

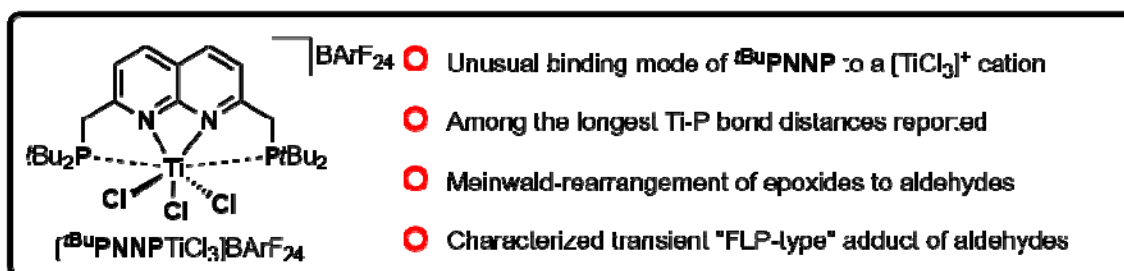
# A KINETICALLY TRAPPED $[\text{TiCl}_3]^+$ CATION: COORDINATION AND REACTIVITY

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Over the last years, Frustrated Lewis Pairs (FLPs) have been a staple in heterolytic bond cleavage.<sup>[1]</sup> Using the polarized interaction between the Lewis acid and base, a broad variety of small molecules can be activated. This reactivity is driven by the alleviation of the ‘frustration’ between the nucleophilic and electrophilic components of the FLP. The scope of FLPs extends beyond the stoichiometric reactivity, with the literature being rich with examples of catalytic reactions including hydrogenation of unsaturated bonds and N-heterocycles, hydroamination of alkynes and reduction of  $\text{CO}_2$ .<sup>[1]</sup> Whereas most studied FLPs are based on main-group elements, a far less explored area is that of Transition Metal-based FLPs (TM-FLPs).<sup>[2]</sup> A potential advantage of TM-FLPs is that by using a transition metal as the Lewis acid, the available d-orbitals can get involved in follow-up reactivity.<sup>[2]</sup> This can result in reactions that are typically stoichiometric for main-group FLPs being catalytic when TM-FLPs are used, *e.g.* the dehydrocoupling of amine-boranes.<sup>[3]</sup> TM-FLPs are however underexplored compared to main-group FLPs in literature, with the most studied TM-FLPs being cationic, group IV metallocene phosphinoaryloxides. In this work, we describe a new type of TM-FLP based on the PNNP expanded pincer ligand developed by our group.<sup>[4]</sup> Although the PNNP ligand is designed to bind two metals, we here show that it can kinetically trap a highly electrophilic  $[\text{TiCl}_3]^+$  fragment. Interestingly, the highly polarized Ti-P bonds of this complex are among the longest reported in literature. We describe the reactivity of  $[\text{PNNPTiCl}_3][\text{BARf}_{24}]$  towards epoxides and lastly we present how this new class of TM-FLP reacts with aldehydes. Lastly, we will show the trapping of the fleeting “FLP-type” adduct, which has been fully characterized with multinuclear NMR-spectroscopy and single-crystal XRD.



[1] Stephan, D.W, *Acc. Chem. Res.* **2015**, 48, 2, 306.

[2] Flynn, S. R. *et.al*, *ACS.Catal.* **2013**, 3, 11, 2574.

[3] Metters, O. J. *et.al*, *ACS.Catal* **2016**, 6, 10, 6601.

[4] Kounalis, E. *et.al*, *Chem.Eur.J.* **2019**, 25, 58, 13280.