

SUPPLEMENTARY INFORMATION

**Large shortening of the lead-lead bond in a diplumbyne upon its one-electron
reduction**

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Experimental Details

General Procedures. All manipulations were carried out using modified Schlenk techniques or in a Vacuum Atmospheres drybox under an N₂ or argon atmosphere. Manipulations of lead compounds were carried out with careful exclusion of light due to their tendency to decompose or disproportionate on illumination. Solvents were dried over columns of activated alumina using a Grubbs type purification system, stored over Na (Et₂O, THF) or K (toluene) mirrors, and degassed via three freeze-pump-thaw cycles prior to use. UV-Visible spectra were recorded in dilute THF solutions in 3.5 mL quartz cuvettes using Cary 60 spectrophotometer. X-band EPR spectra were recorded using a Bruker EMX spectrometer equipped with an ER041Xg microwave bridge and calibrated with DPPH ($g = 2.0036$). Melting point measurements were done in glass capillary tubes sealed under argon using a Mel-Temp II apparatus. ¹H NMR spectra were collected using a Bruker DRX 500 MHz spectrometer and referenced to the solvent residual signal.¹ Magnetic moment measurements were done using Evans' method^{2,3} in *d*₈-THF containing *ca.* 2% C₆H₆ and corrected using an estimated diamagnetic constant.⁴ Ar^{iPr₆}PbPbAr^{iPr₆}, **1**, was prepared according to the literature methods.⁵⁻⁷

[K(18-crown-6)][Ar^{iPr₆}PbPbAr^{iPr₆}], 2. A Schlenk flask was charged with crystals of Ar^{iPr₆}PbPbAr^{iPr₆}·C₆H₁₄ (0.150 g, 0.102 mmol), 18-crown-6 (0.027g, 0.102 mmol), KC₈ (0.014, 0.106 mmol), and a Teflon coated stirbar and wrapped in foil. Et₂O (*ca.* 15 mL) was added and the mixture stirred 18 hours at ambient temperature. The resulting red-orange solution was filtered, concentrated to *ca.* 1 mL, and stored at 8°C overnight to afford orange crystals of [K(18-crown-6)][Ar^{iPr₆}PbPbAr^{iPr₆}], **2** that were suitable for X-ray crystallography. Yield: 0.041 g, 23%. UV-Visible (THF, 25°C): λ_{max} , nm (ϵ , L mol⁻¹ cm⁻¹): 320 (shoulder, 3800), 452 (3400) 778 (670). Magnetic moment (Evans, *d*₈-THF): 1.8 μ_B . M.p.: rapidly decomposes to lead metal above 130°C.

Reaction of $\text{Ar}^{\text{iPr}_6}\text{PbPbAr}^{\text{iPr}_6}$ with 2 equivalents of KC_8 . A stirred suspension of KC_8 (0.071 g, 0.526 mmol) in *ca.* 5 mL of THF was cooled to -78°C in a dry ice/ethanol bath and covered in foil. To this, a solution of $\text{Ar}^{\text{iPr}_6}\text{PbPbAr}^{\text{iPr}_6}\cdot\text{C}_6\text{H}_{14}$ (0.366 g, 0.250 mmol) in *ca.* 30 mL of THF was added dropwise over 20 min. After stirring for *ca.* 30 min the solution had become dark red. The mixture was slowly warmed by *ca.* 20°C every 30 min until it reached ambient temperature then the solvent was removed under reduced pressure. Subsequent extraction of the resulting residue with toluene or THF gave colorless filtrates and a residual grey precipitate of elemental Pb.

General procedure for the reaction of $\text{Ar}^{\text{iPr}_6}\text{PbPbAr}^{\text{iPr}_6}$ with 2 equiv of M (M = Na, K, Rb).

A Schlenk flask was charged with a stirbar and 2.00 equivalents of alkali metal and was then cooled to -78°C in a dry ice/ethanol bath and covered in foil. A solution of $\text{Ar}^{\text{iPr}_6}\text{PbPbAr}^{\text{iPr}_6}\cdot\text{C}_6\text{H}_{14}$ (0.146 g, 0.100 mmol, 1.00 equivalent) in *ca.* 15 mL of solvent (THF or toluene) was added dropwise to the cooled flask via cannula. The solution took on a dark red color which faded rapidly at ambient temperature with concomitant precipitation of lead powder. Attempts to filter the red solution cold only yielded colorless filtrates due to rapid decomposition of the product.

X-ray Crystallography

Crystals of **2** were removed from a Schlenk flask under a stream of argon and immediately covered with hydrocarbon oil. A suitable crystal was selected, attached to a MiTeGen microloop, and mounted on the goniometer of the diffractometer under a cold stream of N_2 . Data were collected at 90 K on a Bruker Duo APEXII CCD diffractometer with $\text{Cu K}\alpha$ radiation $\lambda = 1.54178$. Data were integrated with SAINT⁸ and an absorption correction (multi-scan) was applied using SADABS.⁹ The structures were solved using SHELXTL program package¹⁰ by intrinsic phasing methods using SHELXT¹¹ and were refined by full matrix least-squares procedures using SHELXL.¹² All non-H atoms were refined anisotropically. Disordered diethyl ether solvent (1.25

molecules in the asymmetric unit) in the structure was accounted for with the PLATON SQUEEZE routine.¹³

Table S1. Crystal data and structure refinement for [K(18-crown-6)][Ar^{iPr6}PbPbAr^{iPr6}](C₄H₁₀O)_{1.25}, **2**.

Empirical formula	C ₈₉ H _{135.5} O _{7.25} KPb ₂ ,	
Formula weight	1773.94	
Temperature	90(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	a = 15.9819(4) Å	α = 75.3410(10)°
	b = 16.1583(3) Å	β = 70.5950(10)°
	c = 22.8325(5) Å	γ = 65.8440(10)°
Volume	5027.2(2) Å ³	
Z	2	
Density (calculated)	1.172 Mg/m ³	
Absorption coefficient	7.133 mm ⁻¹	
F(000)	1819	
Crystal size	0.255 × 0.112 × 0.096 mm ³	
Theta range for data collection	3.025 to 68.334°	
Index ranges	-19 ≤ h ≤ 18, -17 ≤ k ≤ 19, -27 ≤ l ≤ 27	
Reflections collected	26313	
Independent reflections	17458 [R(int) = 0.0163]	
Completeness to theta = 67.679°	95.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.297 and 0.161	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	17458 / 518 / 952	
Goodness-of-fit on F ²	1.069	
Final R indices [I > 2σ(I)]	R1 = 0.0654, wR2 = 0.1985	
R indices (all data)	R1 = 0.0713, wR2 = 0.2089	
Largest diff. peak and hole	2.730 and -0.982 e Å ⁻³	

UV-Visible Spectrum

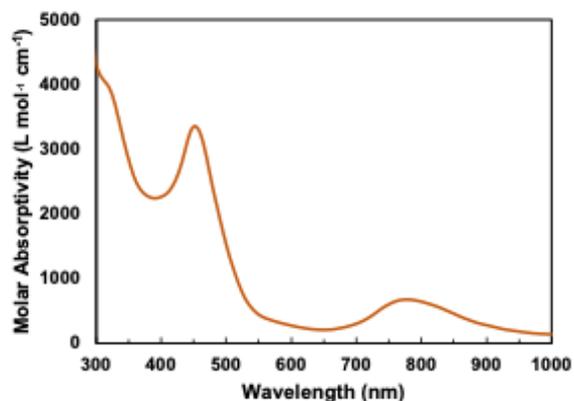


Figure S1. UV-visible spectrum of **2** in THF.

EPR Spectroscopy

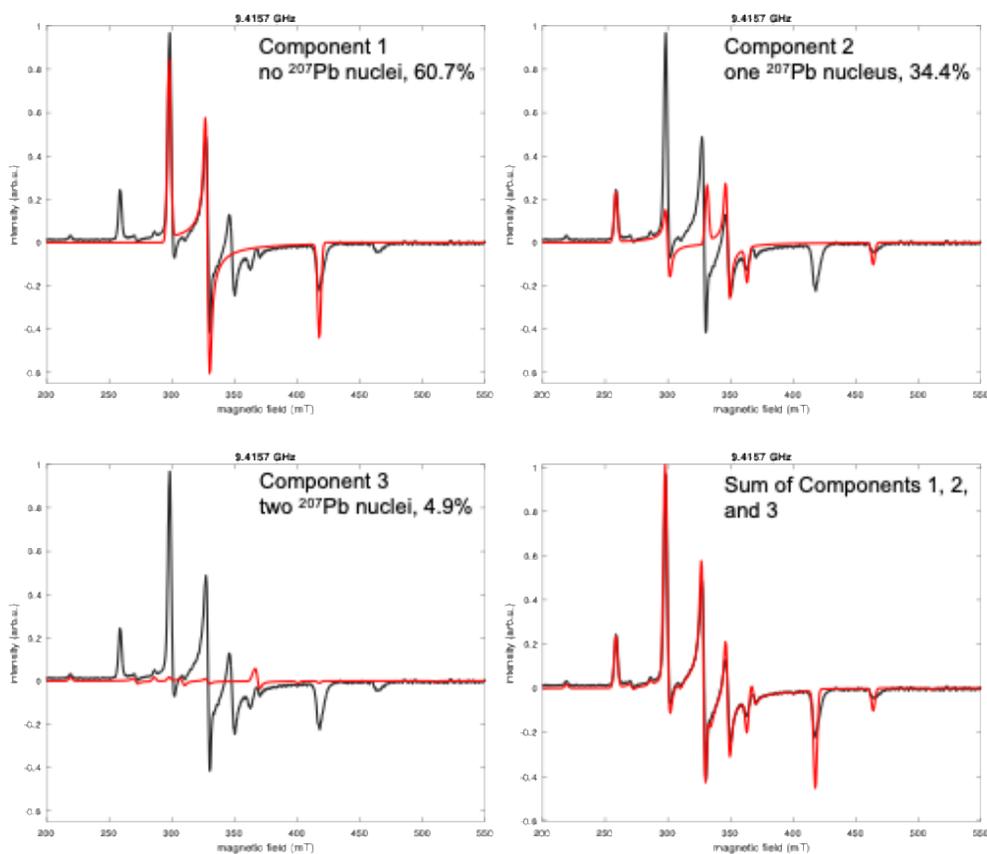


Figure S2. Simulated (red) EPR spectra for the components that contribute to the total experimental frozen solution spectrum (black) of the $[\text{Ar}^{\text{iPr}_6}\text{PbPbAr}^{\text{iPr}_6}]^-$ radical anion. Simulations were performed using the *pepper* function in EasySpin.¹⁴

NMR Spectroscopy

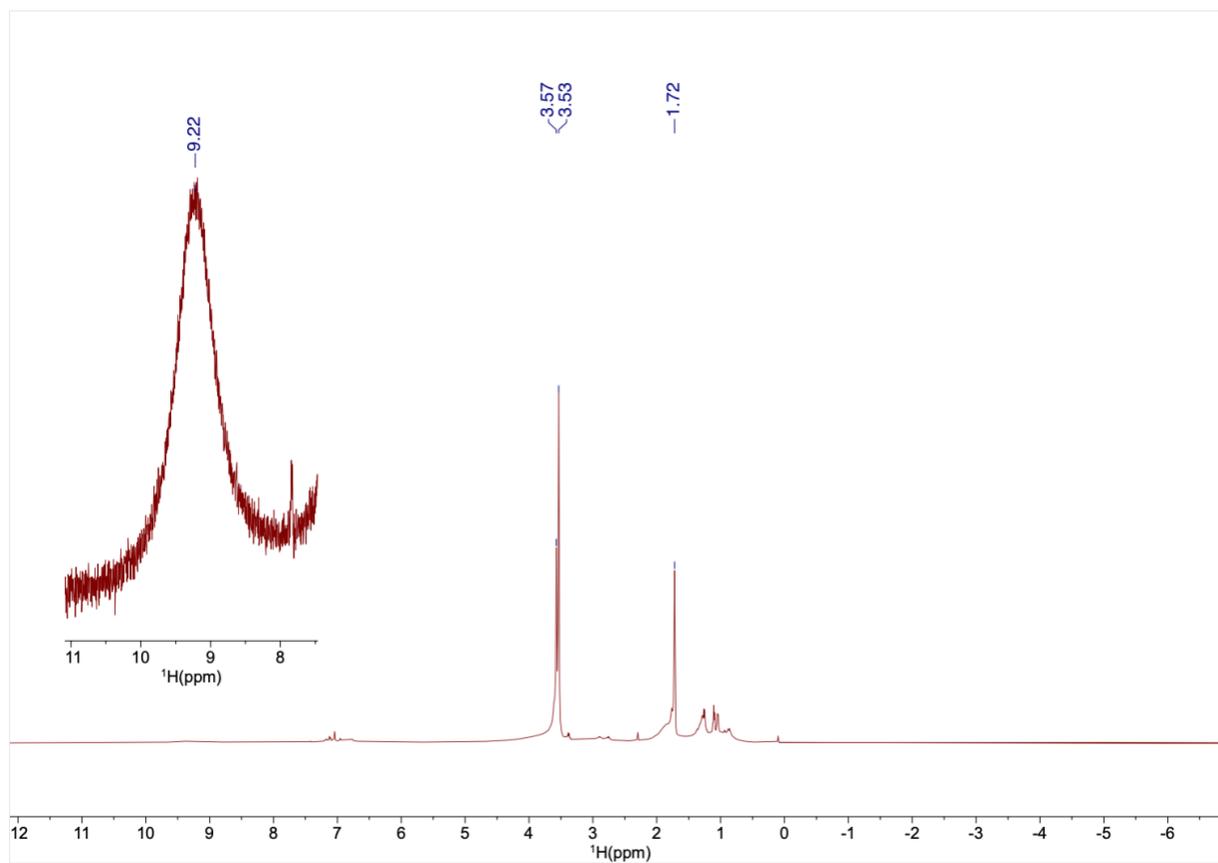


Figure S3. ^1H NMR spectrum of **2**, *ca.* 9 mM in d_8 -THF. The inset shows the only tentative broad resonance assigned to this compound at 9.22 ppm.

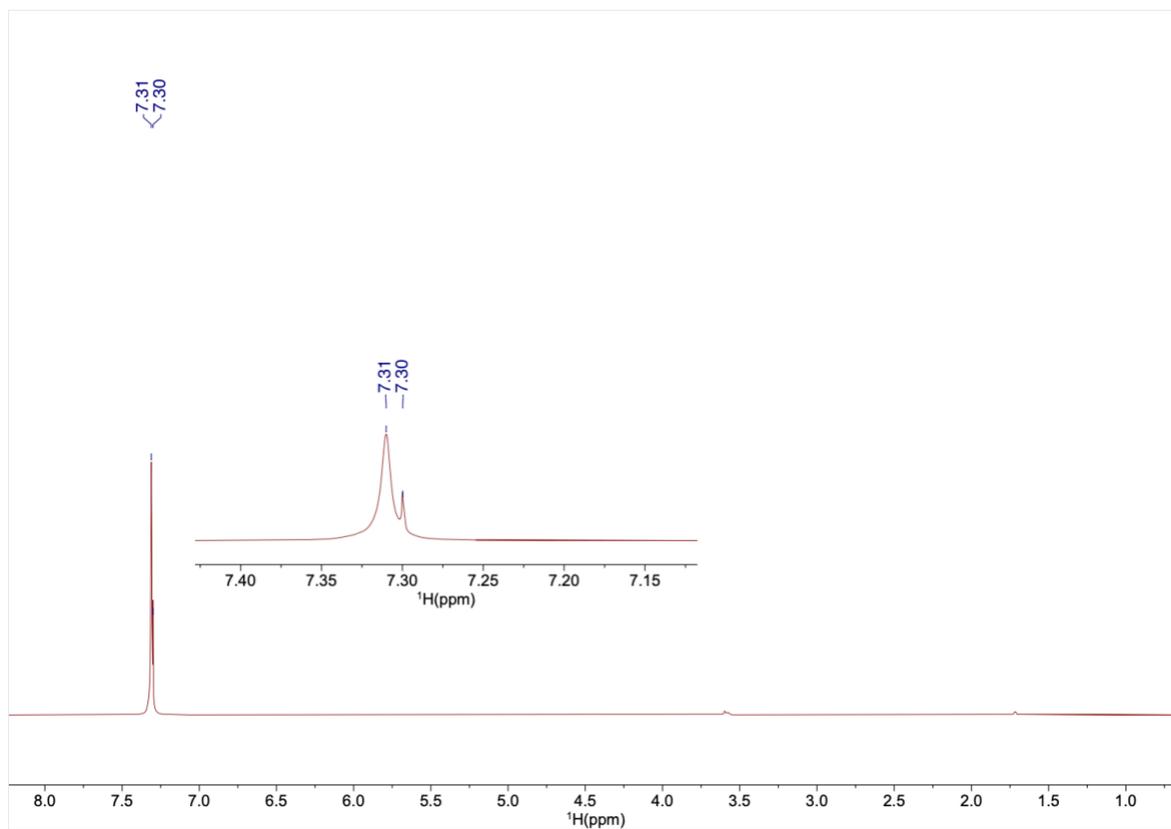


Figure S4. ¹H NMR spectrum of **2**, 5.8 mM in *d*₈-THF doped with C₆H₆ used for the magnetic moment measurement. An estimated diamagnetic correction of 101×10^{-6} emu mol⁻¹ was used.

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