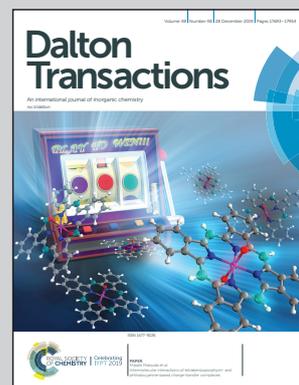


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Institute of Chemistry, Karlsruhe Institute of Technology,
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A highly stable, Au/Ru heterobimetallic photoredox catalyst with a [2.2]paracyclophane backbone

The unique "bent and battered" structure of [2.2]paracyclophane features planar chirality, high rigidity and enables transannular electronic communication which makes this scaffold an ideal playground for the investigation of cooperative effects in distance-defined heterobimetallic complexes. In the featured heterobimetallic Au/Ru complex, [2.2]paracyclophane acts as a backbone, holding the two metal centers in a fixed spatial orientation and distance. The Au/Ru complex is easily accessible, exhibits high stability and shows promising properties as photoredox catalyst in a visible-light mediated arylyative Meyer–Schuster rearrangement.

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A highly stable, Au/Ru heterobimetallic photoredox catalyst with a [2.2]paracyclophane backbone†

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We report the synthesis and catalytic application of a highly stable distance-defined Au/Ru heterobimetallic complex. [2.2]Paracyclophane serves as a backbone, holding the two metal centers in a spatial orientation and metal–metal fixed distance. The Au/Ru heterobimetallic complex is highly stable, easily accessible and exhibits promising catalytic activity in a visible-light mediated dual Au/Ru Meyer–Schuster rearrangement.

Catalysis with mononuclear complexes employs sophisticated ligands to fine-tune the coordination sphere of the metal centre to achieve the desired reactivity.^{1–5} An elegant way to introduce electronic flexibility into the catalytic cycle and additionally enable cooperative or tandem catalysis is found in heterobimetallic complexes.^{6–8} Here, two possibilities arise. In one mode, one metal fulfils the classic activation of the substrate, whereas its catalytic activity is enhanced by the second metal centre. Alternatively, both metal centers can work together in a truly cooperative fashion, as has been demonstrated for metallosalens.^{9,10} This latter concept is widely found in enzyme bio-catalysis, which rationalizes their outstanding activity and selectivity.^{11–13} Despite the vast number of examples for enzymatic catalysis and even their diverse applications in industry, only a few examples for defined binuclear organometallic complexes which exhibit cooperative effects are known.^{14–16}

Enabling chemical synthesis with low-energy visible light can be used to promote photoredox reactions. One of the highest achievements of chemistry as a field is the use of sustainable practices employing low-cost and nature abundant visible-light energy to drive reactions instead of thermal, electrical or mechanical energy. Visible-light mediated photoredox catalysis has seen a rapid growth over the past 20 years.^{17–22} Similarly, gold catalysis has gained new prominence for driving efficient and selective processes under mild conditions,^{23–25} especially in combination with photoredox catalysis.²⁶

However, to date, heterobimetallic complexes with molecular architectures of spatial orientation and metal–metal fixed bond distance have seldom been explored. Exploring distance-defined visible light absorbing coordination complexes based on PCP as a new platform might allow to study the effect of metal–metal distance and their electronic communication on cooperativity. The unique “bent and battered” structure of [2.2]paracyclophane (PCP) features planar chirality, high rigidity and transannular electronic communication which makes this scaffold an ideal playground for the synthesis of distance-defined bimetallic complexes.³⁸ Disubstituted PCPs with two substituents located on different decks display four different regioisomers that are named pseudo-geminal, -ortho, -meta and -para shown in Fig. 1. The short distance between the two decks of the [2.2]paracyclophane causes an overlap of the π -system and leads to a transannular electronic communication.^{27–29} The through-space conjugation effect is

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† Electronic supplementary information (ESI) available: Experimental procedures, analytical data, crystallographic data and kinetic data. CCDC 1958713 (5). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9dt04366g

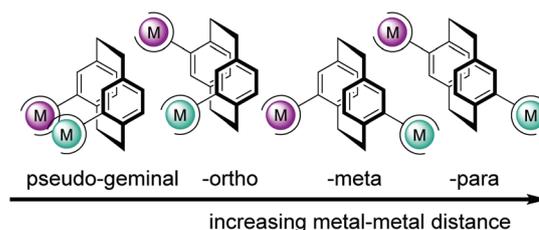


Fig. 1 Design of heterobimetallic PCPs with increasing M–M distance.



especially interesting in the case of the pseudo-*para* and -*meta* isomers. In these isomers, no direct metal–metal interaction is possible and the electronic communication *via* PCP between the two metal centres can be studied selectively.

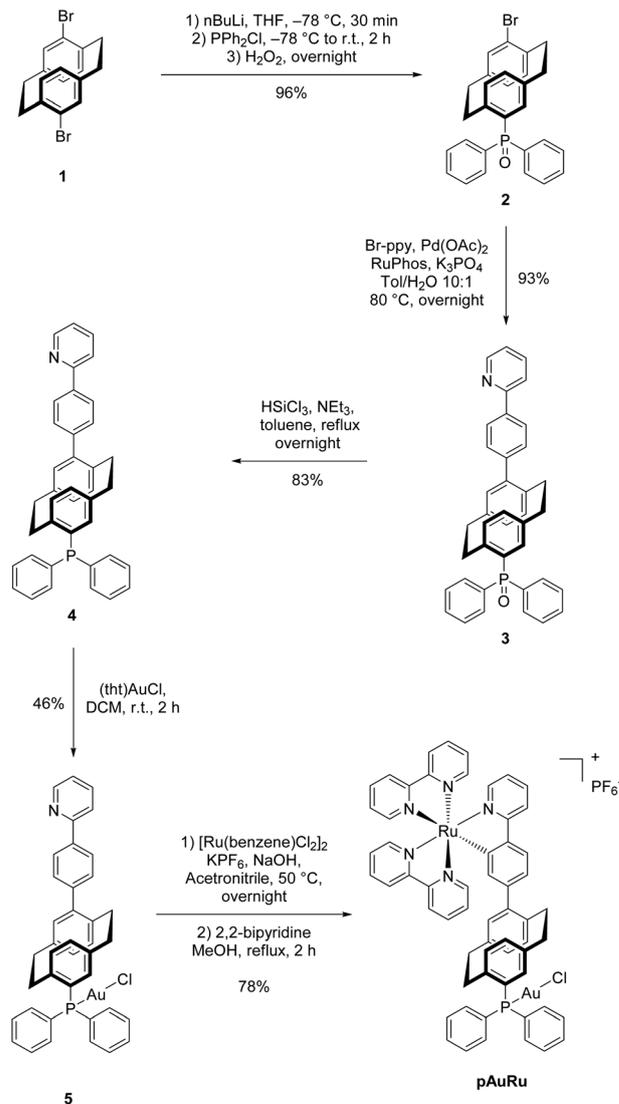
To evaluate the catalytic performance of the newly synthesized heterobimetallic PCP Au/Ru complexes, skeletal rearrangements are good probes and the visible-light mediated arylyative Meyer–Schuster rearrangement also is known to be a good “acid test” to examine stability and catalytic potential. We investigated a well-studied reaction in which both metals participate in the mechanism instead of one metal only being the “fine-tuning” for the other.

Results and discussion

Inspired by recent investigations on the visible-light mediated arylyative Meyer–Schuster rearrangement by the groups of Glorius, Luna and Shin,^{30–32} we focused on a new heterobimetallic version of the photoredox catalyst system employed. The gold(I) catalyst, PPh₃AuCl can be incorporated by replacing one of the phenyl rings with PCP. We changed the Ru(bpy)₃²⁺ cation for Ru(bpy)₂ppy⁺ because of easier synthetic access,⁵ a wider spectral excitation window and its suitability as a photosensitizer.³³ Furthermore, the reaction studied in detail entails oxidative quenching of the excited state of the photocatalyst, which is facilitated for cyclometalated ruthenium complexes when compared to their non-cyclometalated counterparts.²⁰

To be able to compare the influence of PCP on the outcome of catalysis, we first set out to prepare the respective PCP-Au and PCP-Ru, resembling the coordination environments found in the later heterobimetallic complex (Scheme 1).

Starting from PCP dibromide **1**, selective monolithiation⁵ and reaction with chlorodiphenylphosphine gave 4-bromo-16-diphenylphosphoryl[2.2]paracyclophane (**2**). The high selectivity of the monolithiation allows for a further functionalization at the 4-position *via* a cross-coupling reaction. Under optimized Suzuki–Miyaura reaction conditions for PCP,⁵ a new C–C bond to 2-phenylpyridine was formed. After two steps, compound **3** was obtained which bears the (oxidized) phosphine as a selective binding site for Au(I) and the 2-phenylpyridine moiety for the incorporation of Ru(II). Reduction of the phosphoryl moiety with trichlorosilane to the free phosphine **4**³⁴ directly followed by auration provided us with the Au(I) complex **5**. Initial efforts to introduce ruthenium into the

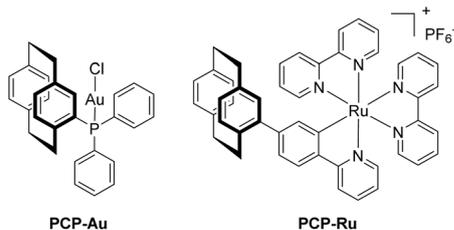


Scheme 2 Synthetic access to target complex pAuRu.

2-phenylpyridine moiety were met with failure, presumably due to the use of commonly employed AgBF₄.³³ However, a milder and silver-free method³⁵ was successfully applied to obtain the cationic heterobimetallic complex pAuRu in 27% yield over 5 steps (Scheme 2). Due to the chiral-at-metal centre and the inherent planar chirality of heterodisubstituted PCP, pAuRu was obtained as a mixture of diastereomers. Despite our efforts, we did not succeed in separation of the diastereomeric mixture by HPLC.

Absorption spectra of the complexes PPh₃AuCl (red), [Ru(bpy)₂(ppy)]PF₆ (blue), PCP-Au (black), PCP-Ru (orange) and pAuRu (green) were obtained in MeOH/MeCN, 3 : 1 at 298 K (Fig. 2). Absorption maxima in the UV-vis spectra and molar extinction coefficients are summarized in Table 1.

The absorption bands in the ultraviolet region below 350 nm arise from spin allowed ligand centered (LC) $\pi \rightarrow \pi^*$ transition. As the only feature, PCP-Ru and pAuRu exhibit an additional LC band at 320 nm which arises from the PCP



Scheme 1 Monometallic complexes PCP-Au and PCP-Ru.



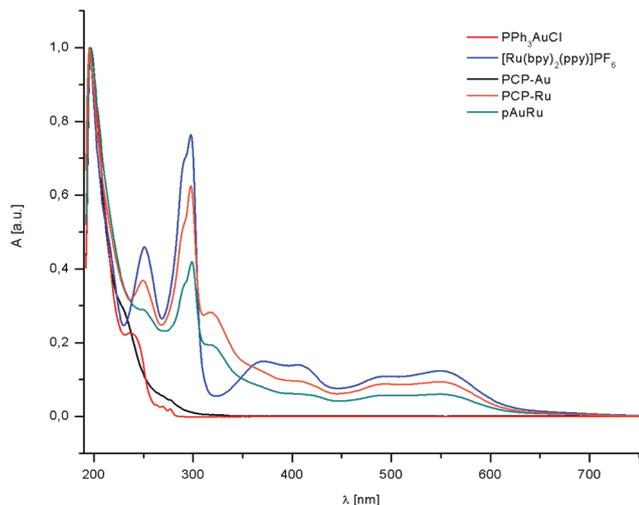


Fig. 2 Absorption spectra in MeOH/MeCN, 3 : 1 at 298 K.

Table 1 Absorption spectral properties of metal complexes^a

Entry	Compound	$\lambda_{\text{max}}^{\text{abs}}$ [nm] (ϵ [$10^4 \text{ M}^{-1} \text{ cm}^{-1}$])
1	[Ru(bpy) ₂ (ppy)]PF ₆	371 (0.99)
		410 (0.91)
		490 (0.71)
		552 (0.81)
2	PCP-Ru	366 (1.21)
		414 (0.89)
		490 (0.83)
		552 (0.89)
3	pAuRu	366 (0.87)
		414 (0.62)
		490 (0.60)
		552 (0.63)

^a MeOH/MeCN, 3 : 1, 298 K.

backbone. Examination of the lower energy absorption bands reveals a large spectral envelope which arises from the cyclometalated phenylpyridine ligand. This also causes additional features below 300 nm which can be assigned to intraligand $\pi \rightarrow \pi^*$ transitions. In the spectra, two bands which are consistent with metal-to-ligand charge transfer (MLCT) are found in the region between 350–450 nm and 450–600 nm.

The first band can be assigned to an MLCT from the ruthenium center to the cyclometalating phenylpyridyl ligand, whereas the band at higher wavelengths is primarily localized on the polypyridyl ligands.

The absorption of PCP-Ru and pAuRu is slightly red-shifted compared to [Ru(bpy)₂(ppy)]PF₆. The heterobimetallic complex pAuRu also shows lower molar extinction coefficients than the monometallic counterparts. This trend can be observed already when going from [Ru(bpy)₂(ppy)]PF₆ to PCP-Ru. Therefore, we postulate that this decrease in molar extinction coefficient as well as the red-shift is due to the increase in electron density by the introduction of the electron-rich PCP moiety and the additional electron-rich phosphine respectively.

Excitation of the pAuRu complex at wavelengths defined by the absorption maxima at 485 nm and 548 nm produces emission bands that are substantially shifted to longer wavelengths. At both excitation wavelengths, strong fluorescence at 795 nm is observed. Upon excitation at 485 nm, the compound shows additional emission at 543 nm and 507 nm (Fig. 3).

No single crystals of pAuRu suitable for X-ray diffraction were obtained. However, the direct precursor 5 did provide us with suitable single crystals and confirmed the molecular structure as shown in Fig. 4. The phenylpyridine moiety (plane through C17–C22) is twisted out of the PCP deck plane (C12–C16) by 41.8°. This angle is significantly larger than comparable PCP pyridyl scaffolds.³⁶ The P–Au and Au–Cl distances are in the expected range with bond lengths of 2.236 Å and 2.292 Å respectively.³⁷ The gold atom is almost linearly coordinated, displaying a gold(i) typical twofold coordination mode [P–Au–Cl: 176.2°]. The P–Au–Cl “tail” is turned towards the PCP scaffold rather than the phenyl substituents to form a 98.6° torsion angle (C5–C4, P–Au).

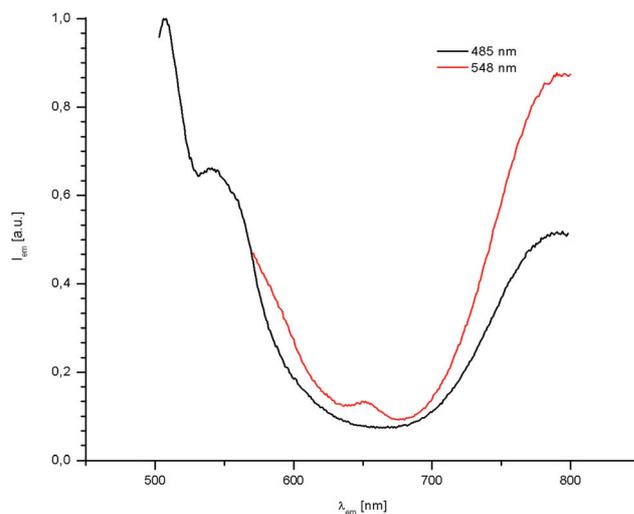


Fig. 3 Emission spectra at absorption maxima 485 nm (black) and at 548 nm (red) for pAuRu in MeOH/MeCN, 3 : 1 at 298 K.

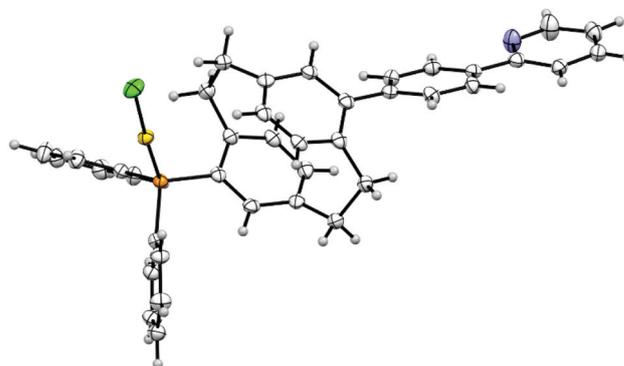


Fig. 4 Molecular structure of complex 5 (orange – P, yellow – Au, green – Cl, blue – N, displacement parameters are drawn at 30% probability level).



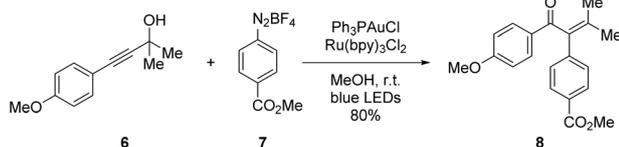
Catalysis application

The model reaction to test **pAuRu** was chosen to be the visible-light mediated arylyative Meyer–Schuster rearrangement (MSR) which was recently published by three groups: Glorius, Luna and Shin.^{30–32} The Shin group reported a Au(I) to Ru(II) ratio of 1 : 1 and was therefore most fit for comparison with our heterobimetallic complex (Scheme 3).

With our setup, the conditions reported by Shin *et al.*, afforded the arylyated enone **11** in 76% yield (Table 2, entry 1). During our investigations, we found that a mixture of methanol and acetonitrile provided overall more consistent results (entry 2). We attribute this to the complete solution of the diazonium salt **10** which is added in four-fold excess and is not well-soluble in methanol.

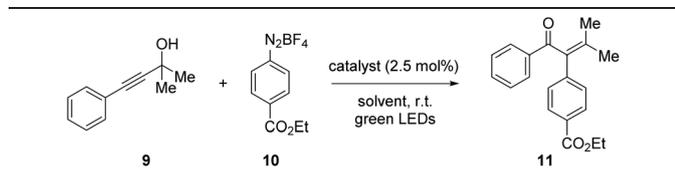
In order to exclude possible electronic effects induced by the different coordination sphere that arises from the 2-phenylpyridine unit within the **pAuRu**, the literature procedure by Shin *et al.* was additionally conducted with the monocationic Ru(bpy)₂(ppy)PF₆ instead of the dicationic Ru(bpy)₃Cl₂ (entry 3). Furthermore, we investigated the impact of the sterically demanding PCP backbone on the overall reaction. The corresponding monometallic PCP derivatives **PCP-Au** and **PCP-Ru** were applied in a test reaction (entry 4). All of those modifications on the catalytic system consistently provided the same results which leads to the conclusion that neither the different coordination sphere that results from exchanging a bpy ligand with a ppy ligand, nor the PCP backbone influence the overall reactivity.

The single-molecule, heterobimetallic **pAuRu** complex could successfully catalyze the Meyer–Schuster rearrange-



Scheme 3 Literature reaction conditions reported by Shin *et al.*

Table 2 Results of the Meyer–Schuster rearrangement with **pAuRu** and the monometallic PCP complexes **PCP-Au** and **PCP-Ru**



Entry	Catalyst	Solvent	Yield ^a [%]
1	PPh ₃ AuCl, Ru(bpy) ₃ Cl ₂	MeOH	76 ^b
2	PPh ₃ AuCl, Ru(bpy) ₃ Cl ₂	MeCN/MeOH 3 : 1	73
3	PPh ₃ AuCl, Ru(bpy) ₂ (ppy)PF ₆	MeCN/MeOH 3 : 1	73
4	PCP-Au , PCP-Ru	MeCN/MeOH 3 : 1	70
5	pAuRu	MeCN/MeOH 3 : 1	63

^a Isolated yields. ^b NMR yields.

ment and afforded the arylyated enone **11** in 63% yield with a reaction time of 25 minutes (see ESI† for kinetics) (entry 5). A comparison of reaction kinetics for the monometallic **PCP-Au** and **PCP-Ru** with those measured for **pAuRu** show no significant difference in induction period or conversion rate. While no mechanistic investigations were performed, this suggests that the reaction follows the mechanistic proposals in literature.^{30–32}

Since both steric and electronic influences that may result from the slightly different coordination environment through the PCP backbone can be excluded, the observed drop in yield when using **pAuRu** could suggest a through-space metal–metal communication and deactivation. This communication would be enabled by the π -conjugated PCP backbone. However, other factors (*e.g.* reduced extinction coefficient) could not be excluded and might influence the outcome of this reaction as well.

The lack of understanding about how heterobimetallic complexes are to be designed for applications in cooperative catalysis demands new frameworks on which to study these complexes systematically. In this work we demonstrated the synthesis and catalytic viability of the heterobimetallic complex **pAuRu** featuring [2.2]paracyclophane as a rigid backbone. The performance of **pAuRu** complex in photoredox catalysis was evaluated and compared to the monometallic approach.

The remarkable stability, high yielding and facile synthetic access of **pAuRu** make it an invaluable first-of-its-kind PCP heterobimetallic complex. The investigated arylyative Meyer–Schuster rearrangement reaction is successfully catalyzed in 63% yield with **pAuRu**. Compared with the respective monometallic complexes, a drop in yield was observed, suggesting metal-to-metal interaction by through-space transannular communication.

We believe that **pAuRu** is the first in a line of distance-modulated bimetallic complexes exploiting the isomeric geometry features of PCP. We hope this will aid in the design and the understanding of metal–metal interactions in bimetallic complexes in catalysis applications. Synthetic routes towards further isomers and PCP-based other heterobimetallic complexes are underway in our laboratories.

Conflicts of interest

No conflicts of interest to declare.

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