Computational Modeling of Phosphorus-Based Metal-Free Hydride Donors

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Phosphorus-based hydrides have recently attracted attention as promising metal-free hydride donors. One important factor that controls their reactivity is the polarity of the P–H bond. By introducing electron-donating groups, the P–H bond becomes more polarized, with increased negative charge on the hydrogen atom [1]. This makes the release of a hydride ion (H^-) easier. A further enhancement in hydride-donating ability can be achieved by stabilizing the positively charged species that forms after hydride release. In the systems studied here, such stabilization is associated with the formation of an intramolecular P→P dative interaction, which lowers the energy of the resulting dication. By combining these two design strategies, electronic tuning and structural stabilization, we designed a series of new compounds with some of the best known hydricities [2]. Hydricities of all compounds were calculated in acetonitrile using density functional theory at the (PCM)ωB97X-D/6-311++G(d,p)//(PCM)ωB97X-D/6-31G(d,p) level. Notably, all designed systems exhibit hydricities sufficiently low to enable the reduction of CO_2, as shown in Figure 1, placing them among the strongest known metal-free hydride donors.

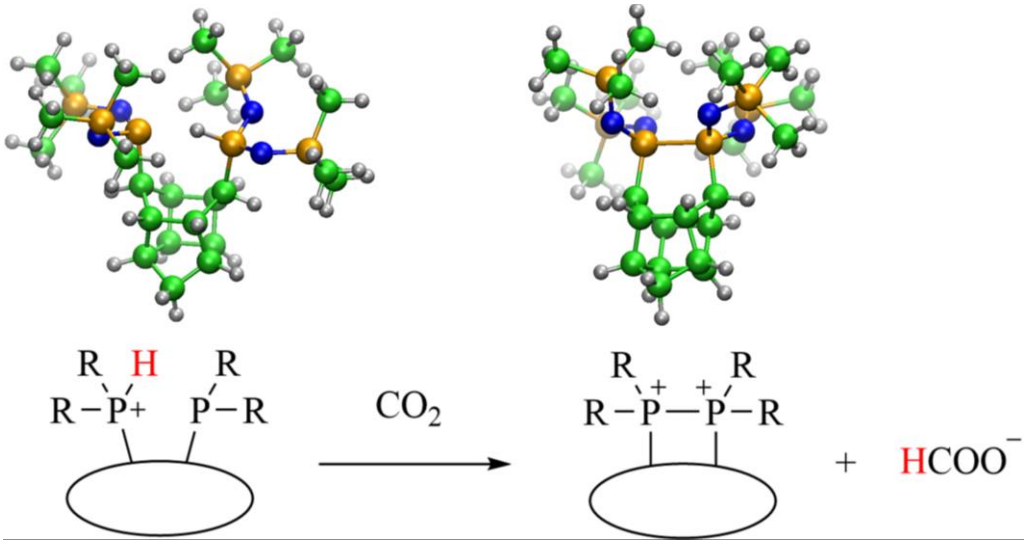

Figure 1. 3D picture of hydride donor with its dication form and scheme of hydride transfer on CO_2

References:

[1] M. B. Röthel, T. Eder, F. Brylak, M. Seidl, P. Löwe, F. Dielmann, *Inorg. Chem.* **64** (2025) 24134–24142.

[2] D. Barić, M. Damjanović, Z. Glasovac, I. Despotović, B. Kovačević, *Chem. Comm.* **62** (2026) 4833–4837.