyanide complexes (e.g. p-RO-Ph-NC-AuCl,³⁴ d(Au-C) =1.918(8) - 1.946(6) Å for R = *n*-alkyl; *p*-MeO₂C-Ph-NC-AuCl,^{32a} d(Au-C) = 1.994(20) and 1.969(12) Å), and are comparable to those of the first set of complexes we reported recently $(Au-C = 1.935(3)-1.927(5) \text{ Å})^{28}$). The bonding angles along the N=C-AuCl group are near linear (5c, \angle (Au-C \equiv N = 176.9(8)°, \angle (C \equiv N-CH) = 176.9(8)°; 5a, \angle (Au-C=N) = 177.3(5)°) except for the \angle (Au-C=N) angle in 5a $(173.5(5)^\circ)$, which deviates more from the ideal 180°. As indicated in Scheme 3, the π -back donation from the gold should weaken the C \equiv N bond, and fractional sp² hybridization would then lead to a more bent $C \equiv N - CH$



Figure 1. Packing diagrams showing π -stacks and Au···Au contacts of the crystal structures of (A) 5a and (B) 5c. Ellipsoids are drawn at the 55% probability level. Hydrogen atoms and two molecules of disordered THF in the structure of 5c were omitted for clarity.

Table 1. Structural Parameters of Ligand 4e and Complexes 5a and 3	Ta	able	1.	Structural	Parameters	of	Ligand	4e	and	Com	plexes	5a	and	5	50
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	Au—C (Å)	N≡C (Å)	N—CH (Å)	CH=C (Å)	CH—N \equiv C (°)	N≡C—Au (°)	Au…Au (Å)
4e		1.161(4)	1.393(3)	1.334(3)	176.2(2)		
5a	1.925(6)	1.144(7)	1.391(7)	1.334(8)	173.5(5)	177.3(5)	3.857(3) 4.201(6)
5c	1.930(7)	1.149(9)	1.388(9)	1.351(9)	176.9(8)	176.7(6)	3.516(1) 4.724(1)

Scheme 3. Resonance structures

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bond angle in **5a** compared to that in **5c**. However, the crystallographic structures show that this effect is marginal, and it is also all but absent in structures optimized by DFT calculations (included in the Supporting Information).

Bulk Packing. The bulk packing of 5a and 5c is governed by extensive π -stacking of the ligands (Figure 1). Neighboring molecules of 5a form tight ring-slipped π -stacks with nearly coplanar fluorenyl moieties (3.3°) spaced 3.460(6) Å apart (Figure 1A). The NC-AuCl moieties show a colinear orientation, which gives rise to infinite chains of gold atoms with Au…Au'…Au" angles of 180.0° and rather loose Au…Au' contacts of 3.857(3) Å between the gold atoms in π -stacked complexes. The NC-AuCl moieties of neighboring stacks are paired in an anti-parallel orientation. Overall, this packing leads to the formation of a double cable of gold(I) atoms wherein each four gold(I) atoms form a lozenge that is $3.857(3) \times$ 4.201(6) Å with internal angles of 104.8(1) and 75.2(1)°. 5c shows a similar packing (Figure 1B). The fluorenyl frames are close to coplanar with angles of $3.2(1)^{\circ}$ between their mean planes, and the staggered positioning of the atoms allows more tight π -stacking with distances of 3.434(9) Å. However, adjacent molecules in the π -stacks are flipped, with their NC-AuCl groups enclosing (ClAu—C \equiv N–CH—CH′—N′ \equiv C-AuCl) torsion angles of ca. 81.8(5)° (Figures S71B and S72). As a consequence, the NC-AuCl groups of neighboring stacks interdigitate to form infinite double-cables of gold(I) atoms similar to those formed by 5a. The Au-Au' contacts of 3.516(1) Å are tighter than those in **5a**, and the parallel chains of gold(I) atoms form regular rectangles with internal angles of $90.0(1)^{\circ}$ and dimensions of $3.516(1) \times 4.724(1)$ Å. The

aurophilic contacts in these complexes are looser than those of compounds for similar solid-state structures $(p \cdot nC_5H_{11}O-Ph-NC-Au-Cl,^{34} d(Au\cdotsAu') = 3.342(1) \text{ or } 3.342(1) Å; (p-MeO_2C)-Ph-Au-CN-Ph,^{32a} d(Au\cdotsAu') = 3.504(1) \text{ or } 4.451(2) Å)$. This would indicate that the bulk packing of **5a** and **5c** is dominated by $\pi - \pi$ -stacking rather than by aurophilic interactions. The systems introduced here may therefore serve as leads for the systematic engineering of the solid-state structures of the corresponding isocyano-gold(I) complexes. However, it has been pointed out^{31a} that extensive π -interactions summarized above, ${}^{30,32-35}$ since they would limit the structural flexibility and possible the packing modes. Conversely, the non-planar ligand backbones of **5e** and **5f** can undergo π -interactions much less effectively, and Au···Au contacts might therefore have a greater impact on their solid-state properties.

Crystallographic data for complexes **5e** and **5f** were obtained. However, both complexes crystallized in the form of very fine needles, and inadvertent twinning and disordering allowed for only a partial structure solution. Still, the packing structure confirms that both complexes adopt a bulk packing mode similar to that of **5a**, which is governed by the stacking of the ligand frameworks and Au···Au' contacts between antiparallel-oriented NC-AuCl groups (Figures S74–S77).

Electrochemistry. The electronic properties of the isocyanofulvenes **4a**–**f**, and chlorofulvenes **2a**,**b** as well as those of their carbonyl-precursors (1) have been characterized by cyclic voltammetry (CV) and square-wave voltammetry (SWV) (Figure S4–S7). The fluorenones all show a reversible first reduction, and the reduction potentials show clear correlations with the Hammett parameters (*meta/para*, σ_m / σ_p^{53}) of substituents present on the fluorenyl frame (∇ in Figure 2). For instance, in 3,6-dimethoxyfluorenone (1c) the MeO groups (σ_p (OMe) = -0.27^{53}) can exert a strong



Figure 2. Correlation of the first reduction potentials of fluorenones $(\nabla, \mathbf{1a}-\mathbf{d} \text{ and } 3,6\text{-dibromofluorenone, half-potentials from CV})$ and fluorene-based isocyanofulvenes (•, $4\mathbf{a}-\mathbf{d}$, peak-potentials from SWV) vs. substituent Hammett parameters.

electron-donating effect due to their direct *para*-conjugation with the carbonyl group at the 9-position. In contrast, the bromo substituents in 3,6-dibromofluorenone (**1h**) act as equally strong acceptors ($\sigma_p(Br) = +0.23$). Hence, **1c** shows the lowest electron affinity ($E_{1/2} = -2.04$ V vs FcH/FcH⁺⁵⁴), **1h** exhibits the highest ($E_{1/2} = -1.66$ V), and **1a** ($E_{1/2} = -1.85$ V, $\sigma_p(H) = 0.0$), and **1d** ($E_{1/2} = -1.96$ V, $\sigma_p(Me) = -0.07$) fall in between. The reduction potential of the 2,7-alkoxyfluorenone **1b** ($E_{1/2} = -1.88$ V) deviates from the linear correlation. Here, the alkoxy group should act as an acceptor due to its *meta*-connectivity to the 9-position and its -I electron-withdrawing effect ($\sigma_m(OEt) = +0.10$). However, the fluorenyl frame allows indirect *para*-conjugation ($\sigma_p(OEt) = -0.24$) to the 9-position across the second benzo ring (Figure S10). In combination with the presence of two alkoxy groups, this less-

effective electron donation seems to largely mitigate the -I effect. The isocyanides 4a-d show a similar Hammett correlation (• in Figure 2) but exhibit lower electron affinities than the fluorenones. Additionally, only irreversible electrochemical processes were observed. The donor-substituted 4c exhibits the lowest electron affinity ($E_p = -2.22$ V), the unsubstituted fulvene 4a exhibits the highest affinity ($E_p = -2.06$ V), and the reduction potential of the alkyl-substituted 4d ($E_p = -2.10$ V) fall in between again. The indirect electron-donation of the alkoxy groups in 4b ($E_p = -2.15$ V) is equally effective in this system as it again shows a low electron affinity that deviates from the linear correlation among the fluorenones even more than that of 1b. The electrochemical analysis of the chlorofulvenes 2a and 2b (see Figure S4 in the ESI) showed

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isocyanovinyl group.

Thioxanthone (**If**, $E_{1/2} = -1.97$ V vs FcH/FcH⁺) shows an electron affinity comparable to that of **Id** ($E_{1/2} = -1.96$ V vs FcH/FcH⁺), while the reduction potential of the corresponding isocyanide **4f** ($E_p = -2.45$ V vs FcH/FcH⁺) is by far the lowest in this survey. However, **4f** was meant to function as an electron donor through resonance of the isocyanomethylene group with the sulphur atom. Hence, the electrochemical oxidation of **4f** was measured in an acetonitrile solution, which yielded an irreversible oxidation with a peak current in SWV at +1.08 V versus FcH/FcH⁺. **4f** is therefore more readily oxidized than thioxanthone ($E_{ox} = +1.34$ V⁵⁵). Overall, we have established a set of electroactive building blocks that cover a broad range of reduction and oxidation potentials.

that the chlorovinyl group is a weaker acceptor than the

Optical Properties. To quantify changes to the optical properties upon metal coordination, UV-vis absorption spectra of the precursors, the free ligands, and the complexes were recorded (Figure 3 and Table 2; see Figure S9 in the Supporting Information for spectra of 2a,b and 3a,b). All ligands show strong absorption bands (λ_2) just outside the



Figure 3. UV-vis absorption spectra of ligands 4a-f and complexes 5a-f. Spectra were recorded in DCM.

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Table 2. Optical Properties of Isocyanides and Precursors^a

compound	$IR (cm^{-1})$	λ_3^{b} (nm)	λ_2^{b} (nm)	$\lambda_{ m max}$	$E_{g,opt}^{c}$ (eV)	
4a	2106	264	323	355 ^d	3.37	
4b	2103	273	322 ^d	425 ^d	2.92	
4c	2114	276	337	365 ^d	3.40	
4d	2103	269	327	375 ^d	3.35	
4e	2112	270		295	4.20	
4f	2102	277		356	3.48	
4g	2106					
5a	2200	267	342	375 ^d	3.31	
5b	2213	283	343	475 ^d	2.61	
5c	2211	283	361	390 ^d	3.18	
5d	2202	274	350	375 ^d	3.31	
5e	2206	264	286	340 ^d	3.65	
5f	2202	283		385	3.22	

^{*a*}For a comprehensive listing, see Table S1. ^{*b*}Additional prominent bands in the absorption spectra. ^{*c*}Calculated from the λ_{max} value in a DCM solution. ^{*d*}Absorption maxima and shoulder bands were derived via a Gaussian deconvolution of the absorption spectra.

visible range ($\lambda_{onset} < 350$ nm; 4f, $\lambda_{onset} = 390$ nm). Upon complex formation, the overall shape of the absorption spectra remains unchanged, but all compounds show a bathochromic shift of the λ_2 band that reflects the increased acceptor strength of the NC-AuCl group and roughly scales with the donor strength of the fulvenyl moiety. Based on the absorption onsets of the λ_2 bands (λ_{max} for 4e,f and 5e,f), the shift is lowest for 4a and 5a($\Delta E = -0.20$ eV), 4d and 5d ($\Delta E = -0.23$ eV), and 4b and 5b ($\Delta E = -0.23$ eV), wherein the alkoxy groups are not directly conjugated with the fulvenyl moiety. The more electron rich system 4c and 5c ($\Delta E = -0.26 \text{ eV}$) and the donors 4e and 5e($\Delta E = -0.28 \text{ eV}$) and 4f and 5f($\Delta E = -0.26 \text{ eV}$) exhibit larger bathochromic shifts.

The bathochromic shift still leaves the absorption of all compounds outside the visible range except for 5f ($\lambda_{onset} = 425$ nm). However, a closer inspection of the absorption spectra reveals that the baseline of several of the fluorene-derived compounds does not drop to zero. Instead, it only gradually drops off (Figure 3A, C, and D) or reveals a very weak additional band at a longer wavelength (Figure 3B, insert). Initially, we presumed that these bands may be caused by inadvertent decomposition products due to the instability of the monomers. However, they were also present in the spectra of the more stable complexes and correctly predicted by DFT calculations (vide infra). The centers of these weak bands were derived by fitting the absorption spectra with Gaussian curves. For the free ligands, this yielded absorption maxima at 355, 425, 365, and 375 nm for 4a, 4b, 4c, and 4d, respectively, and at 375, 475, 390, and 375 nm for the corresponding complexes.

All compounds were nonfluorescent except the chlorofulvene 2a ($\lambda_{max,em} = 475 \text{ nm}$), the ligand 4a ($\lambda_{max,em} = 515 \text{ nm}$), and the complex 5a ($\lambda_{max,em} = 559 \text{ nm}$) (Figure S8). The increasing bathochromic shift of the emission in this series again shows the rising acceptor strength of the fulvene moiety when moving from the chlorovinyl group (2a) over the free isocyanovinyl group (4a) to the isocyano–gold complex (5a). Neither 5a nor any of the other complexes showed fluorescence in the solid state.

DFT Study. To elucidate the origin of their electronic properties, a computational survey was performed. The molecular structures of the free ligands and complexes were optimized at the B3LYP-D3/TZVP level in the gas phase, and

Table 3. Calculated Orbital Energies and Lowest-Energy Transitions

	HOMO - 1	НОМО	LUMO	LUMO + 1	Exc1 HOMO \rightarrow LUMO		Exc2 HOMO $-1 \rightarrow LUMO^{a}$			
	eV	eV	eV	eV	eV	nm	f	eV	nm	f
4a	-7.94	-7.71	-1.44	-0.17	3.56	349	0.008	4.14	299	0.563
5a	-8.09	-7.82	-1.82	-0.27	3.34	371	0.003	3.91	317	0.803
4b	-7.96	-6.96	-1.36	-0.05	3.08	403	0.012	4.19	296	0.427
5b ^{syn}	-8.11	-7.02	-1.81	-0.16	2.70	459	0.006	3.93	316	0.637
5b ^{anti}	-8.10	-7.05	-1.75	-0.13	2.84	437	0.009	3.95	314	0.690
4c	-7.47	-7.35	-1.27	-0.16	3.42	363	0.001	3.96	313	0.761
5c	-7.61	-7.45	-1.65	-0.26	3.19	389	0.006	3.72	334	1.001
4d	-7.71	-7.59	-1.31	-0.15	3.56	348	0.0004	4.07	305	0.644
5d	-7.86	-7.70	-1.71	-0.24	3.33	373	0.0002	3.83	324	0.882
4e ^b	-8.38	-7.47	-0.61	-0.60	4.20	295	0.353	4.29	289	0.146
5e	-8.48	-7.57	-1.13	-0.72	3.97	313	0.222	4.19	296	0.335
$4f^{c}$	-8.29	-7.38	-0.97	-0.26	3.94	315	0.249	4.70	264	0.037
$5f^d$	-8.39	-7.47	-1.41	-0.14	3.66	339	0.364	4.46	278	0.319
4a-AgCl	-8.14	-7.83	-1.79	-0.27	3.35	370	0.004	3.98	312	0.706
4a-CuCl	-8.10	-7.83	-1.83	-0.27	3.33	372	0.003	3.89	319	0.746
4a-W(CO) ₅	-7.36	-7.10	-1.43	-0.42	3.28	378	0.604	HOMO	\rightarrow LUMC) (82%) ^e
4a-Mo(CO) ₅	-7.44	-7.18	-1.55	-0.28	3.40	365	0.658	HOMO \rightarrow LUMO (84)) (84%) ^f
4a-Cr(CO) ₅	-7.67	-7.33	-1.49	-0.18	3.53	351	0.294	HOMO $-2 \rightarrow$ LUMO (53 HOMO \rightarrow LUMO (41%)		40 (53%), 0 (41%)
					3.56 348 0.507 HOMO $- 2 \rightarrow LUM$ HOMO $\rightarrow LUM($				40 (43%), O (55%)	

^{*a*}Unless otherwise indicated, HOMO \rightarrow LUMO or HOMO-1 \rightarrow LUMO is >92%. ^{*b*}Exc1, HOMO \rightarrow LUMO (61%) and HOMO \rightarrow LUMO + 1 (35%); Exc2, HOMO \rightarrow LUMO (33%), HOMO \rightarrow LUMO + 1 (58%), and HOMO $- 2 \rightarrow$ LUMO (3%). ^{*c*}Exc2, HOMO $- 2 \rightarrow$ LUMO (10%), HOMO \rightarrow LUMO + 1 (76%), HOMO $- 3 \rightarrow$ LUMO (2%), and HOMO \rightarrow LUMO + 6 (4%). ^{*d*}Exc2, HOMO $- 1 \rightarrow$ LUMO (88%) and HOMO \rightarrow LUMO + 3 (2%). ^{*e*}HOMO $- 1 \rightarrow$ LUMO + 2 (5%) and HOMO \rightarrow LUMO + 4 (5%). ^{*f*}HOMO $- 1 \rightarrow$ LUMO + 3 (3%) and HOMO \rightarrow LUMO + 4 (5%).



Figure 4. Calculated UV–vis absorption spectra of free ligands and AuCl-complexes. The geometry was B3LYP-D3/TZVP, the TD-DFT was CAM-B3YLP/def2-TZVP (solvent model: PCM; solvent: DCM), and mwb60 was used for gold atoms. Inserts show close-ups of weak HOMO-to-LUMO transitions.

electronic transitions were subsequently computed by timedependent DFT calculations (TD-DFT) at the CAM-B3LYP/ def2-TZVP level using the PCM solvent model (the solvent was dichloromethane). The effective core potential mwb60 was used to emulate the gold atoms. Alkoxy and alkyl groups were shortened to methoxy and methyl groups to reduce the computational effort. Included in the survey were the ligands **4a**-**f** and the complexes **5a**-**f**. For the **5b** complex, two conformers (*syn* and *anti*) were identified wherein the methoxy groups point either towards the AuCl group (*syn*) or away from it (*anti*). The *syn* conformer is more stable ($\Delta G = -6.0$ kJ/mol) and exhibits some structural and electronic differences (for details, see Figure S12 and associated comments in the Supporting Information).

TD-DFT calculations on the fluorene derivatives showed very weakly populated HOMO-to-LUMO transitions, both for the free ligands and for the complexes (Exc1 = 3.56-2.70 eV and f = 0.0057 to 0.0002; Table 3 and Figure 4A–D). These transitions can be assigned to the low intensity λ_{max} bands present in the experimental absorption spectra of all four fluorene derivatives. This confirms that the bands are true absorption features of the compounds, and no artifacts were caused by decomposition or oligomerization. The calculations also predict a second set of more intensely populated transitions (Exc2 = 3.72-4.19 eV and f = 0.563-1.001) that are between 0.5 (4d,c) and 1.1 eV (4b) higher in energy and are near-exclusively HOMO - 1 to LUMO in character. In agreement with the experimental results, we assigned Exc2 to the experimentally observed main absorption bands (λ_2) with maxima between 335 (4b) and 380 nm (5c). Furthermore, the calculations also correctly predict Exc2 to become more intense upon metal coordination (Table 3 and Figure 4A-D,F). A comparison of frontier orbital plots of fluorene derivatives (Figure 5A; see also Section 3 of the Supporting Information), shows that the HOMOs are delocalized across the benzo rings, but do not contain electron density within the isocyanomethylene fragment. In contrast, the HOMO - 1 and



Figure 5. Exemplary frontier orbital plots for (A) **4c** and **5c** and (B) **4f** and **5f**. Plots were generated with the GaussView 6.0 program; the isovalue is 0.035.

LUMO contain strong contributions both from the fluorene framework and the C=CH-NC-(AuCl) group. In both ligands and complexes, the HOMO – 1-to-LUMO transition Exc2 therefore constitutes a π - π * transition, whereas the HOMO-to-LUMO transition Exc1 involves a charge transfer from the π -system onto the C=CH-NC-(AuCl) group. This analysis agrees with reports on the electronic properties of other fluorene-based dyes.⁵⁶

For 4e and 5e and 4f and 5f, the calculations predict the lowest energy excitations to be strongly populated HOMO-to-LUMO⁵⁷ transitions (4e, E = 4.20 eV, f = 0.353; 5e, E = 3.97 eV, f = 0.222; 4f, E = 3.94 eV, f = 0.249; 5f, E = 3.66 eV, f = 0.364). In both types of compounds, the HOMO and LUMO are delocalized throughout the molecules, and both show contributions from the isocyanomethylene group that become stronger upon metal coordination (Figure 5A; see also Section 3 of the Supporting Information). In 4f and 5f, the sulphur

atom also contributes strongly to the HOMO. Overall, the lowest energy transitions in 4f and 5f therefore constitute charge redistributions from sulphur to the isocyanomethylene moiety that can be assigned to the observed main absorption bands centered at 356 (4f) and 385 nm (5f), respectively.

To further demonstrate the possibilities of the ligands in this survey, the structures and electronic properties of additional complexes of ligand 4a were computed (Figure 6). Specifically,



Figure 6. Calculated transitions and UV-vis spectra of other isocyanide complexes. The geometry was B3LYP-D3/TZVP, the TD-DF was CAM-B3YLP/def2-TZVP (the solvent model was PCM and the solvent was DCM), and effective core potentials were used for heavy metal atoms.

the homologous d¹⁰ complexes 4a-AgCl and 4a-CuCl were simulated in addition to 5a (i.e., 4a-AuCl), as well as d⁶ carbonyl complexes of the type $4a-M(CO)_5$ (M = Cr, Mo, or W). 4a-AgCl and 4a-CuCl exhibit electronic properties that are virtually identical to those of 4a-AuCl. The three complexes share the weakly populated HOMO-to-LUMO transitions as well as more strongly populated HOMO - 1-to-LUMO transitions of an almost identical energy. However, the calculations predict markedly different properties for the pentacarbonyl complexes, as exemplified by the discussion of $4a-W(CO)_5$. The HOMO-to-LUMO excitation in this complex is of a similar energy as for 4a-AuCl (4a-W(CO)₅, Exc1 = 3.28 eV and 378 nm, f = 0.604) but is electronically different and expected to be much more strongly populated. In this complex, the highest occupied molecular orbitals (HOMO - 2 to HOMO) are dominated by the occupied d orbitals at the metal center (Figure 7).⁵⁸ The HOMO – 2 (d_{yz}) and HOMO - 1 (d_{xy}) show limited-to-no delocalization into the ligand and do not participate in transitions involving the isocyano ligand. The HOMO, however, is dominated by the $d_{\pi\pi}$ orbital and shows both π -back bonding to the isocyano carbon and strong contributions from the fulvenyl fragment. The LUMO, on the other hand, is delocalized across the whole isocyano ligand. This spatial overlap allows a strong electronic coupling that represents a metal-to-ligand charge transfer upon excitation. The electronic situation is almost identical in 4a- $Mo(CO)_{5}$, while for $4a-Cr(CO)_{5}$ only slightly differing properties were computed.59

CONCLUSION

In summary, we have reported the synthesis and comprehensive characterization of a series of isocyanofulvenes that cover a broad range of electrochemical and optical properties. Through the preparation of their corresponding gold(I) complexes, we also demonstrated their great potential as



Figure 7. Frontier orbital levels of 4a-W(CO)₅. Plots were generated with the GaussView 6.0 software; the isovalue is 0.035.

ligands in coordination and materials chemistry. A notable finding is that the solid-state structures of complexes 5a, 5c, 5e, and **5f** are governed by both $\pi - \pi$ stacking of the ligand frames and by aurophilic interactions. This reoccurring property may be exploited to engineer the solid-state structures of other isocyano-gold(I) complexes. UV-vis absorption spectra of the ligands show a consistent bathochromic shift upon metal coordination that indicates the effective conjugation between the coordinating functional group and the π -systems of the ligand. We further elucidated the origin of the optical properties of the ligands and complexes through DFT calculations. Theses analyses confirmed the presence of weak longest-wavelength absorption bands for all fluorene-based ligands and complexes that originate from charge transfer from the fluorenyl π -system towards the isocyanovinyl moiety. This process is rather ineffective in these systems because the fluorenyl moiety represents an electron-acceptor rather than an electron-donor. More effective charge transfer processes were observed in thioxanthene- and dibenzocyloheptene-based donor fulvenes.

The gold(I) complexes of fluorene-based ligands exhibit weak π -back bonding between the ligand and d orbitals at the metal center. Hence, the metal center is only marginally involved in electronic transitions. In an additional DFT study we could show, however, that carbonyl-complexes of group six

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metals of the type R–NC–M(CO)₅ (M = Cr, Mo, and W) would exhibit very effective metal-to-ligand charge transfer. Since our study also shows that we can readily modify the electronic properties of the ligand π -systems, this indicates that isocyanofulvene ligands may be of interest for (photo-) catalysis and optical applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02435.

Experimental procedures for syntheses, spectroscopic and electrochemical data, a detailed listing of the physical properties of ligands and complexes, Khon– Sham frontier orbital plots, NMR spectra, and details on crystal structure data collection (PDF)

Crystallographic data on 5e and 5f as well as molecular structures and electronic transitions computed by TD-DFT (ZIP)

Accession Codes

CCDC 2022537–2022542 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

S.S., J.T., and F.P. thank the German Science Foundation (DFG, project no. FP 2217/3-1) and the German Chemical Industry Fund (FCI, Liebig scholarship to F.P.) for financial support. A.O. thanks the Swedish Research Council (Vetenskapsrådet) for support.

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(58) In the following discussion, the x-axis was arbitrarily assigned to the direction of C—M bond, and the z-axis was assigned perpendicular to the fluorenyl plane. Consequently for 4a-W(CO)₅, the HOMO – 2 shows contributions from the d_{yz} orbital, the HOMO – 1 shows contributions from the d_{xy} orbital, and the HOMO involves the d_{xz} orbital.

(59) For 4a-Cr(CO)₅, two conformeric structures were found wherein the fluorenyl moiety stands either staggered or eclipsed to the CO ligands. The eclipsed conformation is $\Delta G = 2$ kJ/mol more stable, and the data for this conformer are included in the listing of electronic transitions included in the Supporting Information. However, computed electronic properties differ only marginally, and data for both conformers are included in the Supporting Information.