Metal-to-Metal Distance Modulated Au(I)/Ru(II) Cyclophanyl Complexes: Cooperative Effects in Photoredox Catalysis

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Abstract: The modular synthesis of Au(I)/Ru(II) decorated mono- and heterobimetallic complexes with π-conjugated [2.2]paracyclophane is described. [2.2]Paracyclophane serves as a rigid spacer which holds the metal centers in precise spatial orientations and allows metal-to-metal distance modulation. A broad set of architectural arrangements of pseudo -gemininal, -orth, -meta, and -para substitution patterns were employed. Metal-to-metal distance modulation of Au(I)/Ru(II) heterobimetallic complexes and the innate transannular π-communication of the cyclophanyl scaffold provides a promising platform for the investigations of structure-activity relationship and cooperative effects. The Au(I)/Ru(II) heterobimetallic cyclophanyl complexes are stable, easily accessible, and exhibit promising catalytic activity in the visible-light promoted arylative Meyer-Schuster rearrangement.

Introduction

Heterometallic complexes have received considerable attention due to their distinctive magnetic and optical properties and further their emerging synthetic applications in catalysis.[1] Installation of heterometallic moieties in one framework – each intended to serve a particular, independent purpose, can execute precise sequences of multiple reactions in a one-pot fashion. The activity of one metal is enhanced by the other and in combination, may reduce the activation barrier by cooperative effects.[2] Incorporating a second metal center into mononuclear organometallic complexes can lead to novel reactivity and enhanced selectivity compared to the reaction performed with a mixture of related monometallic complexes.[3] However, it remains a synthetic challenge to position heteronuclear metal centers with a well-defined electronic environment in a pre-defined orientation to one another to achieve cooperative effects. Among various contributing factors based on the nature of the metal, oxidation state, and coordination number, metal-to-metal (M–M) distance modulation has been a promising approach to identify and fine-tune cooperative effects in (hetero)bimetallic systems.[4] Especially the bridging ligand design is decisive to incorporate multiple metal centers in defined orientations and stands in the center from a perspective of application.[5] The choice of the coordination environment, ligand effects like flexibility, steric, electronic parameters, and an appropriate spacer that allows for systematic variation of M–M distances are crucial contributing factors.[6] The presence of two or more metal centers with defined M–M distances can be achieved either by a conjugated or non-

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conjugated tether. Both types of tethers have been reported for bimetallic ruthenium complexes,[9] whereas a conjugated tether allows an electronic communication between the metal centers and thus an alteration of the electronic properties of one or both metal centers.

Our research group has a long-standing interest in the chemistry of [2.2]paracyclophane (PCP) scaffolds for a diverse range of applications, including developing versatile PCP-derived planar chiral ligands and catalysts – employed most notably for various enantioselective transformations.[10] PCP is a co-facially stacked prochiral scaffold that displays unusual characteristics caused by transannular π-π electronic interactions of the benzene rings fixed in close proximity and exhibits unique stereochemical features on selective functionalization.[10] When employing carefully chosen transformations, different substituents can be positioned selectively either at only one or both benzene rings, i.e., mono-, and differently functionalized disubstituted PCP regioisomers including pseudo-, ortho-, meta-, and geminal, derivatives can be synthesized (Figure 1). The prefix pseudo refers to substituents positioned on different decks of the PCP scaffold. From a geometric point of view, the two moieties on PCP can be held parallel to each other, i.e., pseudo-geminal, anti-parallel in pseudo-orthal, and pseudo-meta position. The substitution pattern on PCP heavily influences the nature of the respective compound and even minor changes can alter its properties significantly.[10]

The application of PCP derivatives as chiral ligands or catalysts for stereoselective syntheses have been extensively investigated.[10-13] Installation of (hetero)bimetallic centers using PCP as a bridging ligand can bring the metals in a well-defined and spatially-oriented relation to one another where M–M distance modulation and the extent of through-space electronic communication can be studied with regard to a structure-activity relationship and cooperative effects. Recent examples of PCP as a bridging ligand include distance-modulated cyclo-ruthenated complexes holding two ruthenium metal centers selectively either at only one or both decks with varying M–M distances.[12] PCP porphyrin conjugates allow convenient access to modular fixed-distance bimetallic Cu/Zn complexes.[13] In the context of π-electronic communication, “through-space” (i.e., π-stacking) via the co-facially stacked benzenes, various constitutional isomers of bis(ferrrocenylvinyl)-substituted PCPs and diruthenium cyclophanyl complexes have been investigated and compared to their non-PCP analogues, where electron delocalization is a prominent contributing factor.[14] The regioselective substitution pattern of PCP can be used for M–M distance modulation. PCP-derived homobimetallic gold(I) complexes with varying intramolecular Au–Au distances based on the diposphine ligands Ph₂-GemPhos and PhanePhos have previously been reported. By single crystal X-ray diffraction, the Au–Au distance in pseudo-geminal (2.98 Å) and pseudo-ortho (3.23 Å) position, as well as the respective P–P distances of 4.068 Å and 5.014 Å, in case of the corresponding ligands were found.[15] In this work, we report the modular synthesis of a series of cyclophanyl-derived mono- and M–M distance modulated (hetero)bimetallic complexes by combining Au(I) with Ru(bpy)₃ppy as a photosensitizer to explore the structure-activity relation and their synthetic applicability. Merging transition metal and photocatalysis to enable chemical synthesis with naturally abundant, visible light will significantly impact the emerging field of photocatalysis.[16]

Results and Discussion

Synthesis: The Au(I) was to be incorporated by coordination with a triarylphosphine ligand while a cyclometallated phenylpyridine substituent would allow installation of the Ru(II).

Starting from 4,16-dibromo[2.2]paracyclophane (1),[17] selective mono-lithiation and reaction with chlorodiphenylphosphine gave 4-bromo-16-diphenylphosphoryl[2.2]paracyclophane (2, Scheme 1). The phosphine is prone to oxidation in air and is rapidly converted to the phosphine oxide, making its isolation by column chromatography impractical. Therefore, before purification, the phosphine was oxidized with hydrogen peroxide to the corresponding phosphate oxide 2, which simplified its isolation. Under optimized Suzuki-Miyaura reaction conditions, a new C–C bond to 2-phenylpyridine was formed. After two steps, compound 3 was obtained in 92% yield and bears both the phosphate oxide as a precursor for the selective binding of Au(I) and 2-phenylpyridine for the incorporation of Ru(II).[18]

Reduction of phosphate oxide 3 with trichlorosilane/triethylamine[11a] and reaction of the phosphate, which was obtained after rapid aqueous workup, with [tth]AuCl,[19] gave compound 4 in 36% yield (Scheme 2).

Initial attempts to incorporate the Ru(II) complex structure into compound 4 were made by using [Ru(bpy)₃]Cl₂ and silver(I) tetrafluoroborate as dechlorination agent to aid the cyclometallation reaction.[19] This method was unsuccessful, presumably due to the chlorine-abstracting properties of the silver salt,
which led to the decomposition of the gold moiety. The alternative approach that forgoes any dechlorination agent involves the formation of a cyclometallated tetraacetonitrile Ru(II) complex.\textsuperscript{[21]} Complex 5 is formed by the reaction of ligand 4 with benzeneruthenium(II) chloride dimer in acetonitrile and sodium hydroxide as a base. Displacement of the labile acetonitrile ligands with 2,2'-bipyridine gave the final \( p \AuRu \) complex 6 in 26\% yield over four steps. The final complex 6 was obtained as a mixture of diastereomers with a planar chiral and a chiral-at-metal stereocenter. The molecular structure of the \( p \AuRu \) precursors 3 was confirmed by single-crystal X-ray diffraction (Figure 2).

The selective bromination of 4-diphenylphosphonyl [2.2]paracyclophane (7), in pseudo-\textit{geminal} position, gave compound 8 in 94\% yield.\textsuperscript{[16c]} Thermal isomerization of 8, which involves the homolytic cleavage of one ethylene bridge (under the formation of a diradical, rotation, and subsequent ring closure), gave the pseudo-\textit{meta} derivative 9 in 85\% yield (Scheme 3, A).\textsuperscript{[17b,c,22]} Similarly, pseudo-\textit{ortho} derivative 10 was obtained by isomerization of 1 at 215 °C, in 85\% yield. Followed by monolithiation and reaction with diphenylphosphine chloride gave 4-bromo[2.2]paracyclophane-12-diphenylphosphin oxide (11) in 61\% yield (Scheme 3, B).\textsuperscript{[23]}

The general synthesis route established for the preparation of \( p \AuRu \) was also applied in the synthesis of the pseudo-\textit{meta}, -\textit{ortho}, and -\textit{geminal} regioisomers, with slight variations. The Suzuki-Miyaura reaction conditions for both pseudo-\textit{ortho} and -\textit{geminal} derivatives 11 and 8 were modified since the standard protocol employing RuPhos as ligand only led to the isolation...
of starting material. The use of (rac)-AntPhos, which is more adapted for the cross-coupling of sterically demanding substrates, gave the corresponding products 12 and 13 in 59% and 60% yield, respectively (Scheme 4).

Successive incorporation of the gold(I) chloride and ruthenium(II) bipyridyl moiety into the pseudo-geminal 13, pseudo-ortho 12, and pseudo-meta isomers 14 enabled to prepare a complete set of differently functionalized Au(I)/Ru(II) heterobimetallic complexes, gemAuRu (18), oAuRu (19), and mAuRu (20), with overall yields ranging from 10% to 28% (Figure 3). All AuRu isomers were obtained as diastereomeric mixtures with a d.r. = 1:1. For the detailed synthesis of the mono-metallic precursors 15, 16, and 17, as well as gemAuRu (18), oAuRu (19), and mAuRu (20), see the Supporting Information. The respective mono-metallic PCP-Au (21) and PCP-Ru (22) were also prepared for their comparison with literature known complexes (Figure 4).

Scheme 4. Suzuki cross-coupling conditions for incorporating the 2-phenylpyridine (ppy) moiety into pseudo-geminal/ortho- and pseudo-meta/para-isomers.

The molecular structure of the mAuRu precursor 14, the oAuRu precursor 11 and monometallic PCP-Au (21) were confirmed by single-crystal X-ray diffraction (Figure 5). Single crystals of the final heterobimetallic AuRu complexes suitable for X-ray diffraction were not obtained.

Mass Spectrometric Analysis: The metal complexes AuRu (6, 18–20), PCP-Ru (22) and Ru(bpy)3(ppy) were analyzed by ESI-MS in their monocationic form, without counterions. In a second step, those were isolated in the ion trap and exposed to collision induced dissociation (CID) and photodissociation (PD). A qualitative examination of the AuRu complexes is exemplarily performed for the pseudo-para isomer pAuRu (6). All complexes were dissolved in acetonitrile and then injected by electrospray ionization into the mass spectrometer.

The molecular peaks for [pAuRu]+, [PCP-Ru]+ and [Ru(bpy)3(ppy)]+ are found at m/z 1190, 774 and 568, respectively, and identified by their isotope patterns. CID of [pAuRu]+ (Supporting Information-Figure S89) takes place by two fragmentation pathways. The first pathway starts with the neutral loss of one bpy ligands forming the fragment with the highest intensity at m/z 1034. Subsequently [AuCl(Ph3P)2-PCP-(ppy)Ru(bpy)]+ either splits off a second bpy ligand giving m/z 878 or is subject to the loss of an HCl molecule at the ClAu(PPh2)-PCP reactive site of the complex forming m/z 998. Since the latter peak appears only at a lower intensity, the loss of the second bpy seems to be favored. However, the loss of HCl takes place even after the loss of the second bpy ligand resulting in a peak at m/z 842. In each case, the proton (or H-atom) for the HCl loss probably stems from the spatially close phenyl group of the PPh2 ligand or from the PCP ligand. Such cleavages are often observed in MS fragmentation. Eventually, the loss of...
the Au atom and a Ph substituent leads to the species [(PPh)3AuCl]PF6−
and formed as discussed before. To confirm the assignment, the ions related to m/z 670 were isolated in a MS2 step and subjected to fragmentation. The resulting fragments at m/z 514 and 412 match the previously discussed fragmentation pathway. However, the photoinduced dissociation only leads to the fragment at m/z 670. The CID fragmentation of [Ru(bpy)ppy]2+ (Supporting Information-Figure S93), results in the loss of one bpy ligand leading to the species [Ru(bpy)ppy]2+ at m/z 412 and the subsequent attachment of one H2O molecule forms [Ru(bpy)ppy(H2O)]2+ at m/z 430, which is a common ion-molecule reaction for undercoordinated Ru6+ complexes in ion traps. The photodissociation approach shows barely any fragmentation yield, probably since the necessary dissociation energy for the bidentate ligands cannot be achieved by one-photon absorption processes.

Ion Mobility Spectrometry: A combination of quantum chemical calculations and ion mobility spectrometry (IMS) was used to obtain structural parameters and estimate the M—M distances of the AuRu complexes (Table 1).

The obtained CCS follow the order [pAuRu]2+ > [mAuRu]2+ > [oAuRu]2+ = [gemAuRu]2+ and are qualitatively consistent with calculated CCS of the complexes (Figure 7, obtained by trajectory calculations with the IMoS package).25b

Additionally, IMS allows the differentiation of isomers and conformers that differ by less than 0.5% in CCS. The diastereomeric nature of the AuRu complexes indicated by a double signal set in NMR spectroscopy was also confirmed by the two peaks present in each mobilogram.

Ground State Studies: Electronically excited states, which are essential in photoredox chemistry, are generated by the light absorption of a molecule in the ground state. Selective and efficient irradiation and the evaluation of redox properties are essential for understanding and ultimately, applying new photoredox catalysts. For this purpose, absorption and emission spectroscopy and cyclic voltammetry were performed.

Table 1. M-to-M distances of the global minima and the Boltzmann average of the possible rotamers.

| entry | compound        | Calculated CCS [Å2][a] | Au-Ru distance [Å][b] | Boltzmann Average [Å][c] |
|-------|-----------------|------------------------|-----------------------|--------------------------|
| 1     | pAuRu (6)       | 325                    | 22.36                 | 22.2                     |
| 2     | mAuRu (20)      | 311                    | 15.49                 | 18.5                     |
| 3     | oAuRu (19)      | 298                    | 11.98                 | 14.4                     |
| 4     | gemAuRu (18)    | 305                    | 11.70                 | 12.3                     |

[a] Global minimal structure; [b] all calculated CCS are scaled by 0.89; [c] Boltzmann average of local minimum structures, 1.5 eV internal energy was assumed. 1 au = 0.529 Å.

Figure 4. Monometallic complexes PCP–Au (21) and PCP–Ru (22).

Figure 5. Crystal structures of mAuRu precursor 17 (top), oAuRu precursor 11 (bottom left) and PCP–Au (21, bottom right). Displacement parameters are drawn at a 50% probability level in case of 17 and 11, and at a 30% probability level in case of 21.
Absorption/Emission Spectroscopy

The room temperature absorption spectra of monometallic and heterobimetallic Au(I)/Ru(II) PCP complexes are shown in Figure 8. The UV region below 310 nm is dominated by spin allowed ligand centered (LC) transitions and additional interligand (ppy – bpy) transitions. Additionally, the monometallic PCP-Ru (22) and the heterobimetallic AuRu isomers 6 and 18–20 show an additional band at 320 nm, where the PCP backbone is likely to contribute.\[26\] Examining the lower energy absorption bands reveals a large spectral envelope that arises from the cyclometalated 2-phenylpyridine ligand. The two absorption bands in the region between 350–450 nm and 450–600 nm result from metal-to-ligand charge transfer (MLCT) transitions.\[20b\] The MLCT bands show similarly high molar extinction coefficients for all heterobimetallic AuRu isomers while being substantially more prominent than the monometallic PCP-Ru (Table 2). The first band can be assigned to an MLCT from the ruthenium center to the cyclometalating 2-phenylpyridyl ligand, whereas the band at higher wavelengths is primarily localized on the bipyridyl ligands, indicating a delocalization of the LUMO mostly on the bipyridyl ligand, whereas the HOMO is most likely localized on the cyclometalating phenylpyridyl.\[20b,27\]

The emission spectra were recorded under argon atmosphere at 20 °C under excitation at wavelengths defined by the absorption maximum at 495 nm (Figure 8, right). This produces an emission band with a substantial Stokes shift at 795 nm. The excited-state energy of the first singlet excited state \(E_{S1} \) was estimated from the crossing point between absorption and emission profile.\[26\] This energy refers to the transition between the lowest energy vibrational state (\(v = 0\)) of \(S_1\) to \(v = 0\) of \(S_0\). Alternative methods to approximate this value use the earliest onset (highest energy) of fluorescence, the midpoint between emission and absorption maxima (one-half Stoke-shift), or the
fluorescence maximum. Each method is an approximation and is likely to over- or underestimate the value for $E_{\text{exc}}$. In combination with the ground state reduction and oxidation potentials, which are obtained from cyclic voltammetry (see below), it is used to estimate the excited state potentials $E^\ast$.

**Action Spectroscopy in Gas-phase and TD-DFT Calculations**

Ion trap UV photodissociation (UV-PD) spectroscopy in gas phase is an established technique, even though its application was realized with different experimental setups and primarily used for the investigation of biomolecular systems.[29] It has recently been applied to study metal complexes or aggregates.[24,30] However, studies for multimetallic, especially heterometallic, molecular systems are still scarce in this field.[30,31] In order to determine the intrinsic UV spectra devoid of counterions and solvent effects, UV photodissociation (UV-PD) spectra of the pseudo-para complex 6, the monometallic complex 22 and $[\text{Ru(bpy)}_6\text{ppy}]^{\text{2+}}$ were recorded. After electrospray ionization and mass-selective ion-trap isolation at room temperature the corresponding cations $[\text{AuRu}]^{\text{2+}}$, $[\text{PCP-Ru}]^{\text{2+}}$ and $[\text{Ru(bpy)}_6\text{ppy}]^{\text{2+}}$ were examined at m/z 1190, 774 and 568.

UV-PD spectra represent gas phase action spectra recorded by UV laser irradiation of the mass-selected and stored species in an ion trap by monitoring their relative photofragment yield (since photoexcitation usually leads to dissociation if the photon energy exceeds possible fragmentation barriers) as a function of laser wavelength. Here, $[\text{AuRu}]^{\text{2+}}$ shows two bands in the CT region ($> 400$ nm) and more intense bands at 350 nm, 295 nm, and 260 nm. The UV-PD spectrum of $[\text{PCP-Ru}]^{\text{2+}}$ exhibits similar band positions as $[\text{AuRu}]^{\text{2+}}$ below 400 nm, however, the bands at 350 nm and 260 nm appear with lower intensity (Supporting Information-Figure S97). The UV-PD spectrum of $[\text{Ru(bpy)}_6\text{ppy}]^{\text{2+}}$ only shows a band at 295 nm with low intensity. For $[\text{PCP-Ru}]^{\text{2+}}$ and $[\text{Ru(bpy)}_6\text{ppy}]^{\text{2+}}$ above 400 nm the fragment yield was too low for analysis, possibly due to the relatively high activation barriers for dissociation, so that the UV-PD spectra could not be obtained in those CT regions.

A comparison of the gas phase to the solution phase spectra reveals similarity for all studied species with the strongest band close to 300 nm. Remarkably, for $[\text{AuRu}]^{\text{2+}}$ a second peak (red-shifted to 350 nm) appears in the gas phase spectrum resembling the double-peak structure observed in other Ru$^{\text{2+}}$ complexes in the gas phase.[32] It could originate from the shoulder or a small peak observed at 320 nm in solution. However, this feature does not appear in the spectrum of the $[\text{Ru(bpy)}_6\text{ppy}]^{\text{2+}}$ species and is related to the PCP and/or the PPh$_2$AuCl unit and constitutes an interesting target wavelength for ultrafast pump-probe studies (see below).

Quantum-chemical calculations based on time-dependent density functional theory (TD-DFT) using the hybrid functional (CAM-)B3LYP with the cc-PVT(D)Z basis set (ECP for Ru and Au, Stuttgart97) were employed to get insight into the underlying electronic transitions. The B3LYP functional delivers satisfying results for Ru(II) polypyrrolid complexes,[33] while CAM-B3LYP corrects for the long/short range correlation issue of larger molecules.[34] From these calculations, theoretical absorption spectra were obtained for all conformational isomers of both diastereomers of $[\text{AuRu}]^{\text{2+}}$ (6) and plotted in Figure 9 and Supporting Information-Figure S101. The spectra are remarkably similar to each other and display only a slight variability in the shoulder at 320 nm. Moreover, the spectra mimic the experimental solution spectra in the short wavelength region quite nicely, although the CT region, especially above 500 nm is not well reproduced. However, the calculated spectrum using the B3LYP functional shows more similarity to the UV-PD gas phase spectrum and reproduces its strong band at 350 nm (Supporting Information-Figure S99).

The type of transition is identified by visualizing the involved molecular orbitals (MOs, Supporting Information-Figure S104). The absorption and UV-PD spectrum of $[\text{AuRu}]^{\text{2+}}$ and the calculated transitions in form of vertical sticks are shown in Figure 10. The broad bands in the experimental data, their intensity, and shape depend critically on the calculated “density”, position and oscillator strength of these electronic transitions. The percentages of the coupled ground and excited state MOs for each transition is shown in Supporting Information-Table S7. Based on the contribution of the involved MOs the type of transition can be estimated. For $[\text{AuRu}]^{\text{2+}}$ only transitions possessing an oscillator strength of $\geq 0.03$ and MOs with a weight $\geq 10\%$ were considered. The bands in the CT region (370 nm–560 nm) are assigned to the states S5, S6, S22, and S29 and characterized as MLCT transition, where the electron density from Ru is moved partially to the ligands bppy and bppy’ (Supporting Information-Figure S103, structural breakdown).

The transitions for the band around 360 nm cannot be clearly and uniformly assigned due to the low contribution of the involved MOs. However, S38, S39 and S40 suggest a MLCT transition partially from AuRu onto the ligands coordinated at Ru (ppy, bppy, bppy’). The transition S45 at 345 nm shows ILCT (interligand charge transfer) character, where the electron
density moves from a ligand coordinated at Au to the ppy ligand. In the UV-PD gas phase spectrum of \( \text{pAuRu}(6) \), a weak shoulder appears around 310 nm. This is assigned to the transitions S79 and S80, characterized as MLCT involving Au and the ligands ppy, bpy and bpy'. This wavelength region was also used for transient absorption spectroscopy in this work (see below). The calculation for S98 did not result in a clear type of this transition. However, an LC transition is assigned to S111. The remaining states do not possess MOs with a significant contribution, so that the characterization of those transitions is unclear. However, the states under 300 nm strongly suggest ILCT and LC transitions. The calculations with the CAM-B3LYP functional (Figure 9, Supporting Information-Figure S107–111, Supporting Information-Table S10–S12) deliver a better description of the MOs and the according transitions. By and large, their assignment follows those obtained with the B3LYP functional. However, the calculated spectrum using CAM-B3LYP is blue shifted in comparison to the results presented in Figure 10. The MLCT transitions involving Au appear at 254 nm, the ILCT transitions involving PCP at 280 nm and the MLCT transitions involving Ru at >300 nm. In summary, the theoretical analysis by TD-DFT agrees only partially with the experimental results but allows for adequate and generic assignment of the transitions in order to characterize the observed bands in Figures 8, and.

Cyclic Voltammetry

The redox behavior of PCP-Ru (22) and all AuRu isomers 6 and 18–20 consists of a reversible metal-based oxidation process in the range of +0.26–+0.51 V, which is assigned to the Ru(III) redox couple (Figure 11, left). An irreversible ligand-based reduction process at −1.67−−2.24 V is observed and can be ascribed to reducing the bipyridyl ligands. The anionic and electron-rich character of the 2-phenylpyridyl ligands makes its reduction more complicated such that it occurs at lower reduction potentials.

CV measurements of PCP-Ru (22) and mAuRu (20) were conducted at different scan rates (see Supporting Information-Figure S77 and S78). The peak current was plotted against the square root of the scan rate to obtain the Randles-Sevcik plots (see Supporting Information-Figure S79 and S80).

The linear relationship between peak current and the square root of the scan rate indicates that the oxidation process is diffusion controlled. The measurements were only conducted for the monometallic PCP-Ru (22) and heterobimetallic complex mAuRu (20). Similar behavior is assumed for all other AuRu isomers.

Figure 10. Gas phase UV-PD spectrum (blue) and calculated transitions (stick) of \([\text{pAuRu}]^+\) calculated with B3LYP, as well as the liquid phase absorption spectrum in CH\(_2\)Cl\(_2\) (red) of \(\text{pAuRu}(6)\). The different ligands of the complex are marked with their abbreviations.

Figure 11. Cyclic voltammograms of PCP-Ru (22) and AuRu isomers 6 and 18–20 (left) and CV spectra of the second oxidation process (right) (0.1 M \(\text{Bu}_4\text{NPF}_6\), CH\(_2\)Cl\(_2\), 100 mV/s).
A second and third oxidation process takes place in the range of 1.45–1.90 V (Figure 11, right) and are irreversible. Upon repeated cycles, an insulating layer forms on the electrode surface, which causes a decrease in current intensity from cycle to cycle. These oxidation processes can either be attributed to a Ru II /III oxidation or ligand decomposition, displayed by cyclo-metallated complexes.33,36 Additionally, the (electro)chemical oxidation of [2.2]paracyclophane and some of its derivatives is well established and leads to the formation of benzyl radical/benzyl cation intermediates under C–C bond scission of the ethano bridges. The highly reactive intermediate readily reacts either with itself or other molecules to form an insulating polymeric species.34,37 The combined data obtained from absorption/emission spectroscopy and cyclic voltammetry measurements are summarized in Table 2. Most ground state parameters such as absorption maxima ($\lambda_{\text{max}}^{\text{abs}}$), molar extinction coefficient ($\varepsilon_{\lambda_{\text{max}}^{\text{abs}}}$), HOMO-LUMO gap ($\Delta E_{\text{HOMO-LUMO}}$), and $E_{\text{red}}$ show only slight deviations among the AuRu isomers 6 and 18–20. The oxidation and reduction potentials $E_{1/2}^{\text{ox}}$ and $E_{1/2}^{\text{red}}$ indicated a significant M–M interaction.

The first oxidation potential describes the oxidation of Ru II to Ru III, whereas the reduction takes place on the 2-phenylpyridine moiety of the AuRu isomers. The order for oxidation and reduction potential is mirrored, where the most substantial oxidation potential and therefore the weakest reduction potential are found for mAuRu (20, Equation 1).

\[
\begin{align*}
E_{\text{ox AuRu}} & > E_{\text{ox gem AuRu}} > E_{\text{ox para AuRu}} > E_{\text{ox AuRu}} \\
E_{\text{red AuRu}} & < E_{\text{red gem AuRu}} < E_{\text{red para AuRu}} < E_{\text{red AuRu}}
\end{align*}
\]

Equation 1 Order of oxidation (top) and reduction potentials (bottom) of AuRu isomers 6 and 18–20 from strongest to weakest (left to right).

These results can be rationalized by transannular and through-space interactions between the gold and ruthenium centers. In pseudo-para position, electron-donation of the gold moiety onto the ruthenium center is possible through-annular communication and leads to an increase of $E_{1/2}^{\text{ox}}$ by 0.09 V. This type of communication is most pronounced in pseudo-ortho position, which leads to an oxidation potential which is 0.10 V less than the monometallic PCP-Ru (22). It is least pronounced in the pseudo-meta position, which accounts for a difference of 0.15 V compared to PCP-Ru (22), such that the value of $E_{\text{red AuRu}}$ is 0.25 V less than for mAuRu (20). The oxidation potential of gemAuRu (18) indicates a very weak interaction between the gold and ruthenium centers, which is a deviation of 0.04 V compared to the monometallic PCP-Ru (22).

From the obtained oxidation and reduction potentials combined with $E_{\text{ox}}$, an approximate value for the excited state potentials $E^*_e$ can be obtained and summarized in Table 2.

The excited state reduction potential $E^*_e$ shows that both monometallic catalyst PCP-Ru (22) and the AuRu isomers 6 and 18–20 are considerably stronger reducing agents in their excited than in their ground state. The order of redox potentials is consistent with the corresponding ground state values, where oAuRu (19) is the most potent reducing agent and mAuRu (20) the weakest. Photoinduced reduction with either PCP-Ru (22) or any of the AuRu isomers is unfavorable since $E^*_e$ is either negative or has small positive values. This is in agreement with the proposed mechanisms presented in the literature where it is shown that the excited state of Ru undergoes oxidative quenching by the aryldiazonium salt.33,34

Ultrafast Transient Absorption Spectroscopy: As a first step to further unravel the M–M interactions via femtosecond (fs) transient absorption spectroscopy, the photo-induced dynamics of pAuRu (6) was compared to the monometallic PCP-Ru (22) and Ru(bpy)$_2$ppy. For pAuRu (6) in CH$_2$Cl$_2$ no significant difference was observed for the photoinduced dynamics when excited at 405 nm or 495 nm (Figure 12A, Supporting Information-Figure S81A). Comparison to Ru(bpy)$_2$ppy in CH$_2$Cl$_2$ excised at 405 nm and 312 nm (Supporting Information-Figure S81B, C), also shows no change in dynamics. Thus, under excitation in the MLCT-bands around 405 nm and 495 nm no significant influence of the PCP-Au-moiety on the photo-induced dynamics of pAuRu (6), but only the dynamics of the Ru-moiety was observed. However, when pAuRu (6) is excited at 312 nm, an impact on the difference spectra is obvious (Figure 12A and B). Even more striking, the difference spectra of PCP-Ru (22) in CH$_2$Cl$_2$ excited at 312 nm (Figure 12C) clearly differ from those of pAuRu (6) as well as Ru(bpy)$_2$ppy. Thus, in contrast to excitation at 405 and 495 nm, excitation at 312 nm dramatically changes the kinetics in pAuRu (6) and PCP-Ru (22), although in a different manner. In other words, the addition of the Au-moiety (which does not exhibit an absorption band at 312 nm) to PCP-Ru (22) (which does exhibit an absorption band at 312 nm, Figure 8) leads to a significant and non-additive change of the excited state dynamics.

| entry | compound | $\lambda_{\text{max}}^{\text{abs}}$ [nm] | $\varepsilon_{\lambda_{\text{max}}^{\text{abs}}}$ [M$^{-1}$ cm$^{-1}$] | $E_{\lambda_{\text{max}}^{\text{abs}}}^{\text{ox}}$ [V] | $E_{\lambda_{\text{max}}^{\text{abs}}}^{\text{red}}$ [V] | $\Delta E_{\text{HOMO-LUMO}}$ [eV] | $\lambda_{\text{max}}^{\text{em}}$ [nm] | $E_{\lambda_{\text{max}}^{\text{em}}}^{\text{ox}}$ [eV] | $E_{\lambda_{\text{max}}^{\text{em}}}^{\text{red}}$ [eV] | $E_{\text{ox}}$ [V] | $E_{\text{red}}$ [V] | $E_{\lambda_{\text{max}}^{\text{em}}}^*$ [V] | $E_{\lambda_{\text{max}}^{\text{em}}}^*$ [V] |
|-------|----------|-------------------------------|--------------------------|-----------------|-----------------|-----------------------------|-------------------------------|--------------------------|-----------------------------|-----------------|-----------------|----------------|----------------|
| 1     | PCP-Ru (22) | 558 | 3.49 | 0.36; 1.45 | 2.24 | 2.60 | 774 | 1.81 | 1.45 | 0.43 |
| 2     | gemAuRu (18) | 562 | 9.07 | 0.32; 1.53 | 1.80 | 2.10 | 781 | 1.79 | 1.47 | 0.01 |
| 3     | oAuRu (19) | 554 | 9.30 | 0.26; 1.60 | 1.95 | 2.20 | 774 | 1.82 | 1.56 | 0.13 |
| 4     | mAuRu (20) | 554 | 9.18 | 0.51; 1.79 | 1.67 | 2.20 | 769 | 1.81 | 1.30 | 0.14 |
| 5     | pAuRu (6) | 557 | 9.31 | 0.42; 1.86 | 1.75 | 2.20 | 777 | 1.81 | 1.39 | 0.06 |

$\lambda_{\text{max}}^{\text{abs}}$ = absorption maximum of MLCT, $\varepsilon_{\lambda_{\text{max}}^{\text{abs}}}$ = molar extinction coefficient, $E_{\lambda_{\text{max}}^{\text{em}}}^{\text{ox}}$ = ground state oxidation/reduction potential, $E_{\lambda_{\text{max}}^{\text{em}}}^*$ = excited state oxidation/reduction potential, $\Delta E_{\text{HOMO-LUMO}}$ = HOMO-LUMO gap energy, $\lambda_{\text{max}}^{\text{em}}$ = emission maximum, $E_{\lambda_{\text{max}}^{\text{em}}}^*$ = excited state energy of the first singlet excited state $S_1$ (zero-zero transition energy).
Independent of excitation wavelength (312, 405, 495 nm), all measured complexes in Figure 12 and Supporting Information-Figure S81 show the excited state absorption (ESA) band at around 355 nm which is typical for the MLCT excited states, in analogy to Ru(II)-polypyridine complexes. This band partially decays as well with \( \tau_2 \). Thus, \( \tau_2 \) seems to represent the depopulation of the MC-excited states and the simultaneous population of a state X (which is not yet specified in more detail) around 475 nm (see \( A_1 \) in Supporting Information-Figure S83D). Therefore, we propose an intersystem crossing (ISC) or internal conversion (IC) process from the MC excited states to an unknown state X with \( \tau_2 \). This process is not observed for \( \text{pAuRu} \) excited at 405 nm and 495 nm or Ru(bpy),ppy, excited at 405 and 312 nm.

The monometallic PCP-Ru (22) excited at 312 nm (Figure 12C) only shows a broad ESA band besides the \(^3\)MLCT-ESA band at 355 nm and no bleach band in the examined spectral window. Inspection of Figure 12B and C (and decay associated spectra in Supporting Information-Figure S83D and E) reveal that the spectro-temporal evolution is significantly different from that in \( \text{pAuRu} \), but bears also characteristic similarities: (i) In PCP-Ru (22) the same band (at 475 nm) as in \( \text{pAuRu} \) is formed, but much faster, i.e. with a strong instantaneous component (ca. 70%, see Supporting Information-Figure S83E) and two weak components (\( \tau_1 = 1.1 \) and \( \tau_2 = 42 \) ps), and a lifetime much larger than 1 ns. However, signal decay in the region of MC absorption in synchrony with the ultrafast rise of the band at 475 nm is not observed, possibly due to non-sufficient time resolution. (ii) In contrast to \( \text{pAuRu} \) in PCP-Ru (22) an additional strong band at around 565 nm is formed concomitantly with the band at 475 nm but lifetime of about 2 ns.

The process of the proposed ISC or IC with \( \tau_2 \) in \( \text{pAuRu} \) is not distinctly observed in PCP-Ru (22), where the same state X seems to be populated much faster, and a strong ESA absorption around 565 nm indicates the formation of another

**Table 3.** Time constants resulting from a global analysis of femtosecond transient absorption data in CH\(_2\)Cl\(_2\) (see Supporting Information).

| entry | compound | \( \lambda_{ex} \) [nm] | \( \tau_1 \) [ps] | \( \tau_2 \) [ps] | \( \tau_3 \) [ps] | \( \tau_4 \) [ns] |
|-------|----------|----------------|----------------|----------------|----------------|----------------|
| 1     | Ru(bpy),ppy | 405   | 0.7 ± 0.2 | 17 ± 3 | / | / |
| 2     | \( \text{pAuRu} \) (6) | 405   | 1.0 ± 0.3 | 14 ± 3 | / | / |
| 3     | \( \text{pAuRu} \) (6) | 495   | 1.2 ± 0.2 | 14 ± 1 | / | / |
| 4     | \( \text{pAuRu} \) (6) | 312   | 0.3 ± 0.1 | 5.5 ± 1.0 | 68 ± 3 | / |
| 5     | PCP-Ru (22) | 312   | 1.1 ± 0.2 | 8 ± 2 | 42 ± 6 | (2) |
state, possibly quenched in pAuRu (6). This highlights the influence of the Au-moiety when pAuRu (6) is excited at 312 nm. Analogous investigations are in progress to analyze the underlying processes in the isomers 6 and 18–20, in particular with respect to the varying M–M-distance.

Ultrafast Transient Photodissociation Spectroscopy: In order to obtain intrinsic ultrafast dynamics we have applied our technique of pump-probe photodissociation spectroscopy (τ-PD) to the isolated ions [pAuRu]+ (6, m/z 1190) and [PCP-Ru]+ (22, m/z 774) in an ion trap at room temperature, with the aim to discern the influence of the PPh moiety on the [PCP-Ru]+ unit.[32] We have restricted ourselves to the investigation of the pseudo-para isomer, since its observed photocatalytic efficiency was the highest (Table 4) and hence dynamic effects of energy or excitation transfer from the Ru antenna unit to the reactive Au center are expected. Using τ-PD we record ultrafast dynamics of species produced by electrospray-ionization with subsequent mass-selection in an ion trap mass spectrometer after resonant photoexcitation in gas phase by monitoring their photofragment yield as a function of resonant pump (UV)-nonresonant-probe (NIR) time delay.

Here, the pump wavelength for excitation for both, [pAuRu]+ (6) and [PCP-Ru]+ (22) was set to 350 nm, which stems from the assignment of this peak in the gas phase spectrum (Supporting Information-Figure S100) to a band containing “cyclophane and phenyl-pyridine (π→π*) transitions” (see above). Note, that we assume that in the solution spectra a similar transition is observed at 312 nm (as a shoulder) and subsequently explored by ultrafast transient absorption as described above. However, the transients obtained for the gas phase by τ-PD (Supporting Information-Figure S110–S114) give a relatively limited picture and exhibit for both species a fast sub-picosecond relaxation, possibly internal vibrational redistribution (IVR, with τ ~ 0.5 ps +/− 0.05 and 0.4 ps +/− 0.04, for [pAuRu]+ (6) and [PCP-Ru]+ (22), respectively; Figure 13 and Supporting Information-Table S8) followed by stabilization of a long-lived state with a lifetime τ2 > 1 ns, likely a 3MLCT state. Unfortunately, we cannot conclude on any influence or electronic coupling originating in the PPhAuCl substituent. Remarkably though, the comparison to the solution data above reveals that time constants in the intermediate range of a few ps to a few tens of ps (cf. τ2 and τ3 of Table 3) seem to be completely missing for the gas phase dynamics. A technical possibility, which we cannot completely exclude, is that these intermediate time constants might belong to states with a low probe amplitude and elude our τ-PD analysis technique. However, related complexes containing Ru-polypyridyl units have been successfully analyzed using τ-PD.[32,40]

To sum up, the τ-PD method was successfully applied to the isolated complexes [pAuRu]+ (6) and [PCP-Ru]+ (22) resulting in intrinsic sub-ps formation of a long-lived electronically excited state. However, an influence of the PPhAuCl reactive center on the ultrafast dynamics was not detectable in the gas phase. In contrast, in solution, vibrational cooling or energy transfer to the solvent might be responsible for the richer dynamics and concomitant opening of different relaxation pathways.

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**Table 4. Catalytic application of the Au(I)/Ru(III) model complexes in a Meyer-Schuster rearrangement reaction.**

| entry | catalyst | yield [%] |
|-------|----------|-----------|
| 1     | PPh3AuCl/Ru(bpy)Cl2 | 73[a], 76[b] |
| 2     | PPh3AuCl/Ru(bpy)[bpy]PF6 | 73 |
| 3     | PCC-Au(21)/PCP-Ru(22) | 70 |
| 4     | pAuRu | 63 |
| 5     | mAuRu(20) | 30 |
| 6     | oAuRu(19) | 26 |
| 7     | gemAuRu(18) | 13 |

23 (0.10 M, 156 µmol), 24 (624 µmol), Au/Ru or AuRu (3.90 µmol, 2.5 mol%), CH3OH/CH2CN (3:1), r.t., green LEDs (524 nm, 30 W), 12 h; [a] determined via 1H NMR with 1,3,5-trimethoxybenzene as an internal standard; [b] isolated yield; [c] CH3OH was used as a solvent.

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![Figure 13. Normalized transient fragment ion intensity of [pAuRu]+ (A) and [PCP-Ru]+ (B) recorded at λpump = 350 nm on a 100 ps time window; bi-exponential fit (black) is given along the fit decomposition (green and red). Fit residual is shown below (blue).](image-url)
AuRu Heterobimetallic Cyclophanyl-Complexes in Meyer-Schuster Rearrangement: The Meyer-Schuster rearrangement (MSR) is a useful transformation of bifunctional, readily accessible propargyl alcohols into α,β-unsaturated carbonyl products. Advancing the catalysis concept, Glorius and others have reported visible-light promoted arylative MSR as testing ground to explore dual catalytic pathways under Au(I) and Ru(II) catalysis. The mechanism for the arylative MSR was proposed by Glorius et al. and is based on previous reports on dual gold photocatalysis. The catalytic cycle of the gold species is responsible for the formation of the arylated product. The ruthenium-based photocatalytic cycle of the gold species is responsible for the ultrafast formation of a long-lived electronically excited reactive state.

In summary, the formation of a series of cyclophanyl-derived Au(I)/Ru(II) decorated mono- and tunable heterobimetallic systems is described. Tailoring the cyclophanyl ligand by employing pseudo-geminal, ortho, meta, and para substitution patterns, allow to precisely organize the AuRu metal centers in spatial orientation, and enable M–M distance modulation. The photophysical and electronic ground-state properties of the AuRu isomers were investigated and suggest M–M interactions. Gas phase ultrafast photodissociation dynamics on isolated [AuRu]* confirms the intrinsic nature for the ultrafast formation of a long-lived electronically excited and reactive state.

Conclusion

At this point, a comprehensive interpretation of the ultrafast photo-induced dynamics is not yet possible – with pAuRu(6) being the only isomer investigated with fs time-resolved methods, so far. Hence, the impact of the current results of ultrafast transient spectroscopy on the photocatalytic mechanism is not clear, yet. The ongoing investigations of the other isomers including mAuRu(20), oAuRu(19) and gemAuRu(18) is necessary to get profound insights into the M–M interaction. The data of pAuRu(6) has shown a clear influence of the Au moiety on the dynamics of pAuRu(6), when excited at 312 nm. In contrast, the excitation of pAuRu(6) at lower energy bands (405 or 495 nm) leads only to dynamics analogues to Ru(bpy)$_2$(ppy)$_2$. The wavelength-dependency of the photo-induced dynamics might as well affect the performance in photocatalysis. Thus, the preliminary results of the time resolved data are pointing at the benefits of further investigations on the system in catalysis, for example, considering photoreactivity under irradiation with different wavelengths.

As an initial study, the performance of the AuRu complexes proved viable in visible-light mediated arylative Meyer-Schuster rearrangement and emphasizes the viability of this approach. In this particular setup, the chemical reactivity is influenced by steric effects, electronic parameters, and a reduction in M–M distance between the Au(I) and Ru(II) moieties, which is likely to play a crucial role.

Developing catalysts by combining multiple metal centers is an emerging field of interest. The underlying mechanisms and influences that govern activity and selectivity in catalysts that combine multiple metal centers in a single molecule are scarcely understood. This is especially the case in light-driven reactions, where the different timescales for light absorption, generation of the excited state, and the actual chemical
reaction are crucial parameters. Concerning the net effects of changing metal to metal distance in complexes, more research represents an important step forward for its practical applications. With this work we hope to spark further investigations which will help in the design of enhanced catalysts.

Experimental Section

Deposition Numbers 2080313 (3), 2080314 (11), 2080315 (21), and 2080316 (17) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Experimental procedures and spectral data for all these new compounds are available in the Supporting Information. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: metal-to-metal distance modulation · heterometallic complexes · cooperative effects · photoredox catalysis · [2.2] paracyclophane · gold · ruthenium

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