Stabilisation of an inorganic digallane by the phosphinobisthiolato *P,S,S* pincer ligand PPh(2-SC$_6$H$_4$)$_2$

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UV-Vis spectroscopy – comparison between experimental and theoretical data

Photochemical experiments were undertaken and followed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy to understand the decomposition mechanism of **4**.

The absorption spectra of both the ligand and complex recorded in CH$_2$Cl$_2$ are shown in Figure S1. There are two absorption bands at 260 and 328 nm in the spectra of the complex **4** and two, at 255 and 280 nm, in the spectra of the ligand. By comparison of the two compounds, the absorbance of the complex at 260 nm can be assigned of π→π* transitions due to the ligand, while the other absorbance is the results of ligand→gallium transitions. Thus, in order to decompose the complex further UV irradiation of **4** was performed with a UV lamp at 366 nm. For the calculation of the molar absorptivity ε, Lambert-Beer's law was used.

Table S1. UV data of **PS$_2$H$_2$** and complex **4**

Compound	λ (nm)	A	ε (l·mol^{-1}·cm^{-1})
PS$_2$H$_2$	255	2.65	91.912·10^3
	280	4.60	52.949·10^3
4	260	2.46	117.943·10^2
	328	0.49	23.494·10^2
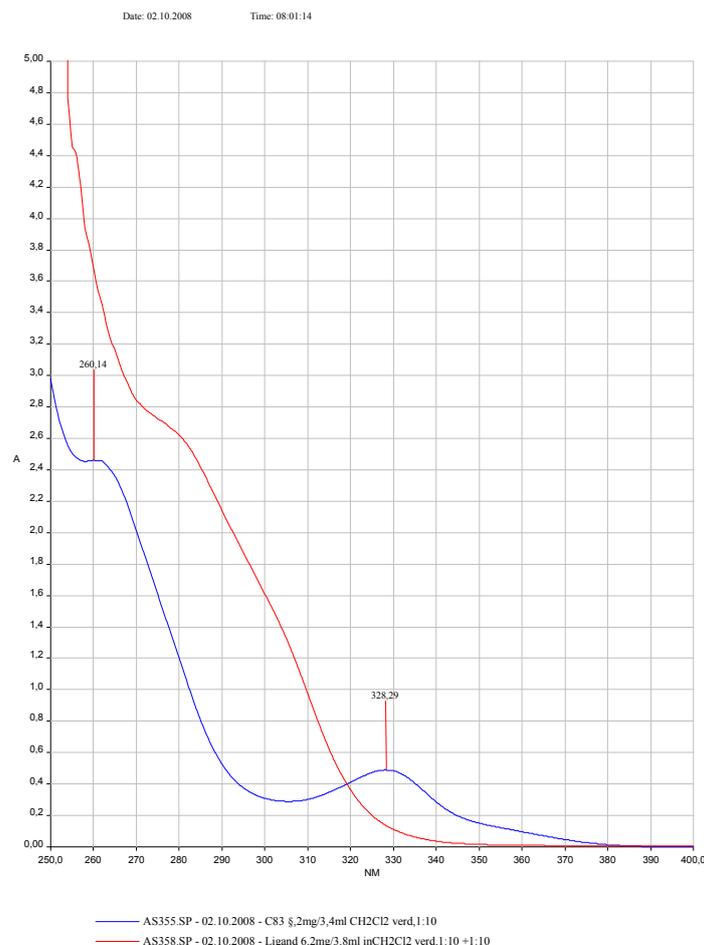
Figure S1. Absorption spectra of **4** and **PS₂H₂** (*vs.* CH₂Cl₂ blank, c_4 = 2.086·10⁻³ mol l⁻¹) and c(**PS₂H₂**) = 5.005·10⁻⁵ mol l⁻¹)

In order to study the way the irradiation of **4** affects the absorption spectra, an additional absorption test was performed. Thus, a solution of **4** in CH₂Cl₂ was irradiated at 366 nm with a UV lamp using different exposure times of 1 h, 12 h, and 25 h, and the samples were studied by UV spectroscopy. Only a slightly hypsochromic effect was observed, the absorption was shifted to smaller wave numbers relative to a fresh solution of **4** (328 nm), i.e., to 322 nm after 1h and 12 h irradiation and to 319 nm after 25 h irradiation.

The electronic spectrum of **4** was also calculated (TD-DFT calculation using the Spartan'06 package) in order to understand the nature of the absorbance transitions. The excitation energies for the first 10 singlet states are summarised in Table S2. By comparison, it was observed that the calculated UV spectrum (Figure S2) reproduces very well the main features of the experimental data (Figure S1).
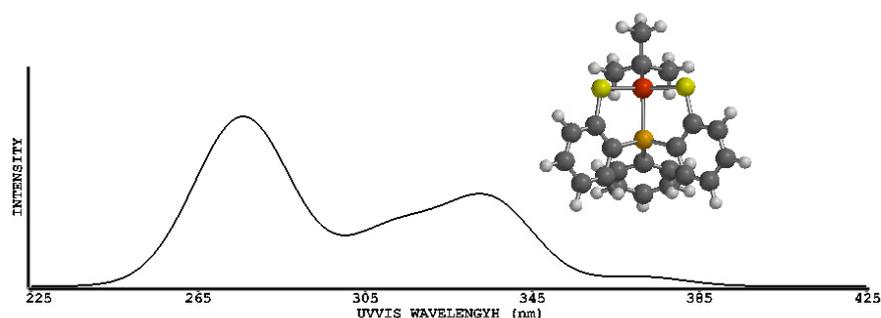
Figure S2. Calculated absorption spectrum of **4**

Table S2. TD-DFT/TDA excitation energies in **4**

Excited state	Transition	Excitation energy (cm^{-1})	Total energy of the state	Strength	Wavelength (nm)
1	HOMO→LUMO	26982.65	-3913.9309	0.0033	370.6
2	HOMO−1→LUMO	29837.07	-3913.9179	0.0276	335.1
3	HOMO→LUMO+1	30345.20	-3913.9156	0.0016	329.5
4	HOMO−1→LUMO+1 HOMO→LUMO+2	31755.88	-3913.9092	0.0124	314.9
5	HOMO−1→LUMO+1 HOMO→LUMO+2	32516.46	-3913.9057	0.0085	307.5
6	HOMO−1→LUMO+2	33623.33	-3913.9007	0.0004	297.5
7	HOMO−2→LUMO HOMO→LUMO+3	35623.33	-3913.8916	0.0183	280.72
8	HOMO−2→LUMO HOMO→LUMO+3	36262.93	-3913.8886	0.0147	275.76
9	HOMO−1→LUMO+3 HOMO→LUMO+4	36427.47	-3913.8879	0.0207	274.52
10	HOMO−1→LUMO+3 HOMO→LUMO+4	37473.58	-3913.8831	0.0099	266.86

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The shapes of the orbitals involved in the transition are depicted in Figure S3A (HOMO) and S3B (LUMO). HOMO−1 and HOMO−2 have Ga−C bonding character so any transitions from these levels should weaken this bond, which is in line with the observed breaking of this bond during the UV irradiation.

Thus, the electron transitions which determine the breaking of the Ga−C bond occur in the range of 267−335 nm, which is in agreement with the experimental UV tests presented above. These values are also in concordance with the calculated UV spectrum presented in Figure S2. Moreover, this lability of the Ga−C bond might also be associated with the high electrostatic positive charges on these atoms (Ga +0.603, C +0.552).
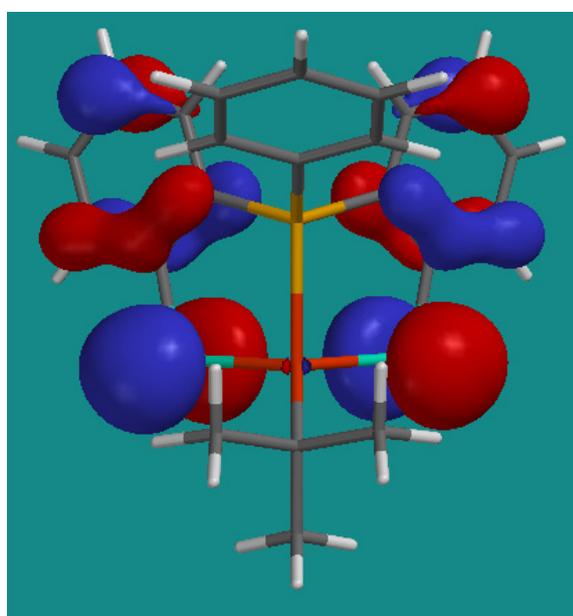
HOMO
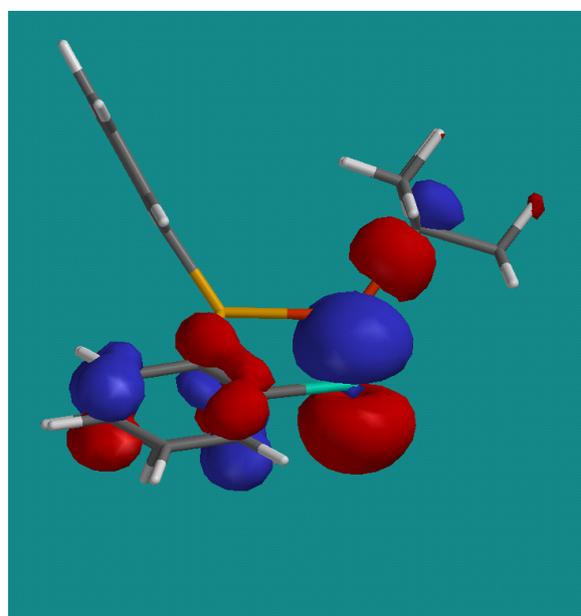
HOMO−1 (side view)
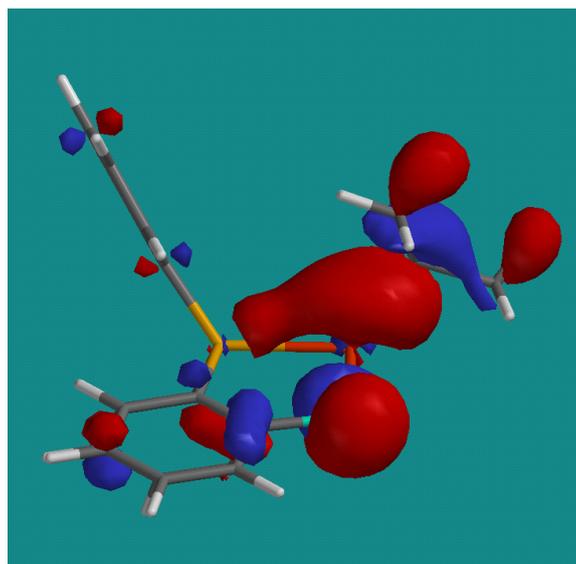
HOMO−2 (side view)

Figure S3A The shape of the HOMO orbitals
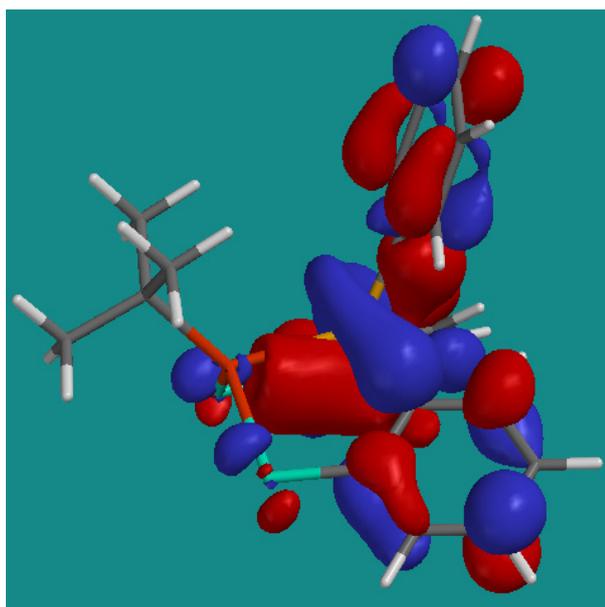
LUMO
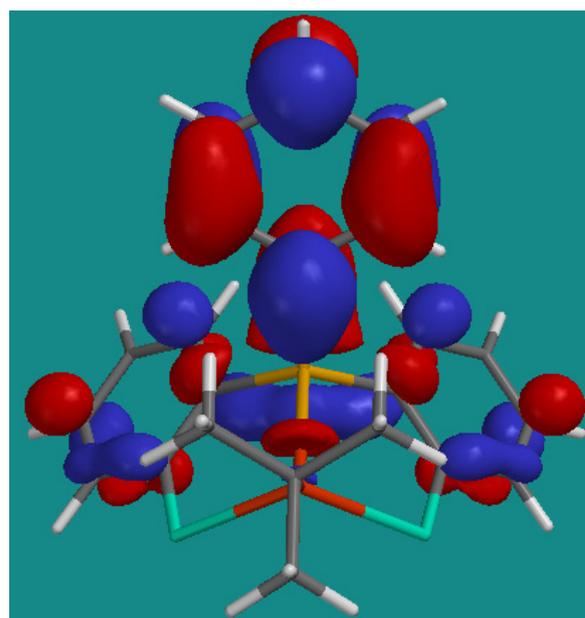
LUMO+1
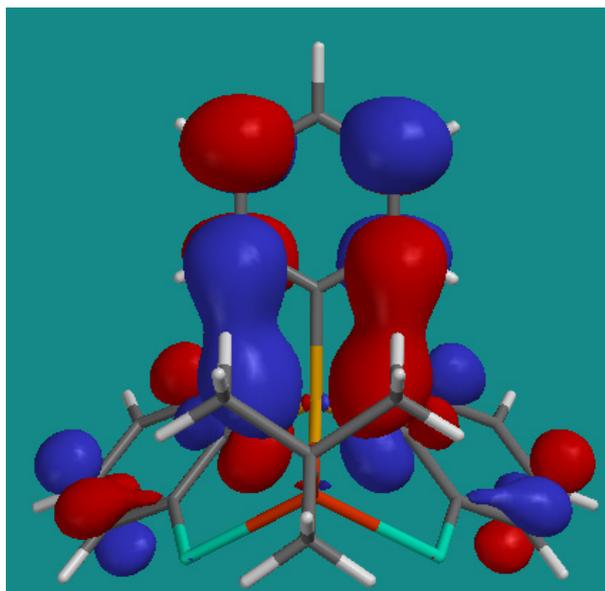
LUMO+2
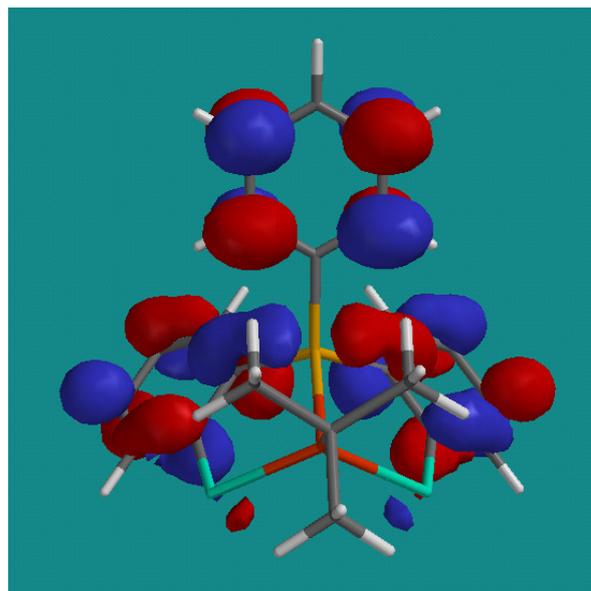
LUMO+3
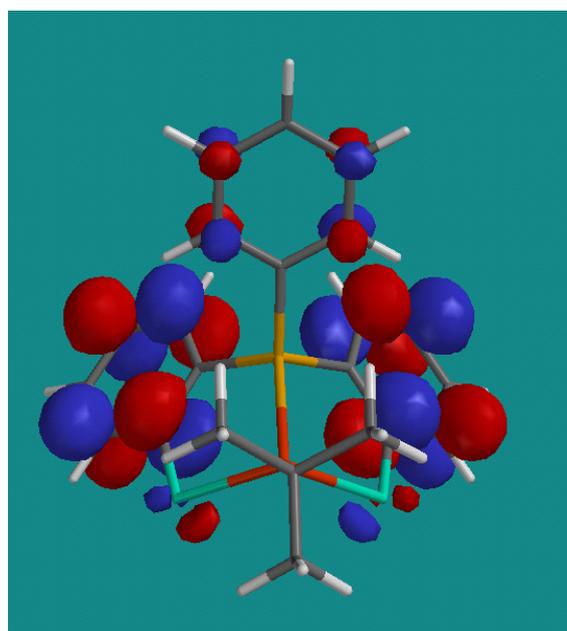
LUMO+4

Figure S3B. The shape of the LUMO orbitals