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Supporting Information

12-Vertex Zwitterionic Bis-phosphonium-*nido*-carborates through Ring-Opening Reactions of 1,2-Diphosphetanes

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DFT Calculations

Density functional theory (DFT) calculations for the lithiated intermediate [{1-P*t*BuLi(THF)-6-P*t*Bu-4,1,6-*closo*-Li(THF)$C_2B_{10}H_{10}$}{Li(THF)$_3$}]$_2$·2 THF (**2a**) were examined using the ORCA 3.0.3 software package by Neese.[1] However, the large molecule was simplified to [{1-P*t*BuLi(Me_2O)-6-P*t*Bu-4,1,6-*closo*-Li(Me_2O)$C_2B_{10}H_{10}$}]$^{2-}$ (**2a'**), to avoid a large number of flexible conformations of the THF molecules which would give no further insides into the electronic structure of the interesting part of the molecule only problems for the convergence within the geometry optimisation procedure. The geometry optimisation was performed based on the atomic coordinates from X-ray single crystal diffraction for **2a** on the BP86 density functional (Becke 88 exchange function[2] and Perdew 86 correlation function[3]) utilising the atom-pairwise dispersion correction with Becke-Johnson damping scheme (D3BJ) [4] and Ahlrichs' def2-TZVP basis set.[5] For the frequency calculations, the same setting as for the geometry optimisation were used as it was performed on the optimised geometry. Density fitting techniques, also called resolution-of-identity approximation (RI),[6] were applied throughout to speed up the calculations. Based on the optimised geometry, a single-point energy evaluation using the M06-2x[7] level of theory again with the Ahlrichs' def2-TZVP basis sets[5] was performed, from which also the molecular orbitals were taken. Within the used RIJCOSX approximation, the COSX can additionally accelerate the numerical integration for the HF exchange in the hybrid functional, where it needed to have a higher COSX grid (GridX6).[8] In order to consider solvent effects (THF), the conductor-like screening model (COSMO) by Klamt, where the solvent is represented by a dielectric polarisable continuum, was used, as implemented in ORCA 3.0.3.[9] The convergence thresholds for SCF and geometry optimisations were set to VeryTightSCF, the FinalGrid was turned off (NoFinalGrid) and a large damping factor for the SCF converger (SlowConv) activated. The frontier orbitals (isosurface = 0.04) are visualised using the UCSF Chimera visualisation system. [10] The LOEWDIN reduced orbital population analysis was used for discussing each molecular orbital and the MULLIKEN atomic charges are taken from the MULLIKEN population analysis.

NMR Spectra of the Lithiated Intermediate

The NMR spectra of **2a** are in good accordance with the molecular structure observed in the solid state. Firstly, the downfield shift of both signals in the $^{31}P\{^1H\}$ NMR spectrum compared to the starting material indicate that these P atoms are connected with Li atoms. More importantly, the right assignment of the spin systems supports the observed binding modes (Figures S1-S4).

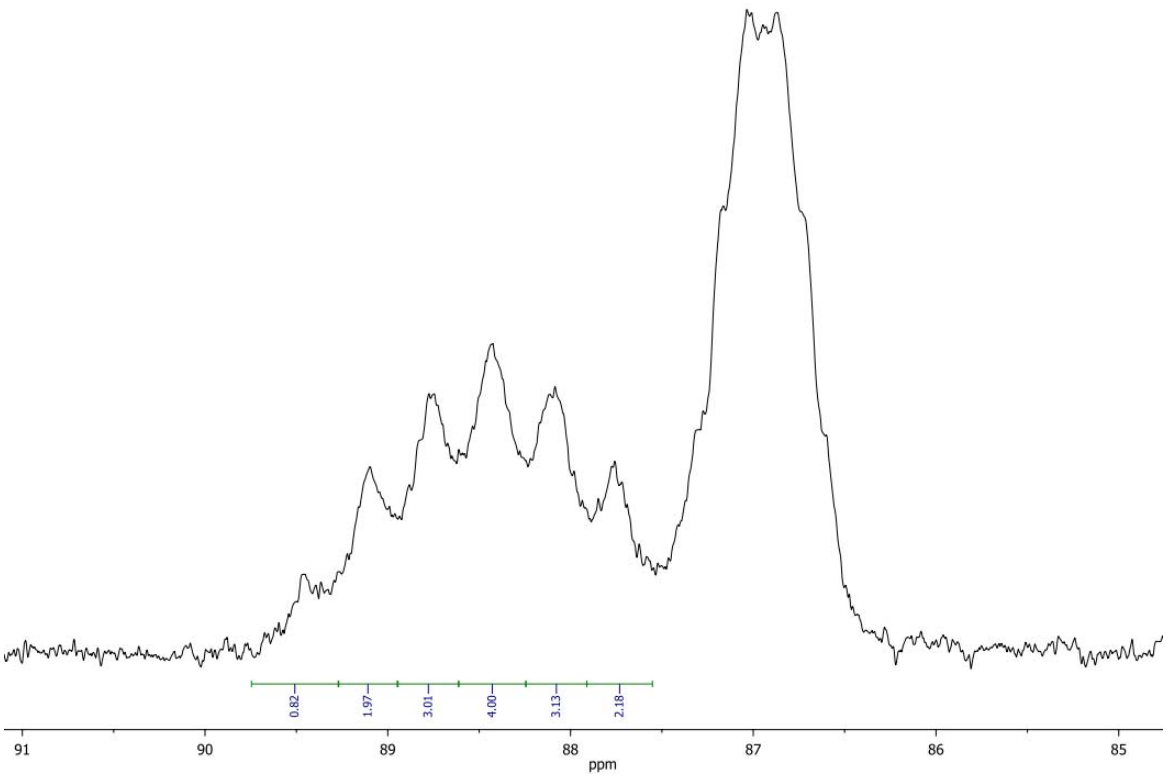

Figure S1. $^{31}P\{^{1}H\}$ NMR spectrum of lithiated intermediate **2a**

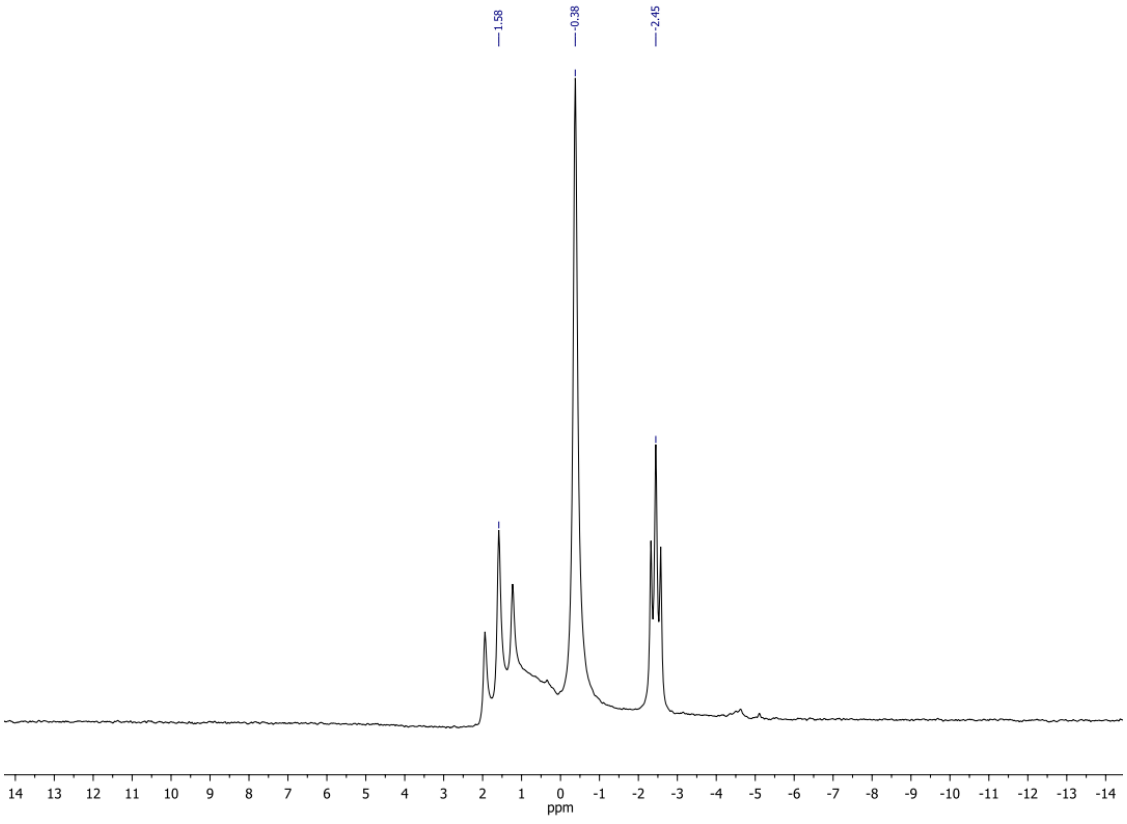

Figure S2. $^{7}Li\{^{1}H\}$ NMR spectrum of lithiated intermediate **2a**

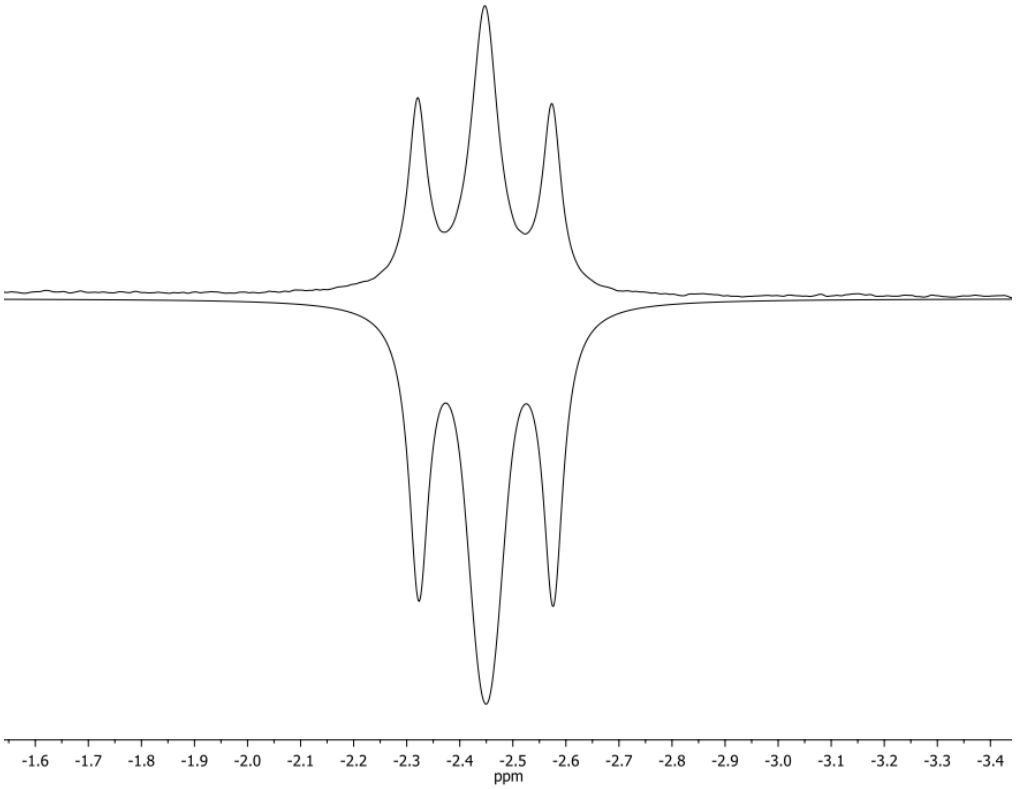

Figure S3. Experimental (top) and simulated (bottom) $^{7}Li\{^{1}H\}$ NMR spectrum of lithiated intermediate **2a**

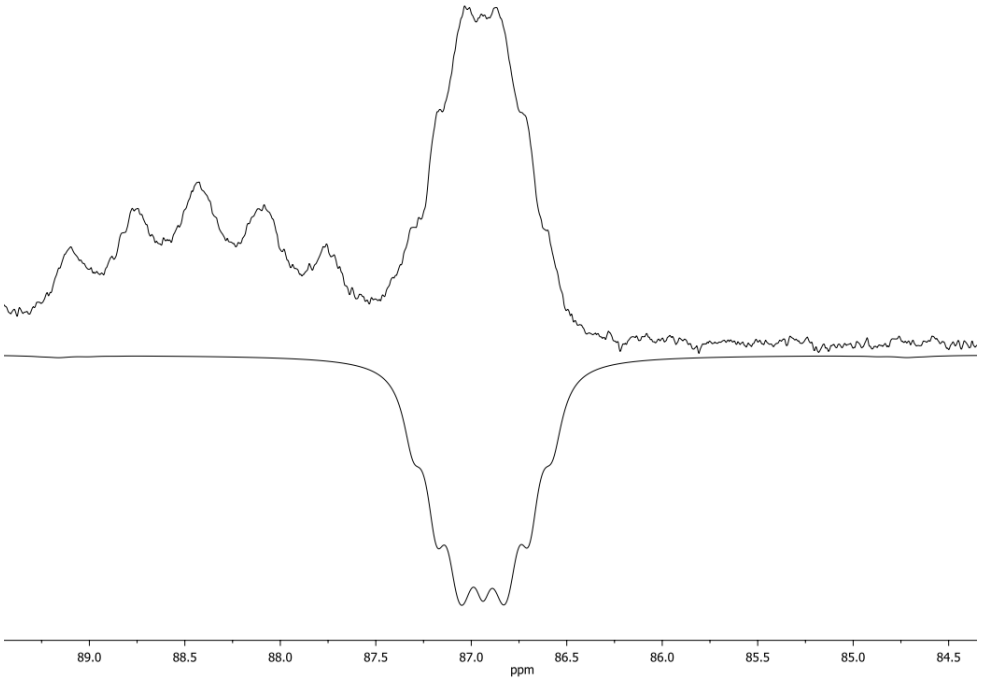

Figure S4. Experimental (top) and simulated (bottom) $^{31}P\{^{1}H\}$ NMR spectrum of lithiated intermediate **2a**.

Due to the nuclear spin of ^{7}Li (I = $^{3}/_{2}$),[11] the two spin systems observed in the NMR spectra of **2a** give a more complicated shape than usual. In both spin systems, this affects the core which couples to the nucleus with I = $^{3}/_{2}$, whereas the signal of the nucleus with I = $^{3}/_{2}$ itself is unaffected. Accordingly, a 1:2:3:4:3:2:1 septet instead of a 1:2:1 triplet is observed in the ^{31}P{^{1}H} NMR spectrum.

The signal for the group P1-P1'-Li1-Li1' in the ^{7}Li{^{1}H} NMR spectrum appears to be a triplet, but is in fact a multiplet of an AA'XX' spin system. These multiplets usually consist of two ab quartets and a doublet with double intensity. In this case the two ab quartets overlap since J(A,A') = ^{3}J(Li1,Li1') is zero. Furthermore, J(X,X') = ^{1}J(P1,P1') is relatively large, thus leading to collapse of the ab quartet to a single line, *i.e.* the intensity of the outer lines were too weak to be detected and the splitting of the inner lines could not be resolved. Nevertheless, we were able to determine a value of –350 Hz as the lower limit for this coupling constant (considering the line width). From the spectral simulation, only the relative sign of ^{1}J(P1,P1') and ^{1}J(P1,Li1) could be extracted. ^{1}J(P1P1') was set negative, since for oligophosphanes and oligophosphanides these coupling constants are usually negative and have large values.[12] All these findings are supported by the ^{31}P{^{1}H} NMR signal of this spin system which matches the simulated multiplet with the extracted coupling constants from the ^{7}Li{^{1}H} NMR spectrum. In analogy to the A_2X_2 spin system, this is not identical to the multiplet in the ^{7}Li{^{1}H} NMR spectrum but shows more lines due to the nuclear spin of ^{7}Li which is only be partially resolved due to the large line width.

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