Supplementary Information

EPR spectroscopy

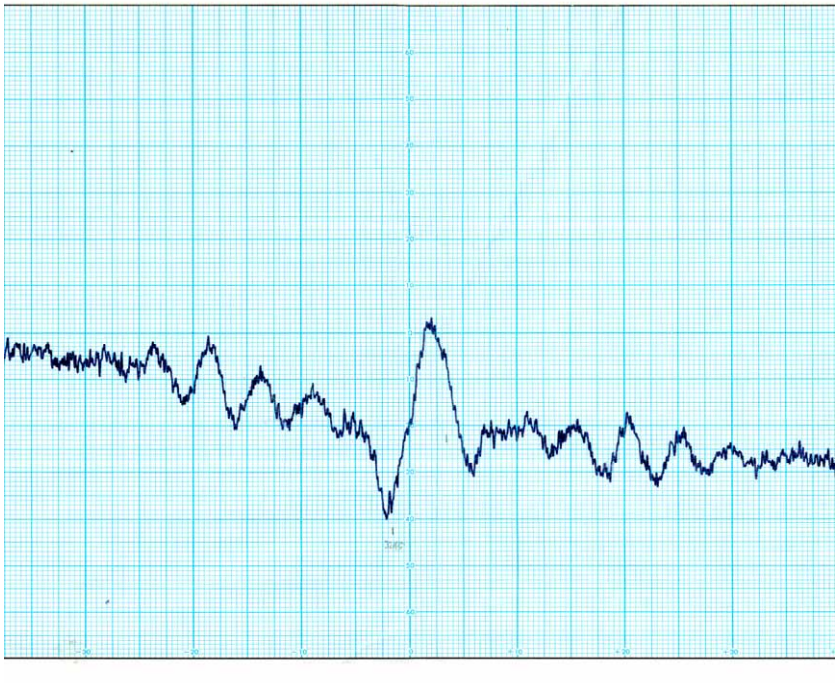


Figure ESI 1. EPR spectrum of **1b** at 315 K in thf.

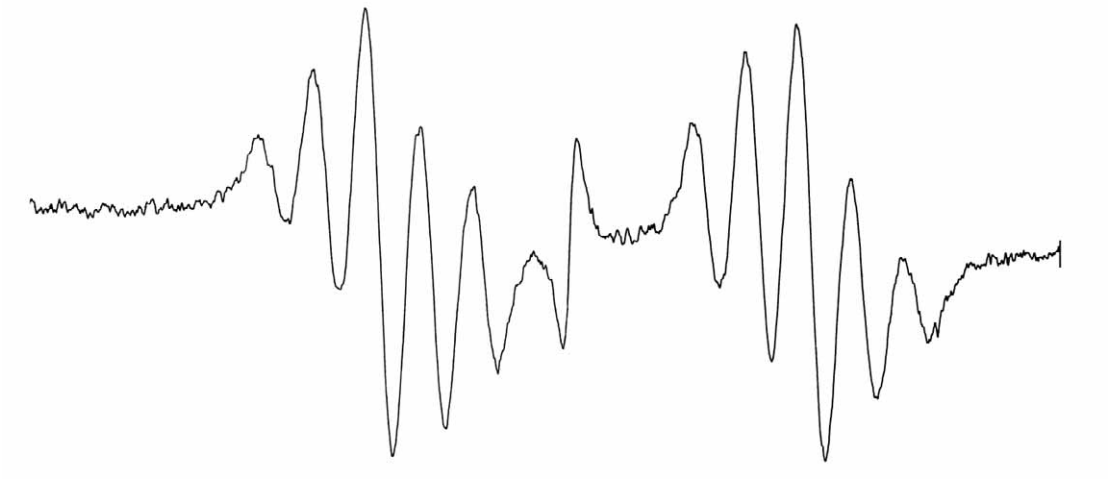
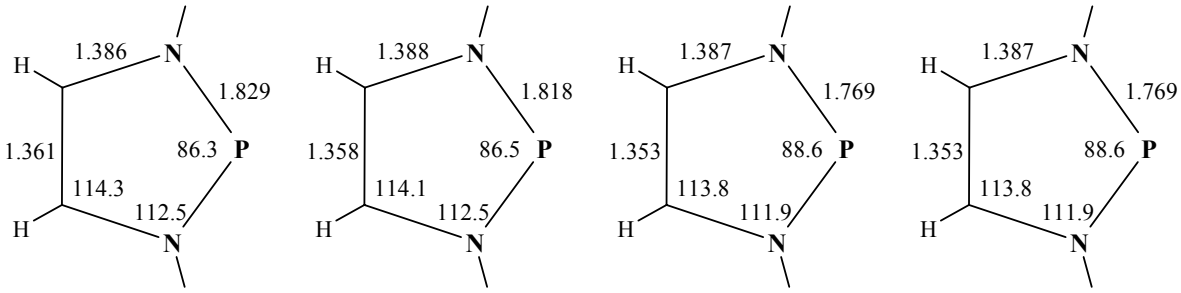


Figure ESI 2. EPR spectrum of **1c** at room temperature in thf.

DFT calculations

All DFT calculations were undertaken using GAMESS-UK using the unrestricted Hartree-Fock UB3LYP functional with double zeta 6-31G, 6-31G* or triple zeta 6-311G and 6-311G* basis sets.



-607.95065179691 83 | -608.0420305357 123 | -608.0605691132 149 | -608.1530053077 189

Figure ESI 3. Calculated heterocyclic bond lengths (Å), angles (°) and energies (Hartrees) of the model heterocyclic $C_2H_2(NMe)_2P^{\bullet}$ system at UB3LYP/6-31G, UB3LYP/6-311G and UB3LYP/6-31G* and UB3LYP/6-311G* levels (alongside the number of basis functions).

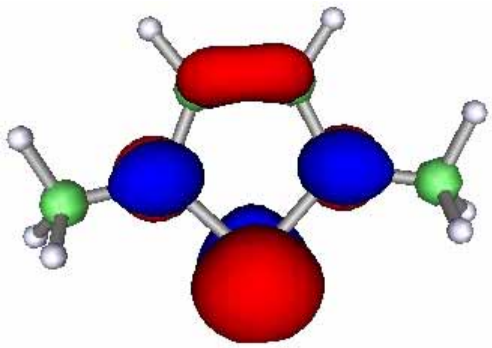


Figure ESI 4. SOMO of $C_2H_2(NMe)_2P^{\bullet}$ determined at the UB3LYP/6-311G* level.

The RHF $[(CH)_2(NMe)P]_2$ dimer (-1215.902403au) is slightly more stable than two UHF monomers $[(CH)_2(NMe)P]$ (-1215.901303au).