Gold Catalysis

Observing Initial Steps in Gold-Catalyzed Alkyne Transformations by Utilizing Bodipy-Tagged Phosphine–Gold Complexes

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Abstract: The Pd-catalyzed reactions of 3-chloro-bodipy with R_2PH (R=Ph, Cy) provide nonfluorescent bodipy-phosphines 3-PR₂-bodipy **3a** (R=Ph) and **3b** (R=Cy; quantum yield $\Phi < 0.001$). Metal complexes such as [AgCl(**3b**)] and [AuCl(**3b**)] were prepared and shown to display much higher fluorescence ($\Phi = 0.073$ and 0.096). In the gold complexes, the level of fluorescence was found to be qualitatively correlated with the electron density at gold. Consequently, the fluorescence brightness of [AuCl(**3b**)] increases when the chloro ligand is replaced by a weakly coordinating anion, whereas upon formation of the electron-rich complex [Au(SR)(**3b**)] the fluorescence is almost quenched. Related reactions of [AuCl(**3b**)] with [Ag]ONf)] (Nf= nonaflate) and

Introduction

Understanding catalytic processes is of essential importance for enhancing catalysts and catalytic transformations.^[1] Acquiring such an understanding critically relies on spectroscopic techniques, which are able to probe the status of the species under study with sufficient precision and sensitivity.^[2] In this respect, fluorescence spectroscopy could be a useful method,^[3] since the high sensitivity of detection perfectly suits the monitoring of catalytic species, which (almost by definition) are present in very small concentrations during catalytic reactions.

Ligand-exchange reactions constitute elementary steps in the chemistry of metal complexes and are crucial in catalytic transformations. It would thus be highly enlightening to synthesize a fluorescent reporter ligand for catalytically active metals, the fluorescence properties of which are modulated by such elementary reactions. Only a few examples related to catalysis in single-molecule studies^[4] and in ensemble measurements in solution have been realized,^[5] despite the fact that related approaches are very popular in photoluminescent sensing.^[6]

The detection processes in such complexes reported to date have been relatively simple, in that only two states are consid-

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phenyl acetylenes enable the tracking of initial steps in gold-catalyzed reactions by using fluorescence spectroscopy. Treatment of [AuCl(**3 b**)] with [Ag(ONf)] gave the respective [Au(ONf)(**3 b**)] only when employing more than 2.5 equivalents of silver salt. The reaction of the "cationic" gold complex with phenyl acetylenes leads to the formation of the respective dinuclear cationic [{(**3 b**)Au}₂(CCPh)]⁺ and an increase in the level of fluorescence. The rate of the reaction of [Au(ONf)(**3 b**)] with PhCCH depends on the amount of silver salt in the reaction mixture; a large excess of silver salt accelerates this transformation. In situ fluorescence spectroscopy thus provides valuable information on the association of gold complexes with acetylenes.

ered (signal on/off) depending on the presence or absence of quencher. A transition metal and a ligand tagged with a fluorescent dye associate to form a fluorescent or a nonfluorescent complex, the brightness of which is reversed by a reaction. This principle has been put to good use to clarify mechanistic issues concerning the postulated release-return mechanism in olefin metathesis (Scheme 1 a).^[7] Mirkin and co-workers reported a Pt complex in which the bodipy-centered fluorescence is reversibly modulated by an added aminophosphine ligand L (Scheme 1 b).^[8] This ligand L releases a nitrogen donor from the coordination sphere of platinum, which then guenches the fluorophore. We recently realized that changes in the fluorescence signal of bodipy-tagged N-heterocyclic carbene metal complexes also occur as a consequence of changes in the coordination sphere of a metal, despite the fact that the spatial relationship of fluorophore and transition metal remains unchanged. In this case, the substitution of a 1,5-cyclooctadiene (cod) ligand in an Ir complex by two CO molecules converts an initially dark complex into a brightly fluorescent complex (Scheme 1 c).^[9] This modulated fluorescence intensity was attributed to changes in the electron density at the transition metal and indicates that the photoinduced electron transfer (PET) mechanism appears to be primarily responsible for fluorescence quenching. The oxidative addition of H₂ to a fluorophore-tagged Crabtree-type complex is another example of a fluorogenic reaction (Scheme 1 d) that is useful for the detection of H₂.^[10]

For this study, it was our target to synthesize metal complexes of bodipy-tagged phosphines, in which one phosphorus donor is directly connected to the bodipy core. The resulting

Chem. Eur. J.	2016, 2	2, 6353 – 636	50
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Scheme 1. Examples of switched fluorescence (on/off) in transition metal complexes with an appended fluorophore. Mes = 2,4,6-trimethylphenyl, bdp = bodipy, SIMes = 1,3-bis(2,4,6-trimethyl)phenyl-4,5-dihydroimidazol-2-ylidene.

phosphine should be dark, due to PET quenching by the phosphorus lone pair. However, coordination of this lone pair to a transition metal should restore fluorescence when using metals that do not open other quenching pathways (for example, heavy atom effect or through minor changes in the electronic structure).^[11] Such a partially quenched fluorescence signal can be sensitive to subtle changes in the coordination sphere of the metal and translate such changes into an increase or a decrease in the bodipy fluorescence.

Results and Discussion

Synthesis of bodipy-tagged phosphines

Only a few examples of bodipy-tagged phosphines have been reported to date.^[12] Higham and co-workers recently reported the synthesis of several bodipy-phosphines, as well as metal complexes with coinage metals ions such as Cu, Ag, Au and with Re.^[13] Bodio and co-workers also reported such phosphines and the derived Ru, Os and Au complexes,^[14] whereas Lim and Blum reported a related Pd complex.^[15] Most of the previously reported metal complexes are highly fluorescent, because the distance between the phosphorus (or the transition metal) quencher and the bodipy is rather large. Our strategy is different, in that the phosphorus donor and the bodipy core are to be connected directly, to initially generate fluorescence-quenched bodipy-phosphines.

We first tested fluorescence properties of the known $8-Ph_2P$ bodipy (Scheme 1).^[16] However, we learnt that this ligand and the respective gold complex show unfavorable properties (low fluorescence quantum yields, very broad emission band, and instability). Therefore, another synthetic approach leading to different bodipy-phosphines was required.

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The reaction of 2,2'-(p-tolylmethylene)bis(1H-pyrrole)^[17] with *N*-chlorosuccinimide followed by chloranil and BF₃·Et₂O provides 3-chloro-bodipy 2 in a three step, one-pot procedure involving two chromatographic purifications in an acceptable overall yield of 19% (Scheme 2). An experimental procedure and spectroscopic data for this compound were reported only very recently.^[18] Our procedure reported herein is based on the synthesis of the closely related 3,5-dichloro-bodipy.^[19] In the latter compound, the chlorine atoms are highly activated towards nucleophilic substitution and Pd-catalyzed cross coupling reactions^[20] and can be replaced with various nucleophiles (amines, alcohols, thiols, etc.) in good yields employing mild reaction conditions.^[21] Consequently, reactions of 2 with Ph₂PH or Cy₂PH and base (Et₃N) provide the respective bodipy-phosphines 3a and 3b, but better yields (72-76%) were obtained, when the same reactions were carried out in the presence of catalytic amounts of Pd(OAc)₂.^[22] Additional phosphine for the activation of the palladium catalyst was not required and we assume that the secondary



 $\label{eq:scheme 2. Synthesis of bodipy-phosphines. Reaction conditions: a) Ph_2PH, CH_2Cl_2, 15 min; b) N-chlorosuccinimide, -78 °C, THF, followed by chloranil, followed by BF_3·Et_2O, NEt_3; c) R_2PH (R=Ph, Cy), Pd(OAc)_2, Et_3N, toluene.$

phosphine used as a reagent forms a sufficiently active crosscoupling catalyst with palladium.^[23] The bodipy-phosphines **3a** and **3b** are slightly sensitive towards oxidation and in a few reactions under ambient atmosphere, small amounts of phosphine oxide **4a** were formed and separated by chromatography.

Metal complexes of bodipy-phosphines

The new metal complexes of bodipy-phosphines (Scheme 3), like [AuCl(1)] and [MX(3b)] (M = Cu, Ag, Au) were synthesized



Scheme 3. Synthesis of metal complexes of bodipy-phosphines. Reaction conditions: a) [AuCl(Me₂S)], CH₂Cl₂, RT, 30 min; b) Cul, MeCN, RT, 1 h; c) AgNO₃, KCl, water/THF, RT, 3 h; d) [PdCl₂(MeCN)₃], CH₂Cl₂, RT, 12 h.

following established procedures for complexes of Ph_3P with copper (X=I),^[24] silver (X=CI),^[25] and gold (X=CI).^[26] The copper and the silver complexes with **3a** and **3b** are significantly less stable than the respective gold complexes. Solutions of the copper complexes decompose within a few hours, whereas the silver complexes decompose when the solutions are exposed to air. The most stable complexes are formed with the electron-rich phosphine **3b** and gold. Nonetheless, NMR

spectra of all Cu⁺, Ag⁺, and Au⁺ complexes could be recorded. However, based on the optical data, which are the same as those of phosphine **3a**, [Cul(**3a**)] appears to dissociate at the low concentrations used to record such spectra ($c=1.0 \times 10^{-6}$ mol L⁻¹). Complex [PdCl₂(**3b**)₂] was synthesized from [PdCl₂(MeCN)₂] and **3b** in 88% yield.^[27]

NMR spectra

The bodipy-phosphines are characterized by the presence of several NMR active nuclei and, in particular, the ³¹P NMR spectra display interesting features. In the ³¹P spectra of **3a** and **3 b**, large ${}^{4}J({}^{31}P-{}^{19}F)$ coupling constants are observed (**3 a**: J =45.5 Hz; **3b**: J=52.4 Hz; Figure 1).^[28] The same corresponding ⁴J(³¹P-¹⁹F) values are much smaller in the respective phosphine-metal complexes; for example, in the gold complex ([AuCl(3a)], J is 15.4 Hz, and it is even smaller in [AuCl(3b)] (J < 2 Hz; Figure 1). Our explanation for this observation is based on the Fermi contact term mechanism, which accounts for the coupling between ¹⁹F and ³¹P and the efficiency of which increases with increasing s-orbital participation in the bonds connecting the two nuclei.^[29] In the phosphine, the phosphorus lone pair is partially delocalized into the electrondeficient bodipy π -system. This leads to increased s-content in the respective P-C(bodipy) bond. In the gold complexes, as well as in the other metal complexes, this lone pair is donated to the transition metal rather than to the bodipy, leading to a decrease in the s-content of the P-C(bodipy) bond and consequently to a decrease in the coupling constant. A related phenomenon concerning ¹⁹F-¹³C coupling constants was observed in fluorine-containing crown ether complexes, in which the magnitude of the coupling constants turned out to be an effective gauge of the fluorine-metal interactions.[30]

In [AgCl(**3 b**)], a ^{107,109}Ag-³¹P coupling is detected, with a typical value for Ag-phosphine complexes of J = 617 Hz.^[31] The ³¹P signal is severely broadened ($\nu_{1/2} = 150$ Hz) and this line broadening prevents the determination of the individual ¹⁰⁷Ag or ¹⁰⁹Ag coupling with ³¹P. Such signal broadening is also observed for [Cul(**3 a**)] and [Cul(**3 b**)] and potential ³¹P-¹⁹F coupling could not be resolved. Such exchange-broadened



Figure 1. ³¹P(¹H) NMR spectra of phosphine 3 b (left) and [AuCl(3 b)] (right). Total range displayed for each spectrum is 300 Hz.

Chem. Eur. J. 2016, 22, 6353-6360

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³¹P NMR signals are typical for Ag– and Cu–phosphine complexes and reflect the lability of such species in solution.[31]

The coordination of bodipy phosphines 3a and 3b to Au led to a significant deshielding of the ³¹P resonance from $\delta =$ -20.3 ppm for **3a** to $\delta = 20.2$ for [AuCl(**3a**)] and from $\delta =$ -14.7 ppm for **3a** to δ = 47.5 for [AuCl(**3b**)]. The more pronounced deshielding of the ³¹P NMR resonance in **3b** (compared to 3 a) upon metal coordination is in line with a more efficient donation of the phosphorus lone pair in [AuCl(3b)] to gold.

X-ray crystal structure analysis of [AuCl(3 a)]

Single crystals of [AuCl(3a)] were grown by slow evaporation of a cyclohexane/CH₂Cl₂ solution (Figure 2). The geometrical features of the complex are very similar to those of the related [AuCl(PPh₃)] complex [Au–P 223.08(5), Au–Cl 229.15(5) pm].^[32] Gold has a coordination number of two and adopts linear coordination geometry. The distance from gold to the nearest fluorine atom is 325.3(5) pm, which is too long to consider a significant Au-F interaction.[30a]



Figure 2. X-ray crystal structure analysis and ORTEP representation of X-ray crystal structure of [AuCl(3 a)]:^[35] Thermal ellipsoids are set at 50% probability (color coding: Au yellow, P orange, F greenish yellow, B pink, Cl green, N blue). Important bond lengths (pm) and angles (°): Au-P 222.7(2), A-Cl 229.8(3), Au…F 325.3(5), 377.1(6); P-Au-Cl 174.88(8).

Optical properties

Fluorescence quantum yields and absorbance and emission maxima of the newly synthesized bodipy compounds are summarized in Table 1. All fluorophores reported herein display a strong UV/Vis absorbance at 506-552 nm and are characterized by small Stokes shift of approximately 15 nm. The small Stokes shifts point to a similar geometry of the excited and the ground state of the fluorophore.^[33] Replacing Cl with PPh₂ or PCy₂ leads to a long-wave shift of the absorbance maximum $(\Delta \lambda = +13 \text{ or } +25 \text{ nm})$; complexation of the phosphorus by group 10 metals leads to short-wave shift in the absorbance

Table 1. Optical properties of bodipy derivatives.				
Compound	$arPhi^{[a]}$	Absorbance λ_{\max} [nm]	Emission λ_{\max} [nm]	
1	< 0.001	529	_	
2	0.093	506	519	
3a	< 0.001	531	-	
3 b	< 0.001	519	-	
4a	0.026	508	524	
[AuCl(1)]	0.008	552	567	
[Cul(3 b)]	0.016	516	527	
[AgCl(3 b)]	0.073	515	528	
[AuCl(3 a)]	0.087	515	531	
[Au(NTf ₂)(3 b)]	0.11	508	523	
[AuCl(3 b)]	0.096	510	526	
[Au(CCPh)(3 b)]	0.070 ^[b]	510	526	
$[PdCl_2(3 b)_2]$	< 0.001	540	-	
[a] Φ values were determined in 1,2-dichloroethane versus rhodamine 101 (Φ = 1.0 in EtOH) at RT with a concentration range of 0.25-1 µm; [b] estimated value (see the Supporting Information).				

(and emission) maxima of approximately 10 nm. Like other 3heteroatom-substituted bodipy compounds, such as the 3amino-substituted bodipy,^[21b] the bodipy-phosphines **3a** and 3b are essentially nonfluorescent with fluorescence quantum yields of $\Phi < 0.001$. It is likely that the phosphorus lone pair engages in PET guenching of the excited state.^[3] In case this is true, the respective complexes of 3a and 3b with transition metals coordinated through the phosphine lone pair can be expected to display brighter fluorescences, unless the presence of the metal opens new relaxation pathways. Indeed, the respective metal complexes of Ag⁺ and Au⁺ are fluorescent with $\Phi \approx$ 0.1, whereas that of Pd²⁺ is nonfluorescent. Spectroscopic reporter groups are important since the d¹⁰ ions Cu⁺, Ag⁺, and Au⁺ do not show d-d transitions in the UV/Vis spectrum. Interestingly, the phosphine oxide 4a is fluorescent ($\Phi =$ 0.026), but less so than the metal complexes, which is consistent with the results of a study on fluorescent phospholes.^[34]

Monitoring ligand substitution reactions by fluorescence spectroscopy

In contrast to the bright bodipy-NHC conjugates recently reported,^[9,10] the fluorescence in the bodipy-phosphines reported herein is largely quenched, probably due to PET-type quenching of the fluorophore. However, once the phosphorus lone pair is donated to a metal, an increase in the fluorescence quantum yields is likely, unless the metal itself opens new quenching pathways. Au^l is normally a non-quenching metal ion and we therefore decided to study different ligand substitution reactions in the stable complex [AuCl(3b)]. This is especially interesting with a view to the prominent role that closely related complexes have played in homogeneous catalysis.^[36]

Gold-thiolato complexes

The addition of an alkanethiol (1-dodecanethiol) to [AuCl(3b)] leads to an exponential decrease in the fluorescence intensity within approximately two minutes; upon addition of base

Chem. Eur. J. 2016, 22, 6353 - 6360





Figure 3. Fluorescence intensity vs. time plot for the reaction of thiol (dodecanethiol) with [AuCl(**3 b**)] in 1,2-dichloroethane ($c = 1.0 \times 10^{-6} \text{ mol L}^{-1}$) and base (Et₃N). Order of addition of reactants: [AuCl(**3 b**)] + Et₃N then thiol (trace a) or [AuCl(**3 b**)] + thiol then Et₃N (trace b).

(Et₃N), the fluorescence of this complex nearly vanishes (Figure 3).^[37] Upon addition of an arylthiol (thiophenol or thiocresol) to [AuCl(3b)] the decrease in fluorescence is more pronounced, leading to an almost quenched complex (the addition of base produces only a small additional decrease in the brightness). The addition of Et₃N alone to [AuCl(3b)] does not have a significant influence on the fluorescence intensity, the fluorescence is only guenched once the thiol is added. This shows that the addition of thiol and Et₃N leads to the formation of the well-established gold thiolato complexes,^[38] with a significantly increased electron density at the gold. It is likely that this increase in electron density enhances the PET quenching of the fluorophore because the electron-rich gold is less willing to accept the phosphorus lone pair.^[11a] This hypothesis is supported by work from Nagano and co-workers on organic fluorophores, who established a qualitative relationship between the electron density (rather the energy of the HOMO) of a quencher and the fluorescence quantum yield.^[39]

It is not clear why the addition of alkanethiol leads to a smaller decrease in the fluorescence intensity than with the arylthiol, but the different acidities of alkanethiol and arylthiol might play an important role. Two explanations are considered: a) the thiol replaces the chloro ligand forming a cationic complex of the type $[Au(RSH)(3b)]^+Cl^-$; b) alternatively, an equilibrium of the type [AuCI(3 b)] + RSH = [Au(SR)(3 b)] + HCI is established. In order to probe hypothesis (a) the reaction of [AuCl(3b)] with thiophene was studied in the fluorescence spectrometer. No change in the fluorescence was observed upon addition of thiophene and therefore coordination of the thiol is less likely. To verify hypothesis (b), different amounts of thiol (50, 100, 200, 400 equiv) were added to [AuCl(3b)]. Depending on the amount of added thiol, a corresponding decrease in the fluorescence intensity was observed, with more thiol leading to successively weaker fluorescence. The fluorescence is always fully quenched upon addition of base to this reaction mixture. This observation is in line with shifting the equilibrium [according to (b)] upon addition of more alkanethiol to the product side. Based on this equilibrium, the much larger initial drop of brightness with aryl thiols as compared to alkyl thiols can be explained based on the much higher acidity of aryl thiols. The analogous experiments (addition of 1 equiv thiol and 1 equiv Et₃N to [AuCl(**3 b**)], albeit at ca. 10000 times higher concentration of gold complex) were carried out in NMR tubes. Resonances detected in the ³¹P NMR spectra of the nonfluorescent solutions show the clean transformation of [AuCl(**3 b**)] (δ = 47.5 ppm) into [Au(SC₁₂H₂₅)(**3 b**)] (δ = 49.6 ppm) or into [Au(SPh)(**3 b**)] (δ = 50.5 ppm); no other peaks are observed in the ³¹P NMR spectra.

Gold complexes with weakly coordinating anions

Based on the results with Au thiolates, a decrease in the electron-density at the transition metal could lead to enhanced brightness. We were therefore interested, whether it is possible to study the formation of "cationic" gold complexes at catalytically relevant concentrations using fluorescence spectroscopy. This was tested by replacing the strongly coordinating chloride in [AuCl(3b)] with weakly coordinating (donating) anions (wca), with the help of silver salts.^[40] Such reactions are very important in gold catalysis, often constituting the crucial activating step in numerous gold-catalyzed transformations.^[41] Complexes such as [LAu(wca)] are generated in situ from [LAuX] (X = Cl, Br, I) through silver salt metathesis involving precipitation of AgX,^[42] but may also be isolated and then used in catalysis.^[43] The nature of the anion and of the solvent, in which such reactions are carried out, exert a very significant influence on the formation of solvent-separated ions (vs. close ion-pairs) and consequently on catalytic activity.^[44]

To a solution of $[AuCl(\mathbf{3} \mathbf{b})]$ in 1,2-dichloroethane were added aliquots corresponding to 0.5 equivalents of [Ag(ONf)] (ONf = $C_4F_9SO_3^{-}$) in the same solvent (Figure 4). The fluorescence intensity of the solution increased following the addition of each aliquot and reaches saturation after adding approximately 2.5 equivalents of silver salt, corresponding to an increase in fluorescence brightness of approximately 20%.^[45,46] Addition of more silver salt (up to 20 equiv) did not lead to significant change in the fluorescence intensity. It is likely that the fluorescence increase is due to ONf⁻ being less electron-donating than chloride. To test this, $[Au(NTf_2)(\mathbf{3} \mathbf{b})]$ was synthesized and



Figure 4. Fluorescence intensity vs. time plot for the addition of six aliquots of [Ag(ONf)] (0.5 equiv; denoted by arrows) to a solution of [AuCl(**3 b**)] ($c = 1.0 \times 10^{-6} \text{ mol } \text{L}^{-1}$) in 1,2-dichloroethane.

Chem. Eur. J. 2016, 22, 6353-6360



CHEMISTRY A European Journal Full Paper

the fluorescence intensity was found to be almost the same as that of the in situ prepared gold nonaflate. However for both [Au(wca)(3b)] complexes, the change in fluorescence intensities are rather modest compared to those seen in the other reactions reported herein. This may well mean that in the 1,2-dichloroethane solvent, cation and anion still form fairly close ion pairs, which is reasonable with a view to the very low donicity of 1,2-dichloroethane.[47,48] The experiments clearly show that the reaction of gold complex with [Ag(ONf)] requires superstoichiometric amounts of silver salt to form the gold nonaflate complex. When smaller amounts of silver salt intermediate species are used, presumably Au-Cl-Au species are formed.^[49] This fits well with results reported by Echavarren and co-workers, who showed that a significant excess of [Ag(OTf)] is required to produce the related [(JohnPhos)-Au(OTf)] from [(JohnPhos)AuCl], as demonstrated by NMR studies.^[49] Our studies confirm the results from Echavarren's group; however, in our study such information are obtained at catalytically relevant concentrations.^[50]

Gold-acetylene complexes

Next, we were interested to learn whether the modulation of brightness could be used to probe the initial steps defining gold-catalyzed reactions with acetylenes. Key species in such reactions include η^2 -bonded acetylenes, $^{[51]}$ σ -bonded acetylides, $^{[52]}$ and the cationic digold species $[(LAu)_2(CCR)]^{+}.^{[52,53]}$ Changes in the coordination sphere should influence the electron density at gold and lead to the characteristic modulation of the fluorescence intensity.

To a solution of [AuCl(3b)] in 1,2-dichloroethane were added 1–30 equivalents of [Ag(ONf)]. The formation of [Au(ONf)(3b)]is accompanied by a modest increase in the fluorescence intensity (figs. 4 and 5). To the in situ-generated gold nonaflate were added 1000 equivalents of phenyl acetylene, leading to a very pronounced increase in the brightness (Figure 5). The



Figure 5. Fluorescence intensity vs. time plot for the reactions of [AuCl(3 b)]($c = 1.0 \times 10^{-6} \text{ mol } L^{-1}$) in 1,2-dichloroethane with different amounts of [Ag(ONf)] (added after ca. 1.5 min: trace f: +1 equiv [Ag(ONf)]; trace e: +5 equiv; trace d: +10 equiv; trace c: +15 equiv; trace b: +20 equiv; trace a: +30 equiv) to [AuCl(3 b)], followed by addition of phenyl acetylene (1000 equiv added after 2.5–3.4 min). Traces a–f denote the fluorescence-time changes after addition of alkyne to gold complexes activated with different amounts of [Ag(ONf)].

amount of silver in the reaction mixture has a significant influence on the evolution of the fluorescence intensity. In the presence of large amounts of [Ag(ONf)] (>10 equiv) a very fast increase in the brightness is observed. When applying less silver salt, the reaction with acetylene is sluggish or does not take place. The need for a large excess of silver salt is not obvious, since our previous experiments had shown that [Au(ONf)(3b)] is already formed with approximately 2.5 equivalents of silver salt. However, it is well known that for many Aucatalyzed reactions, a significant rate acceleration occurs in the presence of a large excess of silver salt.^[42b,44a,54] Based on these results, we conclude that the coordination of the alkyne to the gold and alkyne deprotonation are critical steps. Consequently, the coordination of alkyne to excess silver salt appears to activate this substrate for the reaction with gold, leading to an overall faster reaction.

The reactions of acetylenes with cationic gold complexes can lead to several different species, including a side-on bound complex [LAu(PhCCH)], a terminal acetylide complex [LAu(CCPh)], and a dinuclear species [(LAu)₂(CCPh)]^{+.[55]} Based on the fluorescence intensity alone, it is not possible to identify the formed species, but we were able to gather sufficient evidence to identify the formed complex. The side-on complex is a fragile species and only a few examples of such complexes have been reported.^[51a] In the presence of base, this complex is easily converted into the terminal acetylide.^[56] However, in the reactions presented herein, the addition of an excess of base (Et₃N) does not lead to significant changes in the brightness. The side-on complexes with PhCCH are characterized by modest formation constants,^[52,57] which render their presence in the 10⁻⁶ mol L⁻¹ solutions of Au complex less likely. To probe the potential formation of a side-on bound complex, the cationic gold complex was exposed to 1000 equivalents of 4octyne, which is known to form more stable complexes with LAu⁺ than PhCCH.^[57] However, no change in the fluorescence brightness was observed and based on this evidence we conclude that the side-on acetylene-gold complex is not formed in such dilute solutions.

The terminal acetylide complex is another potential reaction product. However, this neutral complex should not lead to the observed pronounced increase in the fluorescence level, but instead to a significant decrease. To further clarify this, [Au(CCPh)(3b)] was synthesized and the fluorescence quantum yield determined, which is much lower than that of [AuCl(3b)] (Table 1). For this reason, we believe the species formed in our fluorescence experiments to be the dinuclear [{(3b)Au}2(CCPh)]⁺.^[52-53] Closely related species with SIPr-type N-heterocyclic carbene (NHC) ligands instead of 3b are well known.^[51a] The cationic nature of this complex, is in accord with the pronounced increase in fluorescence intensity. A reaction mixture containing the dinuclear species, based on a procedure by Widenhoefer and co-workers,^[52] was probed by NMR spectroscopy (albeit at much higher concentration than in the fluorescence experiment). This experiment provides clear evidence for the formation of the dinuclear species. However, we were not able to isolate this complex in its pure state due to its instability. The phosphine ligand 3b is most likely insuffi-

Chem. Eur. J. 2016, 22, 6353-6360



ciently bulky to render a stable dinuclear complex. Furthermore, NMR signals are observed for the known vinyl triflate, which is the addition product of PhCCH and TfOH. Based on the fluorescence intensity of the insitu-formed [{(**3 b**)Au}₂(CCPh)]⁺, the fluorescence quantum yield of this complex is estimated $\Phi \approx 0.4$.

Finally, we were interested to find out whether the modulation of the electronic nature of the phenyl acetylene has an influence on the fluorescence intensity of the remote bodipy unit. This was tested by using phenyl acetylenes with electronwithdrawing (R=NO₂) and electron-donating groups (R= NMe₂) in the 4-position. The respective digold complexes [{(**3 b**)Au}₂(CCC₆H₄-R)]⁺ were generated with the aid of Hünig's base in the cuvette and the fluorescence intensity measured (Figure 6). The fluorescence experiment proved to have excellent sensitivity, since even the remote 4-NMe₂ substituent led to a significant decrease in the fluorescence brightness of the peripheral bodipy unit, whereas the 4-NO₂ group caused a small increase in the (already high) brightness of the fluorescence emission.



Figure 6. Fluorescence intensity vs. time plot for the reactions of [AuCl(**3** b)] $(c = 1.0 \times 10^{-6} \text{ mol } L^{-1})$ with [Ag(ONf)], Hünig's base, and three different phenyl acetylene derivatives HCCC₆H₄R (1000 equiv; R = NO₂, H, NMe₂), yielding [{(**3** b)Au}₂(CCC₆H₄R)]⁺ ONF⁻ complexes in 1,2-dichloroethane.

Conclusion

We have demonstrated that fluorescence spectroscopy utilizing bodipy-tagged phosphines can be used to monitor introductory steps in gold-catalyzed alkyne transformations in a catalytically relevant concentration range. The reactions involving [AuCl(3b)] show that changes in the electron density at the transition metal, resulting from ligand substitution reactions, translate into characteristic changes in the brightness of the bodipy reporter group. An increase in the electron density at gold leads to a decrease in the brightness, whereas lower electron density at gold results in an increase in the fluorescence brightness. In suitably designed complexes, the fluorophore is highly sensitive to changes in the environment of the gold and even remote substituents in the periphery lead to pronounced changes in the brightness. The phosphine-gold complexes reported herein appear to be ideal in that the initial complex [AuCl(3b)] displays an intermediate level of fluorescence ($\Phi \approx$ 0.1). Consequently, our studies reveal subtle details of the reaction of [AuCl(**3 b**)] with [Ag(ONf)] and different acetylenes. The nature of the silver additive appears to be important both as an activator to generate the "cationic" gold complex and as an activator of the alkyne. The large excess (> 15 equiv) of silver salt needed to accelerate the reaction with the alkyne, may explain why several gold-catalyzed reactions perform better in the presence of excess silver salt—even though the "cationic" species is already formed with approximately 2.5 equivalents of silver salt.

We believe that the observation of the modulated fluorescence intensity in (catalytically active) transition metal complexes with suitable fluorescent tags renders a highly useful tool for the analysis of chemical transformations.

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