

Excited-state dynamics of catalytically active transition metal complexes studied by transient photofragmentation in gas phase and transient absorption in solution

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Abstract: Femtosecond photofragmentation (gas phase) and transient absorption (solution) revealed ultrafast electronic coupling (0.1-3ps) and energy transfer (7-12 ps) in a Ru(II)-complex and ultrafast formation (~ 0.4 ps) of a long-lived triplet state in a Pd₃-complex.

OCIS codes: (300.0300) Spectroscopy; (300.6530) ultrafast.

1. Introduction

Transition metal-ligand complexes are important and selective catalysts or pre-catalysts for homogeneous reactions, among them transfer hydrogenation (addition of H₂) and carbon-carbon bond formation (C-C-coupling) [1]. Moreover, due to their synthetically tunable photophysical properties these complexes succeed in the fields of light-harvesting and photocatalysis. In order to elucidate the primary competing photoreactive pathways, we report here studies on ultrafast excited state dynamics and catalyst activation processes of new Ru(II)- and Pd₃-complexes. This project, encompassing in parallel investigations in gas phase and solution, is part of the collaborative research center "3MET" (SFB/TRR88), focusing on intermetallic cooperative effects in functional homo- and heterometallic complexes [2].

2. Results and discussion

The first molecular target consists of new ruthenium(II) complexes $[(\eta^6\text{-cymene})\text{RuCl}(\text{apypm})]\text{PF}_6$ (apypm=2-NR₂-4-(pyridine-2-yl)-pyrimidine, R=CH₃(**1**) / H(**2**)), which catalyze the transfer hydrogenation of arylalkyl ketones in the absence of a base upon thermal activation [3]. The ultrafast gas phase studies are based on pump-probe transient photofragmentation employing a newly designed setup consisting of a kHz 50fs-amplified Ti:Sa-laser system equipped with two optical parametrical generator/amplifier units for independent wavelength tuning (240-2600 nm) of pump (350-420 nm) and probe pulses (1150 nm) and an electrospray ion trap mass spectrometer for ion selection, storage and mass analysis (up to 3000 m/z) [4].

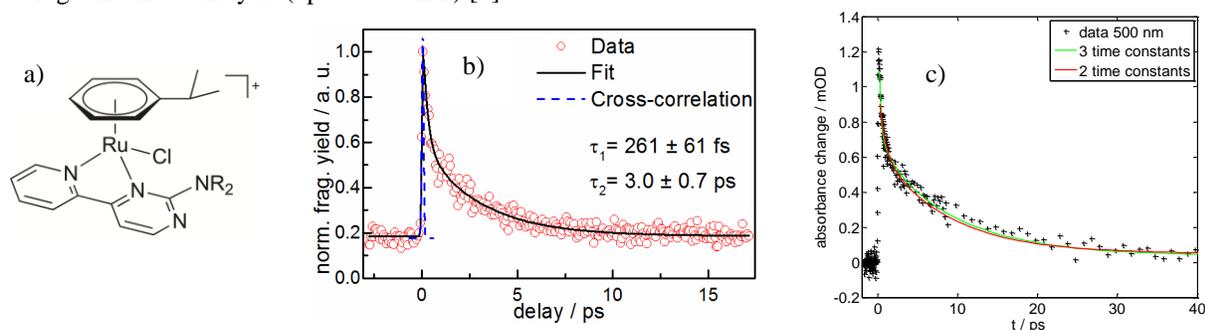


Fig.1. a) Structure of Ru(II)-complex cation, b) transient fragment ion intensity of I^+ ($\lambda_{\text{exc}}:460 \text{ nm}/\lambda_{\text{probe}}:1150 \text{ nm}$) in gas phase c) transient absorption of I^+ in DMSO ($\lambda_{\text{exc}}:400 \text{ nm}/\lambda_{\text{probe}}:500 \text{ nm}$).

Femtosecond transient photofragmentation on mass selected ions (I^+ , 2^+) prove the formation of the activated catalyst species (HCl abstraction) after photoexcitation of the MLCT bands (400-460 nm, Fig. 1b). The excited state dynamics in the gas phase could be fitted to a biexponential decay (time constants <100 fs and 1-3 ps). In parallel, transient absorption spectroscopy in acetonitrile using femtosecond UV/Vis and IR probe laser pulses revealed additional deactivation processes on longer time scales (~ 7 -12 ps, Fig.1c). The formation of the active catalyst

species after photoexcitation could not be observed in solution, emphasizing an efficient deactivation process and strong influence of the solvent-catalyst interaction [4]. Contrary to other well-known Ru(II)-complexes (e.g. $[\text{Ru}(\text{bpy})_3]^{2+}$, bpy=2,2'-bipyridine) we have not observed long-lived triplet states. Probably the fast radiationless deactivation involves metal-centered ^3dd (MC) states, as has been elucidated recently [5].

The second molecular target is represented by a trinuclear Pd-complex ($[\text{Pd}_3\{\text{Si}(\text{mt}^{\text{Me}})_3\}_2]$, **3**, mt^{Me} = methimazole) [6], which acts as a C-C-coupling agent in a Suzuki-Miyaura type reaction. The important questions are here, what is the catalytically active species, can this species be produced by photoactivation and which dynamics are displayed after photoexcitation?

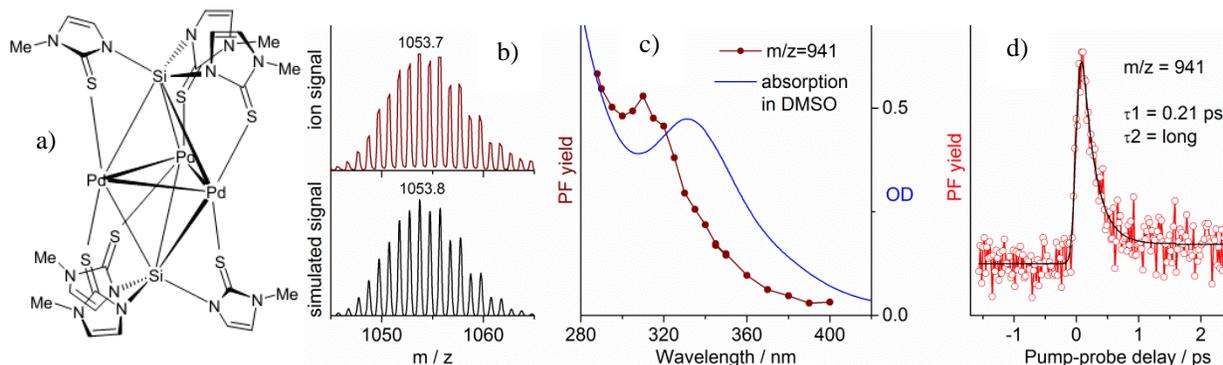


Fig.2. a) Structure of Pd₃-complex [6], b) isotope pattern of 3^+ (top: experiment, bottom simulation), c) UV absorption in DMSO (continuous line) vs. photofragmentation spectrum in gas phase (connected dots), d) transient fragment ion intensity of 3^+ (λ_{exc} :320 nm/ λ_{probe} :720 nm) in gas phase.

Upon electrospray ionization of **3** from acetonitrile solution followed by isolation in the ion trap a mono-cationic species 3^+ could be identified unequivocally by its rich isotope pattern around 1054 m/z (Fig.2b). The large intensity of this mass peak points towards a stable cationic structure. Its fragmentation is dominated by the loss of one methimazole unit ($\text{C}_4\text{H}_5\text{N}_2\text{S}$, remaining ion 941 m/z). Interestingly, the opening of the hemilabile bond between the sulfur donor of the methimazole unit and the Pd₃ core was considered crucial for its catalytic activity [6]. The photofragmentation spectrum (Fig. 2c) shows, besides a blue shift of 15 nm, strong similarity to the absorption spectrum of the neutral species in solution (DMSO, dimethyl sulfoxide). The dynamics of the cationic species (320 nm/720 nm, Fig. 2d) reveal a very fast relaxation of the primary state with a lifetime of ca. 200 fs and an additional long-lived (>100 ps) component which could be related to a triplet state. These observations are remarkably close to the behavior of the neutral compound in solution (static spectrum in Fig.2c). In DMSO after photoexcitation at 330 nm the observed absorption changes are dominated by an instantaneous bleach in the region of electronic ground state absorption and a concomitant fast (~400 fs) build-up of spectrally broad and long-lived (ns time-scale) excited state absorption at 370–750 nm, which is assigned to the lowest triplet state ($^3\text{A}_1$). No hints on ligand dissociation or other structural or electronic changes have been observed in DMSO solution.

3. Conclusions

The ultrafast dynamics of the Ru(II)- and Pd₃-complexes exhibit remarkably similar timescales in both, the gas phase and solution. Whereas the Ru(II)-complex displays a fast and efficient internal conversion into a vibrationally hot ground state, the Pd₃-complex proceeds, independent of charge status (neutral vs. mono-cationic), towards a long-lived triplet state, that might be the starting point for further reactions. For both complexes, the investigation of gas phase fragmentation proved valuable in characterizing the possible catalytically active species.

References

- [1] *Reactive Intermediates: MS Investigations in Solution*, L. S. Santos, ed. (Wiley-VCH, 2010, Weinheim), Chap.7.
- [2] <http://www.uni-kl.de/3met>.
- [3] L. T. Ghoochany, S. Farsadpour, F. Menges, Y. Sun, G. Niedner-Schatteburg, W. R. Thiel, *Eur. J. Inorg. Chem.* **24**, 4305-4317 (2013).
- [4] D. Imanaew, Y. Nosenko, K. Chevalier, F. Rupp, C. Kerner, C. Riehn, R. Diller, W. R. Thiel, submitted (2014).
- [5] Q. Sun, S. Mosquera-Vazquez, L. M. Lawson Daku, L. Guenee, H. A. Goodwin, E. Vauthey, A. Hauser, *J. Am. Chem. Soc.* **135**, 13660-13663 (2013).
- [6] F. Armbruster, J. Meyer, A. Baldes, P. O. Burgos, I. Fernandez, F. Breher, *Chem. Commun.* **47**, 221-223 (2011).