P3.3 Synthesis of biradical metal catalysts and application in activation and coupling of CO_2

Topic and overall goal. In a joint project[1], both research groups succeeded in 2011 in synthesising the first phosphorus-based singlet biradical and demonstrated its great potential in activating small molecules such as CO_2, (**2**).[2] Furthermore, it has already been shown by in situ NMR (under incorporated light switching), UV spectroscopy and structural analysis that the biradical **3** (generated by reaction of **1** with isonitriles)[2c] forms a transannular bond and a closed-shell housane structure (**4**) under red light, which thermally reacts back to **3**. This molecular switching has been applied to switch chemical reactions on and off.[3] The Beweries group has many years of experience in activating small molecules using low valent, cyclic compounds of group 4 metals.[2,4] These metallacycles can be produced by coupling alkenes, alkynes, nitriles, carbodiimides or isocyanides to metallocenes and in some cases also show photochemically induced reactivity.[5]

Specific aims and work plan. In the present project, we would like to combine the biradical chemistry of the Schulz group with the transition metal catalysis from the Beweries group. This can be achieved, for example, by introducing an unsaturated anchor group to the main group fragment (**5**/**6**). Reductive C-C bond formation should lead to novel bis-biradical metal complexes (**7**). The aim of the project is to both the activation of CO_2 and classical C-C coupling reactions with the light-switchable biradical metal catalyst **6**, in particular to study the influence of the molecular switch on the bond activation or product distribution. A special role will be played by operando NMR spectroscopy under photochemical conditions.

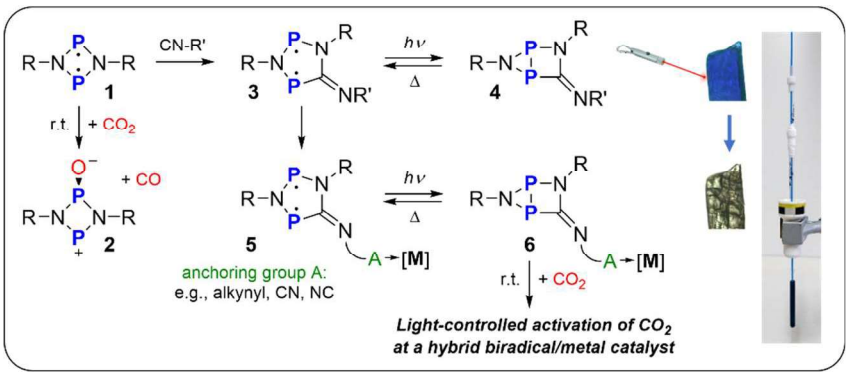

Figure P3.3. Proposed synthesis of hybrid main group/organometallic biradicals.

Within this project the PhD student will receive training in the synthesis of ligands and highly reactive hybrid main group/organometallic compounds, low-temperature synthesis and characterisation, photocatalysis, reaction monitoring by NMR and UV-Vis spectroscopy and modelling of mechanistic steps by quantum chemical calculations.

Connection within the RTG. This PhD project will be jointly supervised by Axel Schulz and Torsten Beweries. Within the RTG there will be a close collaboration with the Brückner (operando spectroscopy), Lochbrunner (time resolved spectroscopy) and Bokareva groups (computational analysis).

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1 T. Beweries, R. Kuzora, U. Rosenthal, A. Schulz, A. Villinger, *Angew. Chem. Int. Ed.* **2011**, *50*, 8974-8978.

2 a) S. Roy, E. D. Jemmis, A. Schulz, T. Beweries, U. Rosenthal, *Angew. Chem. Int. Ed.* **2012**, *51*, 5347-5350; b) C. Godemann, L. Dura, D. Hollmann, K. Grabow, U. Bentrup, H. Jiao, A. Schulz, A. Brückner, T. Beweries, *Chem. Commun.* **2015**, *51*, 3065-3068; c) A. Hinz, A. Schulz, A. Villinger, *J. Am. Chem. Soc.* **2015**, *137*, 9953-9962; d) A. Hinz, A. Schulz, A. Villinger, *Angew. Chem. Int. Ed.* **2015**, *127*, 2815-2819.

3 J. Bresien, T. Kröger-Badge, S. Lochbrunner, D. Michalik, H. Müller, A. Schulz, E. Zander, *Chem. Sci.* **2019**, *10*, 3486-3493.

4 a) C. Godemann, D. Hollmann, M. Kessler, H. Jiao, A. Spannenberg, A. Brückner, T. Beweries, *J. Am. Chem. Soc.* **2015**, *137*, 16187-16195; b) P. Arndt, M. Reiß, A. Spannenberg, C. Schünemann, F. Reiß, T. Beweries, *Dalton Trans.* **2019**, 48, 16525-16533.

5 a) U. Rosenthal, V. V. Burlakov, M. A. Bach, T. Beweries, *Chem. Soc. Rev.* **2007**, *36*, 719-728; b) T. Beweries, C. Fischer, S. Peitz, V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, D. Heller, U. Rosenthal, *J. Am. Chem. Soc.* **2009**, *131*, 4463-4469; c) M. Haehnel, M. Ruhmann, O. Theilmann, S. Roy, T. Beweries, P. Arndt, A. Spannenberg, A. Villinger, E. D. Jemmis, A. Schulz, U. Rosenthal, *J. Am. Chem. Soc.* **2012**, *134*, 15979-15991.