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DNA-based catalytic cyclopropanation in water

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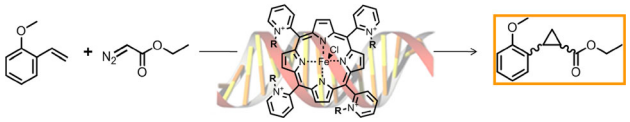
DNA-based asymmetric catalysis represents a powerful tool for the preparation of chiral compounds in water [1]. This novel concept is based on the use of hybrid catalysts, which comprise a transition metal complex (a metal ion coordinated to a non-chiral ligand which is able to bind to DNA) bound to DNA. In this way, the reaction occurs in close proximity to the DNA, allowing chirality transfer and subsequent formation of one of the enantiomers of the reaction product [2]. These hybrid catalysts have been exploited in many Lewis acid catalytic enantioselective reactions, such as Diels–Alder, (oxa)-Michael addition, Friedel–Crafts, syn-hydration of enones and fluorinations [1]. Recently, the catalytic scope of DNA-based asymmetric catalysis has been expanded beyond Lewis acid catalysis when it was applied successfully in a Cu(I) catalysed intramolecular cyclopropanation of α-diazo-β-keto sulfones [3]. Up to now, all the examples of DNA-based catalysis described use copper complexes in combination with DNA. However, alternative metal catalysts can be used as well. Cationic porphyrins (e.g., meso-tetrakis-(*N*-methyl-4-pyridyl)-porphyrin (TMpyP4)), are well known ligands that can bind through π-stacking and electrostatic interactions to DNA. Especially the interactions of these porphyrins with G-quadruplexes have been described [4]. Expanding the scope of DNA-based asymmetric catalysis to other reactions, substrates and novel hybrid catalysts are crucial challenges in our research. Here, we propose the DNA-based catalytic cyclopropanation in water catalysed by iron porphyrin/salmon testes DNA hybrids.

Financial support by the Ramón Areces Foundation is gratefully acknowledged.



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Halogenated gold(I) NHC complexes and their biological evaluation

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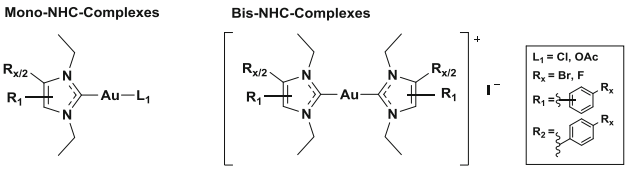
N-heterocyclic carbene metal complexes have already shown antiproliferative effects on tumor cell lines and have proven their potential as anticancer drugs. Thioredoxin reductase (TxrR) is an example for a relevant enzyme, which protects the cells against oxidative stress and apoptosis. It is upregulated in carcinoma cells and represents a possible target in anticancer therapy. Especially gold(I) containing compounds inhibit TxrR in vitro, due to the high affinity of gold to selenocysteine moieties. A well-known drug is auranofin, which is established in the current antirheumatic therapy, shows antiproliferative effects and a remarkable TxrR inhibition [1–5].

New halogenated mono- and bis-NHC-gold(I)-complexes of the imidazole-, benzimidazole- or phenylimidazole-type were synthesized, purified and characterized. Afterwards they were tested against tumorigenic HT-29 colon carcinoma cells, MCF-7 breast carcinoma cells, MDA-MB-231 breast carcinoma cells and non-tumorigenic RC-124 human kidney cells. They all showed cell growth inhibition with IC_{50} values in the submicromolar range. Especially the activities of the bis-NHC-complexes were comparable to auranofin.

The potency of TxrR inhibition of these gold(I) derivatives were determined and cell uptake studies were performed using high resolution continuum source atomic absorption spectroscopy for the quantification of the intracellular amount.



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Synthesis, characterization and cytotoxicity of (η^6-*p* cymene) ruthenium(II) complexes of α-amino acids

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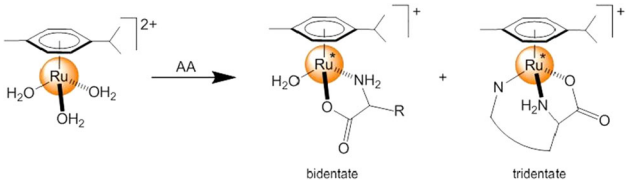
Arene ruthenium complexes of α-amino acids, obtained by mixing aqueous solutions of $[(\eta 6\text{-p-cymene})RuCl_2]_2$ in the presence of $AgCF_3SO_3$with various amino acids, have been studied at 37 °C using NMR spectroscopy and electrospray ionization mass spectrometry (ESI–MS). Presumably, complexes with the general formula $[(\eta^6\text{-p-cymene})Ru(AA)_2]^{n+}$ and bridged complexes with the general formula $[((\eta^6\text{-p-cymene})Ru)_2(\mu\text{-AA})_2(\mu\text{-OH})]^+$ are formed together with the expected bi- and tridentate chelate complexes. All complexes are highly cytotoxic, with IC_{50} values ranging from 0.16 to 19.8 μM. Interestingly, all complexes exhibit selectivity towards A2780 versus A2780cisR cells, indicating a distinct mechanism of action, different from that of many previously reported cytotoxic ruthenium complexes. No direct correlation between the kinetics of formation and the cytotoxicity could be evidenced, suggesting that other physicochemical parameters such as the stability and ligand exchange kinetics may play an important role in their biological activity [1].



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New rhenium complexes for carbon monoxide photorelease

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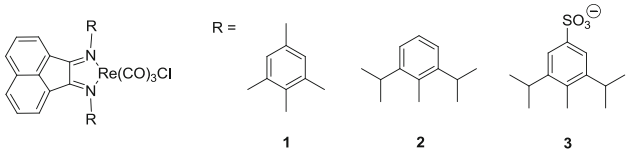
Carbon monoxide has come a long way from just being considered as a silent killer and an environmental pollutant to an important molecular messenger involved in several physiological processes. Recently, important progress has been made towards developing photoactive CO-releasing moieties (PhotoCORMs) for possible therapeutic applications [1]. Here, the synthesis and characterization of new rhenium tricarbonyl diimine complexes of the type *fac*-Re(1,2-diimine)$(CO)_3Cl$, carrying bis-(phenylimino)acenaphtene ligands (BIAN) **1–3** is reported [2].

Among these novel complexes, a special focus will be given to the deeply coloured water-soluble organometallic rhenium(I) derivative **3**, which offers highly desirable features for potential biomedical and catalytic applications such as light-controlled release of carbon monoxide (PhotoCORMs) [3], and homogeneous photocatalytic CO_2 reduction.

CO liberated from the irradiated solutions of CORMs **1–3** has been quantified in the headspace gas using FTIR and GC analysis.

Financial support of this work by the Austrian Science Fund (FWF- Project 25038: Functional Light Responsive Metal Carbonyl Systems) is gratefully acknowledged.



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Expanding the scope of finely tuned asymmetric platinum(IV) complexes

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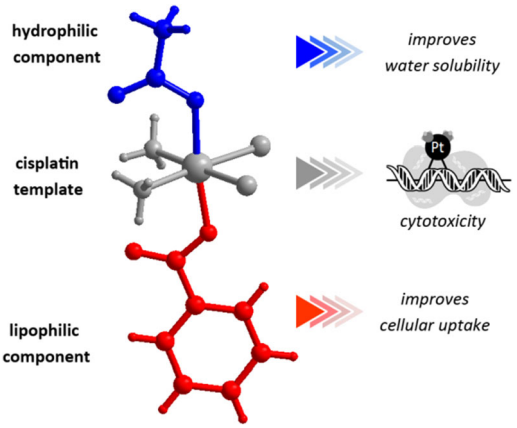
Structure activity relationship studies have previously established a link between the nature of axial ligands and the efficacy of anticancer platinum(IV) prodrug complexes [1, 2]. However, the existing strategy centred on platinum(IV) complexes with symmetrical axial ligands does not fully exploit the vast potential of this class of prodrugs. We therefore adapted this strategy to access asymmetric Pt(IV) complexes with contrasting axial ligands through sequential acylation. By modifying the characteristics of each of the axial ligand, it is now feasible to control the physical and chemical properties of resultant platinum(IV) prodrug complex [3]. To that end, we report a library of finely-tuned asymmetric platinum(IV) complexes and their efficacy against a panel of human cancer cell lines in vitro.

Financial support by the National University of Singapore and Solvay Singapore is gratefully acknowledged.



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Copper, zinc, and lead solubilization from foundry sand and uptake by *Penicillium expansum*

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In nature, microorganisms can act geological agents and, therefore, mediate biogeochemical processes such as e.g., metal solubilization from solid matrices (minerals, rocks, ores), metal speciation as well as immobilization. Generally, microbes are able to mobilize metals from solids by the formation of acids (protons), by oxidation and reduction reactions; and by the excretion of complexing agents or ligands [1]. In the present work, a fungal strain *(Penicillium expansum)* has been investigated for its ability of Cu, Zn, and Pb solubilization from a solid matrix (foundry sand) through the formation of organic acids and its subsequent accumulation in the fungal mycelium. The fungus was grown at 25 °C for up to 2 months in Petri dishes filled with potato-dextrose agar medium enriched. Metal-containing foundry sand containing mainly (in g/kg) Al (31.4), Cu (5.6), Pb (1), Sn (0.3), Zn (5.3) was added at final concentration of 30 g/L during the preparation of the Petri dishes. After cultivation and mycelial growth, the biomass was digested using nitric acid and hydrogen peroxide followed by total metal content analysis by atomic absorption spectroscopy. *P. expansum* was able to solubilize and accumulate Cu from foundry