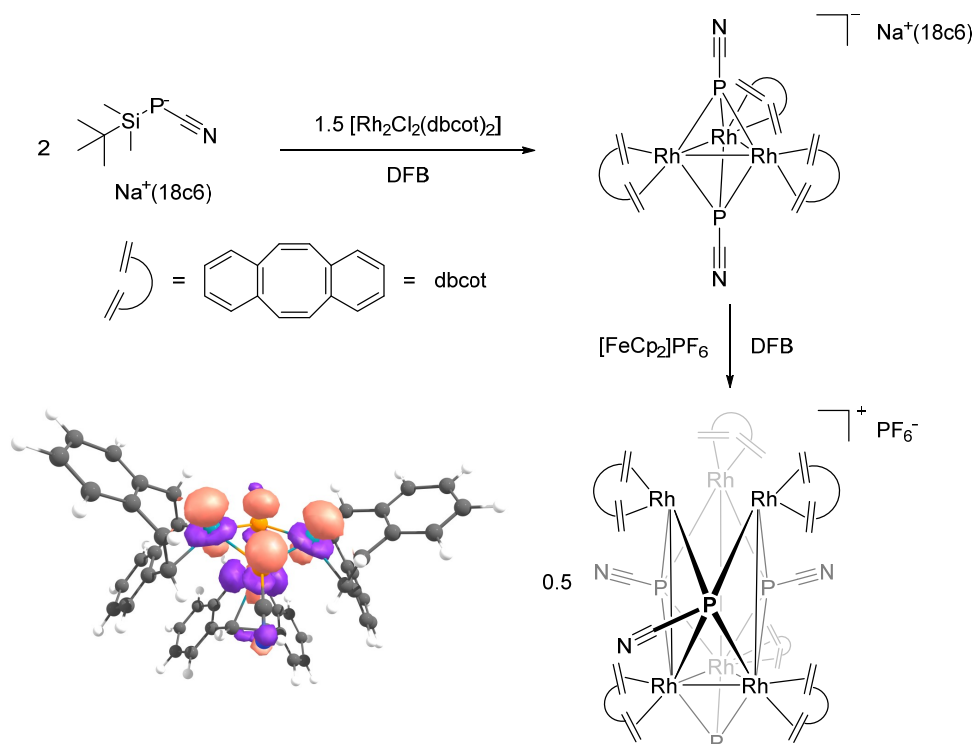


# REACTIVITY OF THE $[\text{PCN}]^{2-}$ LIGAND ON LATE TRANSITION METALS

Stefan Banz, Grégoire Le Corre, Clara Schweinzer and Hansjörg Grützmacher

Laboratory of Inorganic Chemistry, ETH Zurich, Zurich, Switzerland

Our group has recently published the synthesis of a stable  $[\text{PCN}]^{2-}$  synthon, with the general formula  $[\text{Na}(18\text{-c-}6)][\text{P}(\text{CN})(\text{SiR}_3)]$ .<sup>[1,2]</sup> The lability of the P-Si bond enables this salt to transfer  $[\text{PCN}]^{2-}$  units. Indeed, in the reaction with the  $\text{Rh}^{\text{I}}$  chloride  $[\text{Rh}_2(\mu\text{-Cl})_2(\text{dbcot})_2]$ , P-Si bond cleavage and elimination of  $t\text{BuMe}_2\text{SiCl}$  was observed and a highly symmetrical  $\text{Rh}_3\text{P}_2$  cluster with a trigonal bipyramidal structure was obtained (Figure 1, top). Computational studies indicate that upon single electron oxidation one Rh-Rh bond is broken and the  $\text{Rh}_3\text{P}_2$  core opens to form an almost planar  $\text{Rh}_2\text{P}_2$  ring, which is capped by one  $\text{Rh}(\text{dbcot})$  fragment. The SOMO of this intermediate is composed of the bonding interaction of the two  $d_z^2$  orbitals at Rh and two  $p_z$  orbitals at P in the  $\text{Rh}_2\text{P}_2$  ring, which interacts in an anti-bonding fashion with  $d_z^2$  orbital of the capping Rh center (Figure 1, bottom left). We assume that this feature facilitates dimerization, which was indeed observed upon oxidation with  $[\text{FeCp}_2]\text{PF}_6$  to give a cluster with a  $\text{Rh}_6\text{P}_4$  core (Figure 1, bottom right). Formally one  $[\text{PCN}]^{2-}$  ligand is converted into a  $\text{P}^{\text{n-}}$  center under the loss of a CN moiety. The mechanism and oxidation states at the Rh and P centers are not clear, yet, but an oxidative addition of the P-CN bond onto a rhodium center might play a crucial role.



**Figure 1:** Synthesis of  $[\text{Na}(18\text{c}6)][\text{Rh}_3(\text{PCN})_2(\text{dbcot})_3]$  trimer (top). Calculated SOMO (BP86-D3BJ/def2-TZVP) of the oxidized  $[\text{Rh}_3(\text{PCN})_2(\text{dbcot})_3]$  trimer (bottom, left). Structure of the synthesized  $\text{Rh}_6\text{P}_4^+$  cluster (bottom, right).

[1] Le Corre, G.; Gamboa-Carballo, J. J.; Li, Z.; Grützmacher, H., *Angew. Chem. Int. Ed.* **2021**, 60, 24817

[2] Le Corre, G.; Grützmacher, H., *Dalton Trans.*, **2022**, 51, 3497