Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

Triple-decker Complexes Incorporating Three Distinct Deck Architectures

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I. Synthesis and characterization

I.1 General procedures

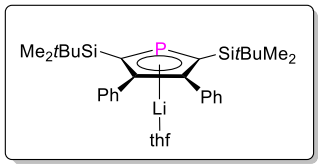
All air- and moisture-sensitive manipulations were performed under dry N_2 or Ar atmosphere using standard Schlenk techniques or in an argon-filled MBraun glovebox, unless otherwise stated. All solvents (Et_2O, *n*-pentane and toluene) were dried using an MBraun solvent purification system (SPS-800) and degassed. Benzene and THF were distilled under nitrogen from potassium benzophenone ketyl before storage over $LiAlH_4$ *in vacuo*. C_6D_6 and toluene-d_8 were dried over Na-K alloy and degassed by freeze-pump-thaw cycles. [Cp*Fe(η^5-P_5)],[1] [Cp*Fe(η^5-As_5)][2] and the dilithioplumbole ([Li_2(thf)$_2$(L^{Pb})], L^{Pb} = 1,4-bis-*tert*-butyl-dimethylsilyl-2,3-bis-phenyl-plumbolyl)[3] were prepared according to the literature procedures. All other chemicals were obtained from commercial sources and used without further purification.

Elemental analyses were carried out with an Elementar vario MICRO cube.

NMR spectra were recorded on Bruker spectrometers (Avance III 300 MHz, Avance 400 MHz or Avance III 400 MHz). Chemical shifts are referenced internally using signals of the residual protio solvent (^{1}H) or the solvent (^{13}C{^{1}H}) and are reported relative to tetramethylsilane (^{1}H, ^{13}C{^{1}H}), or externally relative to LiCl in D2O (^{7}Li), tetramethylsilane (^{29}Si), H_3PO_4 (^{31}P) or Me_4Pb + 5% C_6D_6 (^{207}Pb). All NMR spectra were measured at 298 K, unless otherwise specified. The multiplicity of the signals is indicated as s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet and br = broad. Assignments were determined based on unambiguous chemical shifts, coupling patterns and ^{13}C-DEPT experiments or 2D correlations (^{1}H-^{1}H COSY, ^{1}H-^{13}C HMQC and ^{1}H-^{13}C HMBC).

Infrared (IR) spectra were recorded in the region 4000–400 cm^{-1} on a Bruker Tensor 37 FTIR spectrometer equipped with a room temperature DLaTGS detector, a diamond attenuated total reflection (ATR) unit and a nitrogen-flushed chamber. In terms of their intensity, the signals were classified into different categories (vs = very strong, s = strong, m = medium, w = weak, and sh = shoulder).

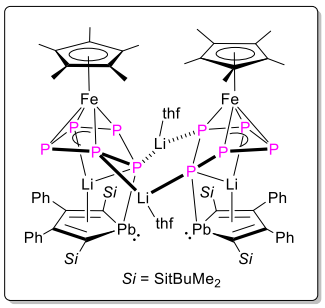
I.2 Synthesis of 1



At -88 °C, toluene (10 mL) to a mixture of dilithioplumbole (0.100 g, 0.125 mmol) and P_4 (0.020 g, 0.161 mmol) was condensed, and the resulting mixture was allowed to warm up to room temperature and kept stirring for 16 h at room temperature. The resulting colorless solution was filtered and concentrated. Crystals suitable for X-ray diffraction analysis were grown from toluene at 5 °C. Yield (based on crystals): 0.041 g (60%).

Anal. Calcd. For $C_{28}H_{40}LiP$ (C_4H_8O) (542.82 g/mol): C 70.81; H 8.91. Found: C 70.79; H 8.82. **^{1}H NMR** (400.30 MHz, C_6D_6): δ (ppm) = 7.16-7.14 (m, 4H, C*H*$_{Ph}$), 7.05-7.02 (m, 4H, C*H*$_{Ph}$), 6.96-6.92 (m, 2H, C*H*$_{Ph}$), 3.22-3.19 (m, 4H, α-C*H*$_2$-thf), 1.13 (s, 18H, SiC(C*H*$_3$)$_3$(CH$_3$)$_2$), 1.07-1.03 (m, 4H, β-C*H*$_2$-thf), 0.28 (s, 12H, SiC(CH$_3$)$_3$(C*H*$_3$)$_2$). **^{7}Li{^{1}H} NMR** (155.51 MHz, C_6D_6): δ (ppm) = -7.0 (d, $^1J_{Li,P}$ = 7.9 Hz). **^{13}C{^{1}H} NMR** (100.62 MHz, C_6D_6): δ (ppm) = 147.0 ($C_{Ph,quart}$), 143.3 (d, $^2J_{C,P}$ = 1.8 Hz, C_β), 142.4 (d, $^1J_{C,P}$ = 75.5 Hz, C_α), 131.9 (*C*H$_{Ph}$), 127.1 (*C*H$_{Ph}$), 125.9 (*C*H$_{Ph}$), 69.3 (C_{THF}), 28.2 (SiC(*C*H$_3$)$_3$Me$_2$), 25.1 (C_{THF}), 18.0 (Si*C*(CH$_3$)$_3$Me$_2$), 1.7 (Si*t*Bu(*C*H$_3$)$_2$), -1.0 (d, $^1J_{C,Si}$ = 8.0, Si*t*Bu(*C*H$_3$)$_2$). (The quaternary carbon of the Ph group could not be detected). **^{31}P{^{1}H} NMR** (162.04 MHz, C_6D_6): δ (ppm) = 154.1 (q, $^1J_{Li,P}$ = 7.9 Hz). **IR (ATR)**: $\tilde{\nu}$ (cm^{-1}) = 3079 (m), 3031 (w), 2958 (s), 2929 (s), 2893 (m), 2856 (s), 1646 (m), 1604 (w), 1576 (m), 1528 (m), 1480 (w), 1468 (s), 1441 (m), 1406 (w), 1390 (w), 1362 (m), 1253 (s), 1233 (m), 1180 (vs), 1062 (vs), 1037 (m), 1010 (vs), 938 (w), 914 (m), 839 (m), 823 (m), 811 (vs), 788 (m), 776 (s), 752 (w), 698 (vs), 678 (m), 646 (w), 562 (m), 512 (m), 458 (m), 436 (m).

1.3 Synthesis of 2

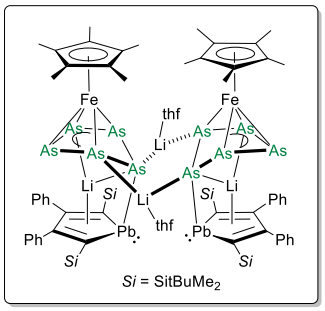


At -88 °C, benzene (10 mL) was condensed to a mixture of dilithioplumbole (0.120 g, 0.150 mmol) and [Cp*Fe(η^5-P$_5$)] (0.052 g, 0.150 mmol) and the resulting mixture was allowed to warm up to room temperature and the reaction mixture turned dark greenish blue. The reaction mixture was kept stirring for 16 h at room temperature before it was concentrated to *ca* 2 mL. Crystals suitable for X-ray crystallography were grown from benzene at room temperature. Yield (based on crystals): 0.066 g (41%).

Anal. Calcd. For $C_{90}H_{132}Fe_2Li_4O_2P_{10}Pb_2Si_4$ (C_6H_6) (2221.97 g/mol): C 48.65; H 5.99. Found: C 48.46; H 5.52. **^{1}H NMR** (400.30 MHz, C_6D_6): δ (ppm) = 8.07-8.05 (m, 2H, C*H*$_{Ph}$), 7.12-7.09 (m,

2H, CH_{Ph}), 7.04-7.02 (m, 2H, CH_{Ph}), 6.96-6.92 (m, 2H, CH_{Ph}), 6.87-6.84 (m, 2H, CH_{Ph}), 3.72 (br, 8H, α-CH_2-thf), 1.63 (s, 15H, C_5(CH_3)$_5$), 1.45 (br, 8H, β-CH_2-thf), 0.99 (s, 18H, SiC(CH_3)$_3$(CH$_3$)$_2$), 0.78 (s, 6H, SiC(CH$_3$)$_3$(CH_3)$_2$), -0.01 (s, 6H, SiC(CH$_3$)$_3$(CH_3)$_2$). **^{7}Li{^{1}H} NMR** (400.30 MHz, C_6D_6): δ (ppm) = 1.2, -3.9. **^{13}C{^{1}H} NMR** (400.30 MHz, C_6D_6): δ (ppm) = 212.5 (C_α), 172.8 (C_β), 153.7 ($C_{Ph,quart}$), 130.5 (C_{Ph}), 130.4 (C_{Ph}), 127.5 (C_{Ph}), 126.8 (C_{Ph}), 125.8 (C_{Ph}), 90.2 (C_5(CH$_3$)$_5$), 69.6 (C_{THF}), 29.1 (SiC(*C*H$_3$)$_3$Me$_2$), 25.5 (C_{THF}), 18.2 (Si*C*(CH$_3$)$_3$Me$_2$), 11.5 (C_5(*C*H$_3$)$_5$), 2.0 (Si*t*Bu(*C*H$_3$)$_2$), -1.9 (Si*t*Bu(*C*H$_3$)$_2$). **^{29}Si{^{1}H} NMR** (59.62 MHz, C_6D_6): δ (ppm) = 2.8 (Si*t*BuMe$_2$). **^{31}P{^{1}H} NMR** (162.04 MHz, C_6D_6, 298 K): δ (ppm) = 42.4 (br), 18.4 (br), -14.3 (dd, $^{1}J_{P,P}$ = 231 Hz , $^{2}J_{P,P}$ = 63 Hz). **^{207}Pb NMR** (62.91 MHz, toluene-d_8): δ (ppm) = 2587. **IR (ATR)**: $\tilde{\nu}$ (cm^{-1}) = 3053 (w), 3018 (w), 2949 (vs), 2924 (vs), 2880 (vs), 2852 (vs), 2706 (w), 2278 (w), 1596 (m), 1557 (w), 1511 (w), 1467 (s), 1440 (m), 1374 (s), 1359 (w), 1329 (w), 1310 (w), 1245 (s), 1212 (w), 1177 (m), 1071 (m), 1040 (vs), 1007 (m), 941 (s), 913 (m), 887 (s), 823 (s), 804 (vs), 764 (vs), 698 (vs), 677 (w), 663 (m), 618 (m), 585 (m), 517 (m), 499 (s), 433 (m).

1.4 Synthesis of 3



At -88 °C, benzene (5 mL) was condensed to a mixture of dilithioplumbole (0.080 g, 0.100 mmol) and [Cp*Fe(η^5-As$_5$)] (0.057 g, 0.100 mmol) and the resulting mixture was allowed to warm up to room temperature and the reaction mixture turned dark green. The reaction mixture was kept stirring for 16 h at room temperature before it was concentrated to *ca* 2 mL. Crystals suitable for X-ray crystallography were grown from benzene at room temperature. Yield (based on crystals): 0.062 g (48%).

Anal. Calcd. For $C_{90}H_{132}Fe_2Li_4O_2As_{10}Pb_2Si_4$ (2583.34 g/mol): C 39.06; H 4.92. Found: C 39.70; H 4.84. **^{1}H NMR** (400.30 MHz, C_6D_6): δ (ppm) = 8.25-8.24 (m, 2H, CH_{Ph}), 7.13-6.86 (m, 8H, CH_{Ph}) 3.80-3.77 (m, 8H, α-CH_2-thf), 1.65 (s, 15H, C_5(CH_3)$_5$), 1.54-1.50 (m, 8H, β-CH_2-thf), 1.01 (s, 18H, SiC(CH_3)$_3$(CH$_3$)$_2$), 0.80 (s, 6H, SiC(CH$_3$)$_3$(CH_3)$_2$), -0.03 (s, 6H, SiC(CH$_3$)$_3$(CH_3)$_2$). **^{7}Li{^{1}H} NMR** (400.30 MHz, C_6D_6): δ (ppm) = 1.1, -3.9. **^{13}C{^{1}H} NMR** (400.30 MHz, C_6D_6): δ (ppm) = 212.5 (C_β), 171.8 (C_α), 154.1 ($C_{Ph,quart}$), 130.6 (C_{Ph}), 128.4 (C_{Ph}), 127.5 (C_{Ph}), 126.7 (C_{Ph}), 125.8 (C_{Ph}), 89.2 (C_5(CH$_3$)$_5$), 69.5 (C_{THF}), 29.2 (SiC(*C*H$_3$)$_3$Me$_2$), 25.6 (C_{THF}), 18.2 (Si*C*(CH$_3$)$_3$Me$_2$), 12.0 (C_5(*C*H$_3$)$_5$), 1.6 (Si*t*Bu(*C*H$_3$)$_2$), -1.9 (Si*t*Bu(*C*H$_3$)$_2$). **^{29}Si{^{1}H} NMR** (59.62 MHz, C_6D_6): δ (ppm) = 2.9 (Si*t*BuMe$_2$). **^{207}Pb NMR** (62.91 MHz, C_6D_6): δ (ppm) = 2096. **IR (ATR)**: $\tilde{\nu}$ (cm^{-1}) = 3053 (w), 3025 (w), 2948 (vs), 2925 (vs), 2880 (vs), 2851 (vs), 2708 (w), 1596 (w), 1557 (w), 1509 (s),

1467 (m), 1440 (m), 1372 (s), 1310 (m), 1244 (s), 1210 (w), 1178 (w), 1071 (w), 1039 (s), 1007 (w), 940 (s), 913 (w), 885 (s), 853 (s), 853 (w), 823 (s), 805 (s), 764 (s), 699 (s), 676 (m), 618 (w), 584 (m), 517 (w), 477 (w), 435 (w).

II. NMR spectra

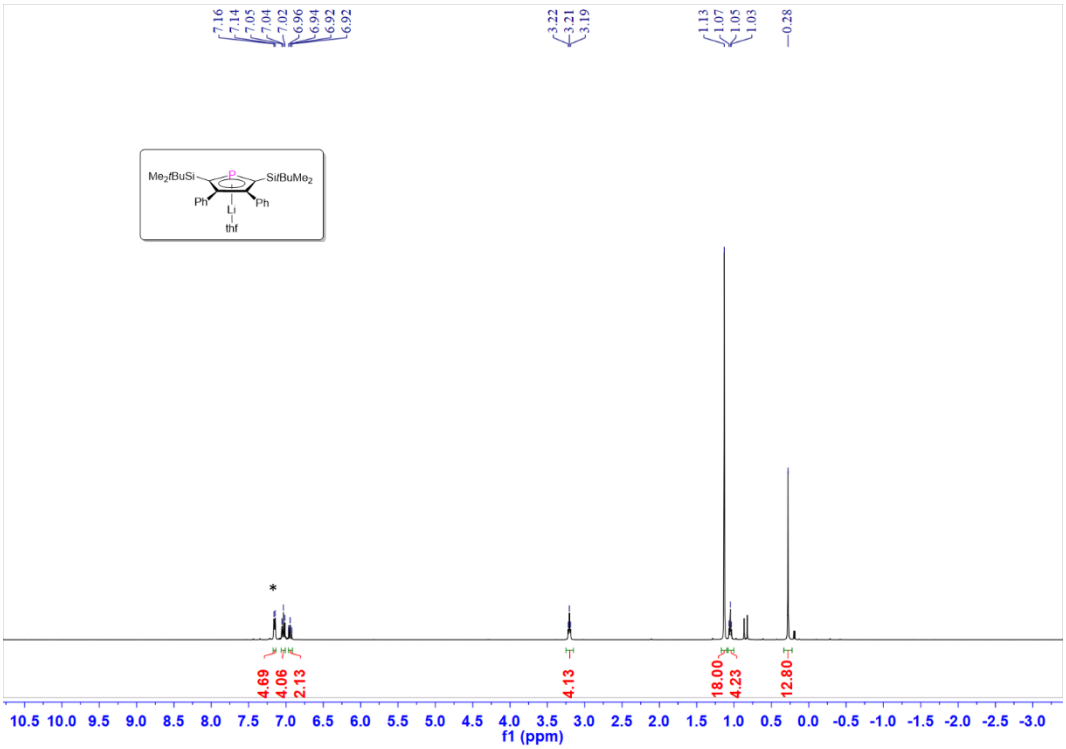


Figure S1. ^{1}H NMR spectrum of **1** in C_6D_6. *, residual protio solvent signal.

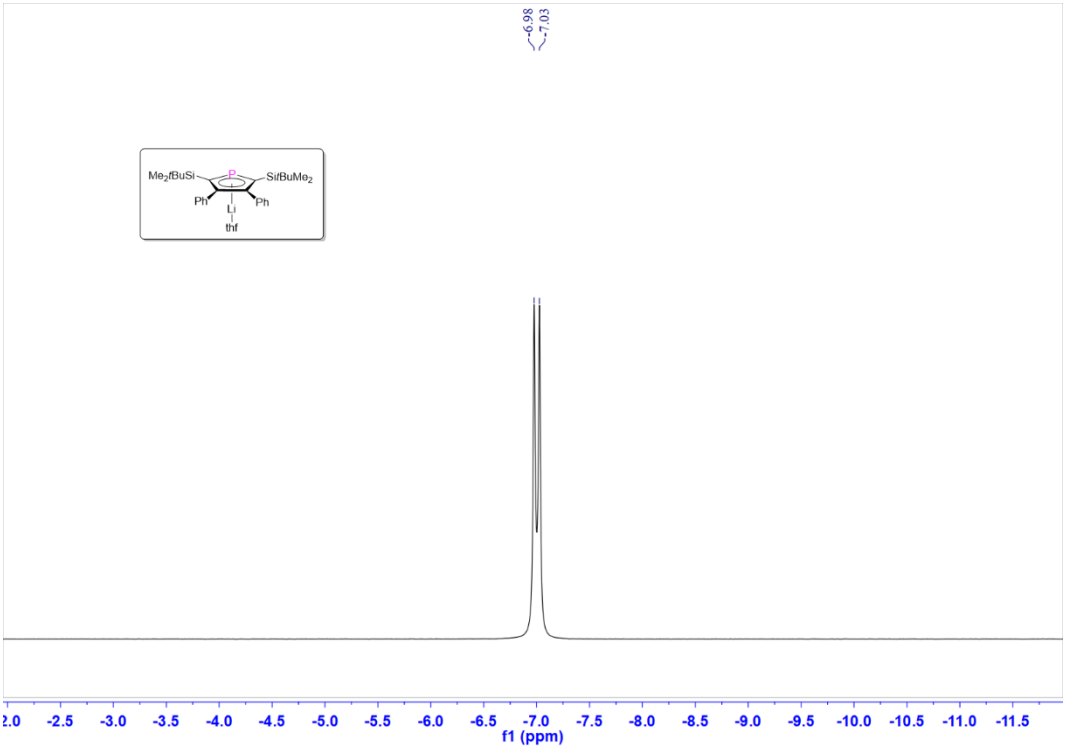


Figure S2. ^{7}Li{^{1}H} NMR spectrum of **1** in C_6D_6.

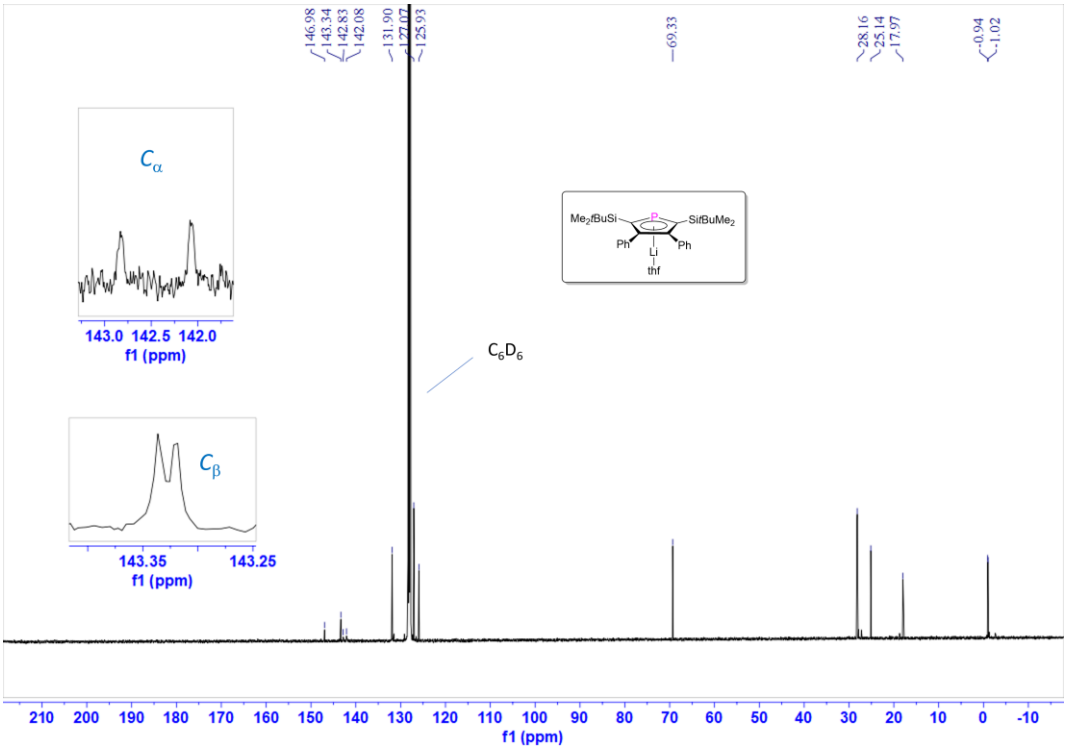


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **1** in C_6D_6.

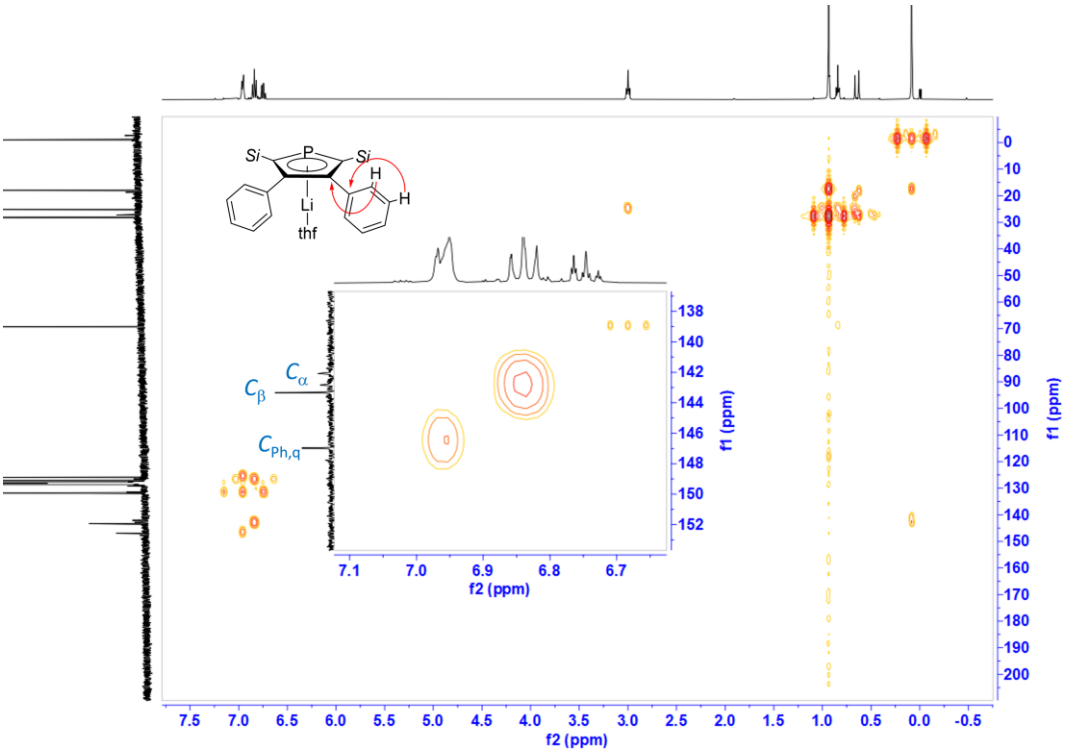


Figure S4. ^{1}H-^{13}C HMBC spectrum of **1** in C_6D_6.

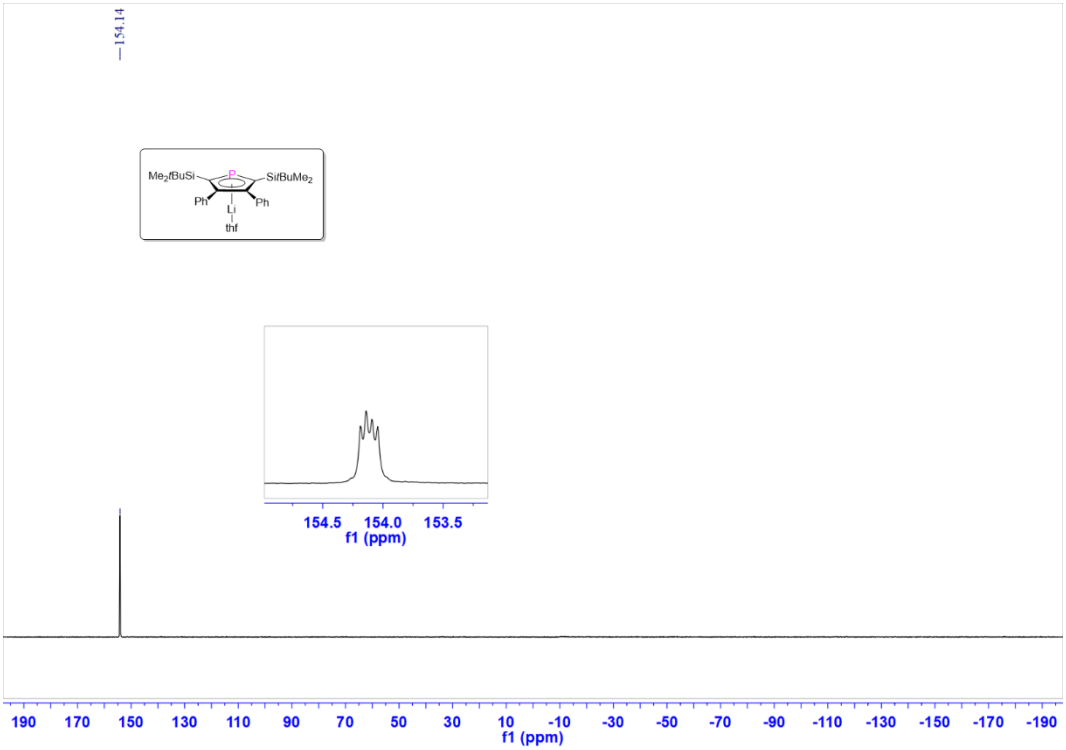


Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum of **1** in C_6D_6.

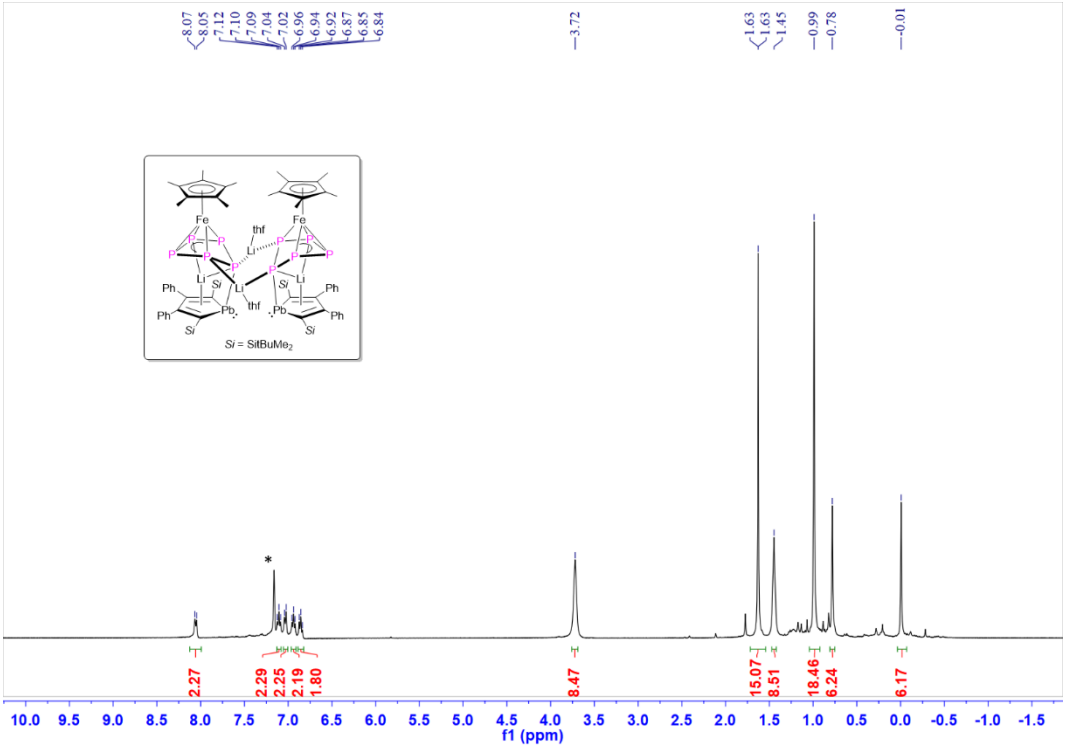


Figure S6. ^{1}H NMR spectrum of **2** in C_6D_6. *, residual protio solvent signal.

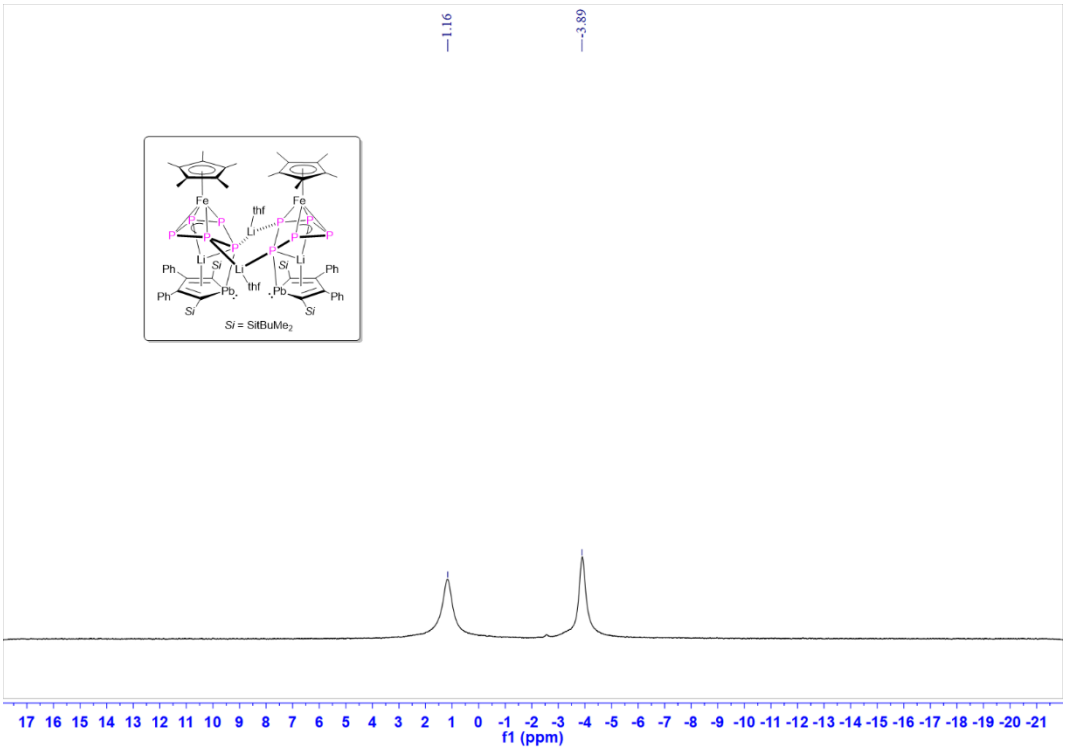


Figure S7. $^{7}Li\{^{1}H\}$ NMR spectrum of **2** in C_6D_6.

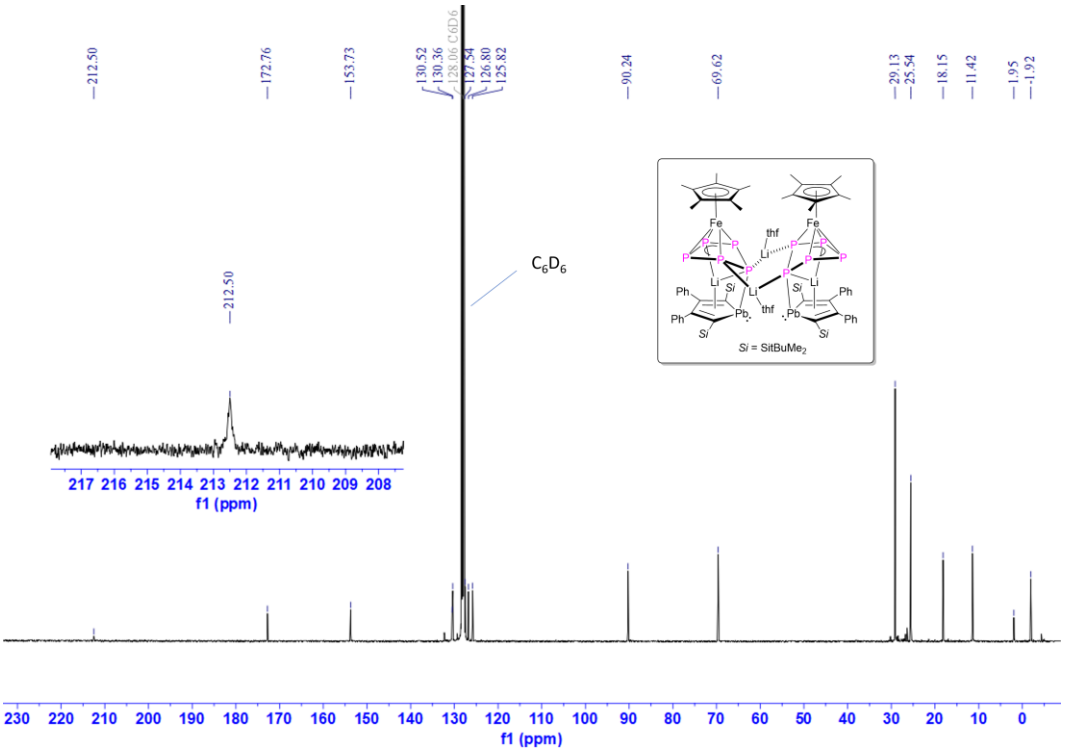


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in C_6D_6.

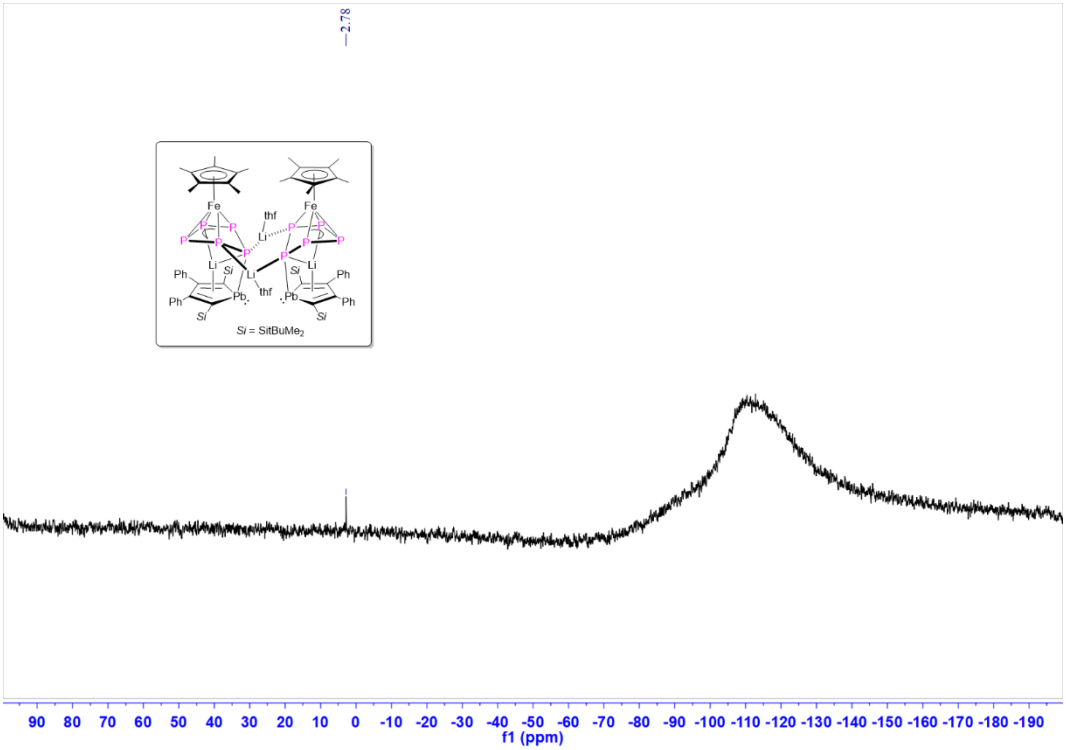


Figure S9. $^{29}Si\{^{1}H\}$ NMR spectrum of **2** in C_6D_6.

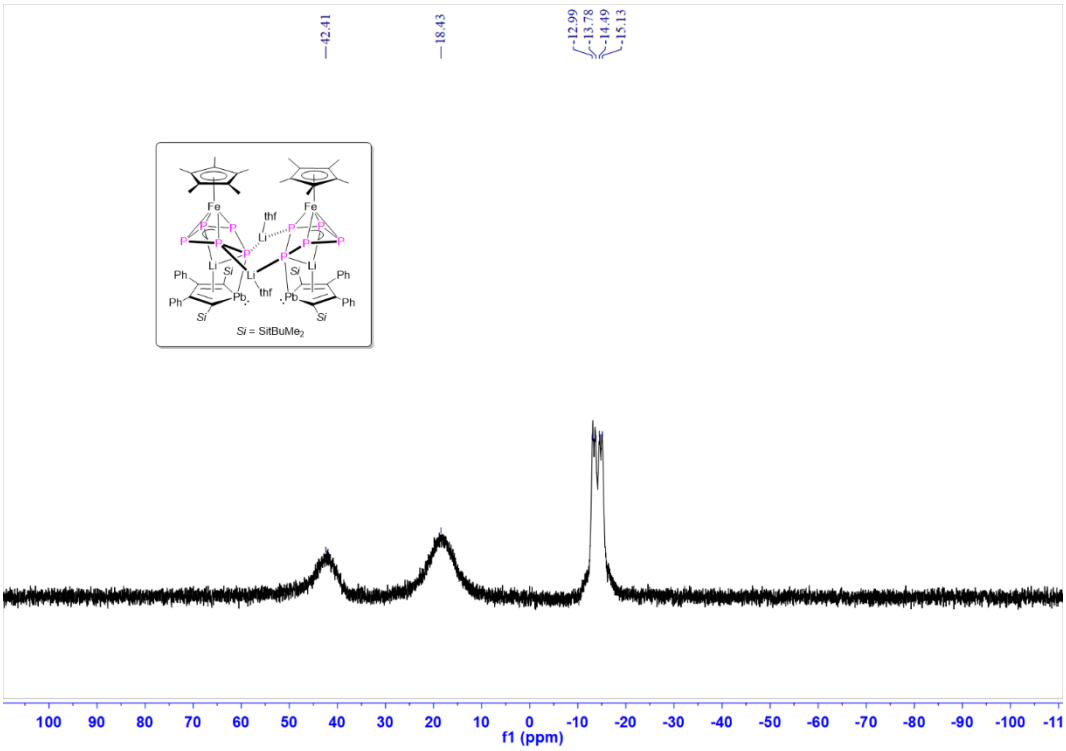


Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of **2** in C_6D_6 at 298 K.

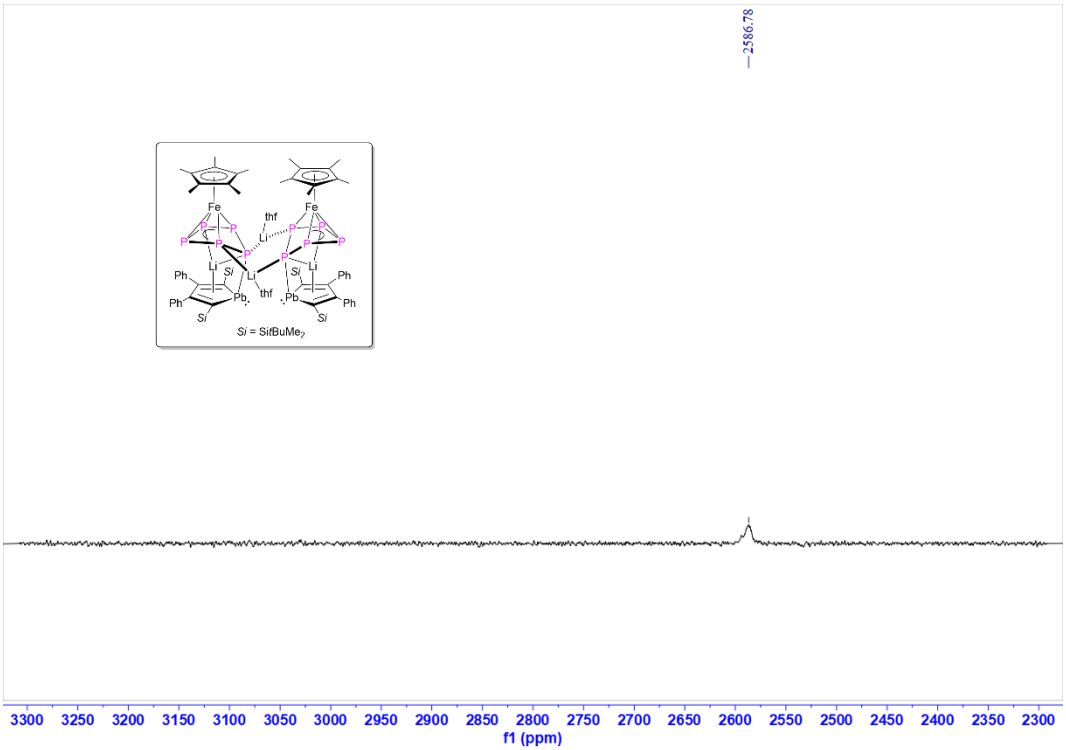


Figure S11. ^{207}Pb NMR spectrum of **2** in toluene-d_8.

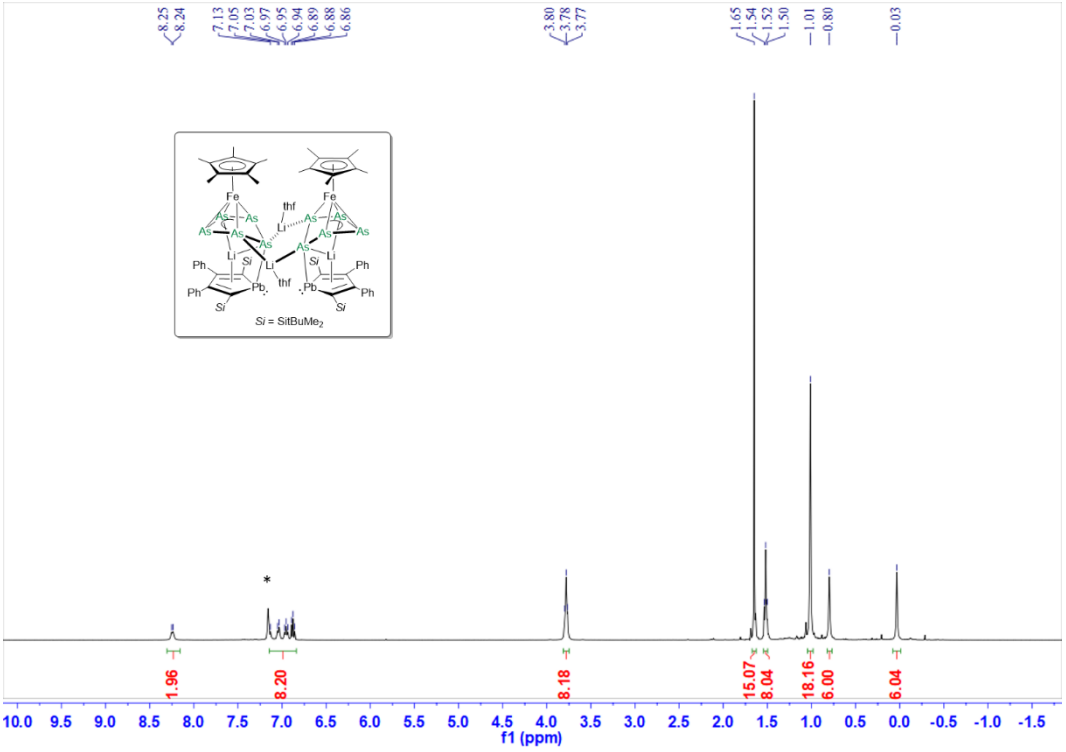


Figure S12. ^{1}H NMR spectrum of **3** in C_6D_6. *, residual protio solvent signal.

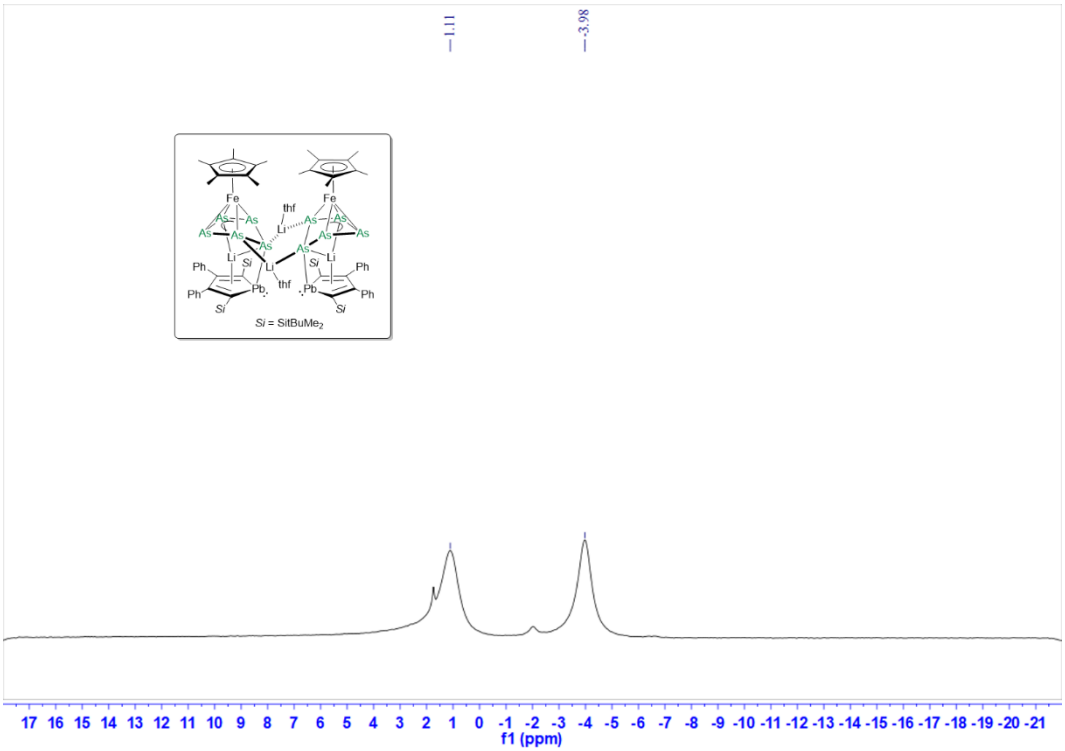


Figure S13. $^{7}Li\{^{1}H\}$ NMR spectrum of **3** in C_6D_6.

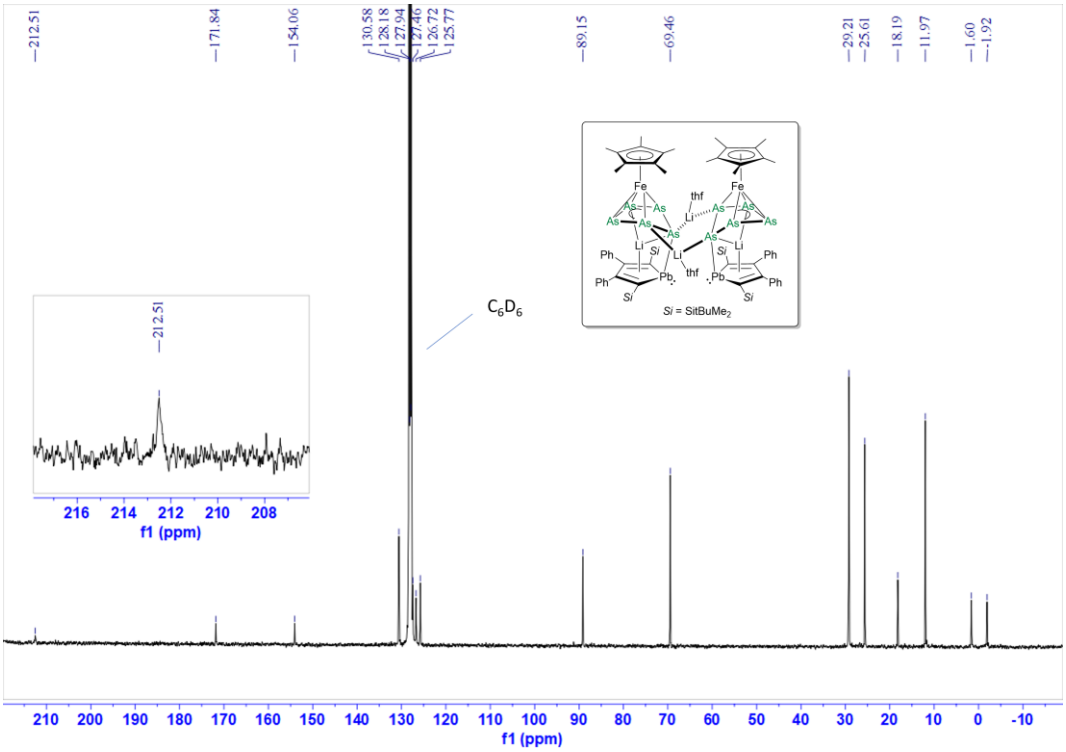


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6.

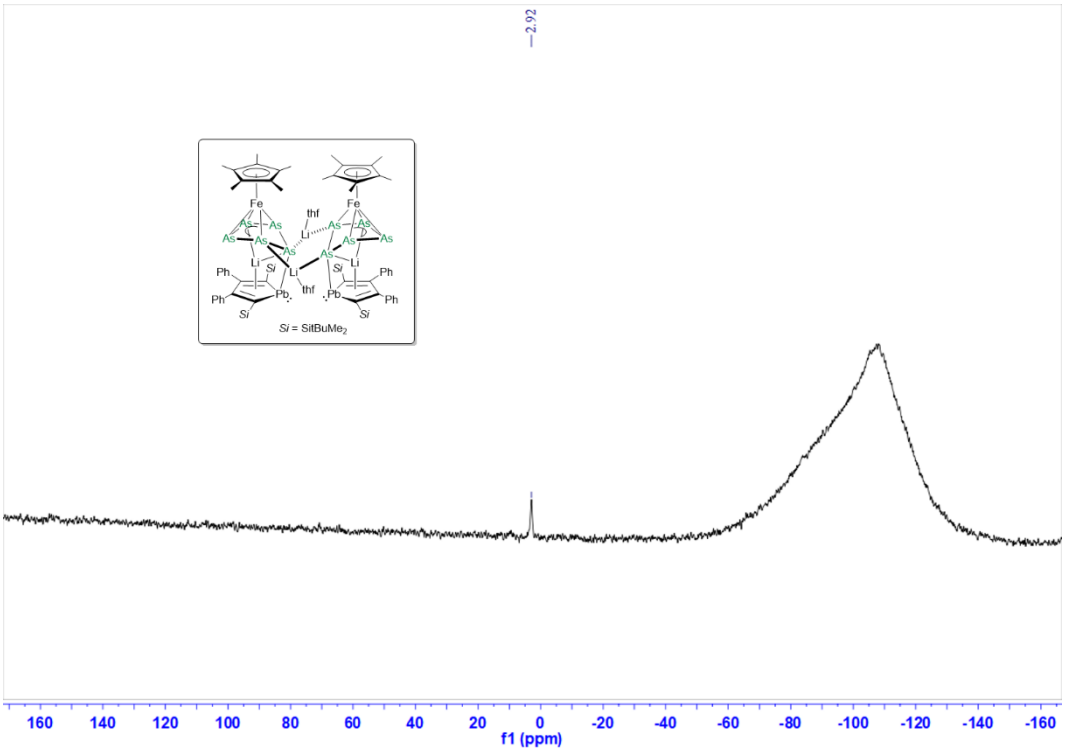


Figure S15. $^{29}Si\{^{1}H\}$ NMR spectrum of **3** in C_6D_6.

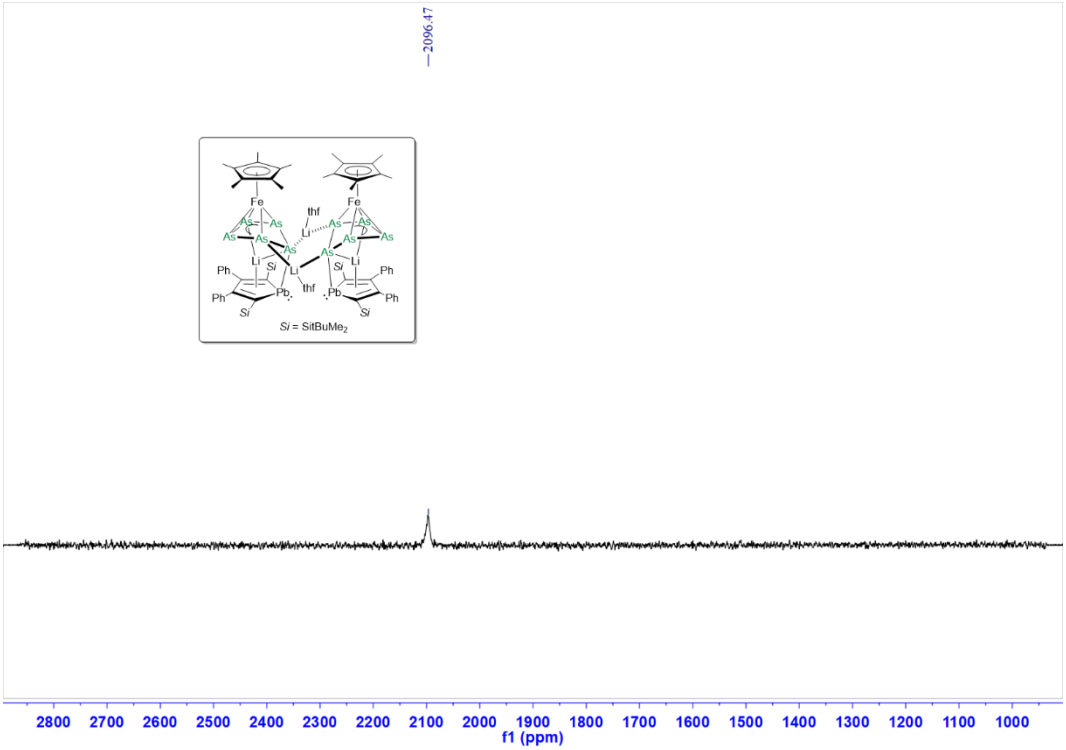


Figure S16. ^{207}Pb NMR spectrum of **3** in C_6D_6.

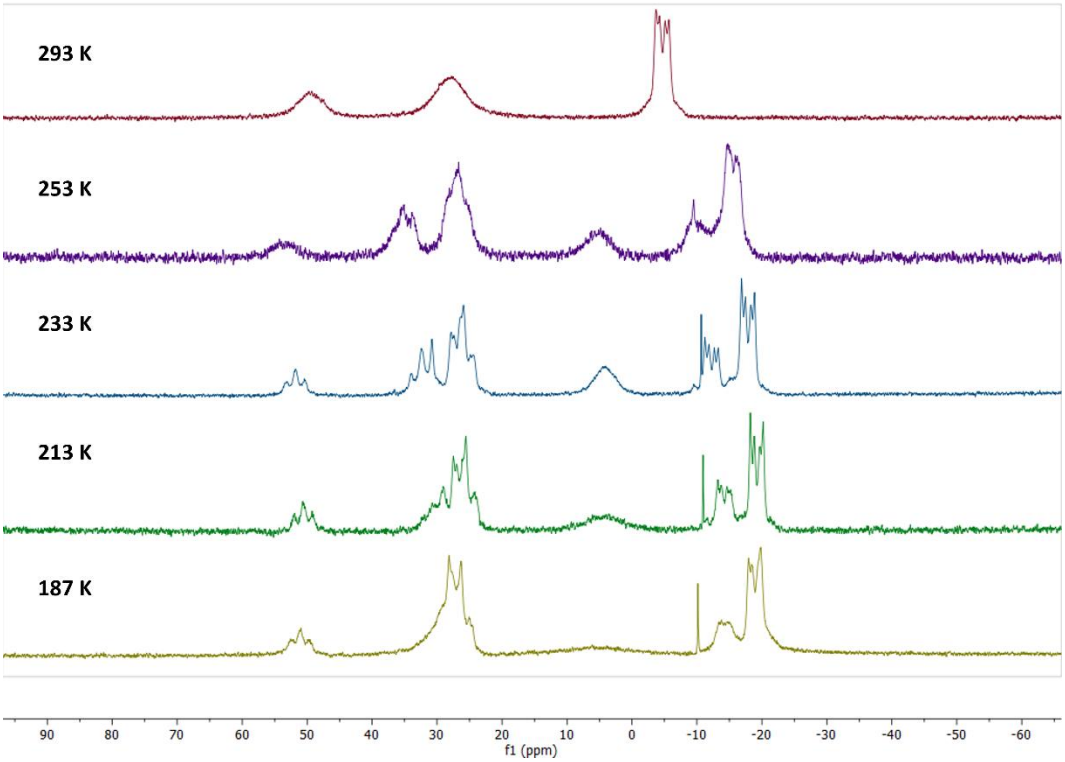


Figure S17. Variable temperature $^{31}P\{^{1}H\}$ NMR (161.98 MHz, toluene-d_8) spectra of complex **2**.

III. IR spectra

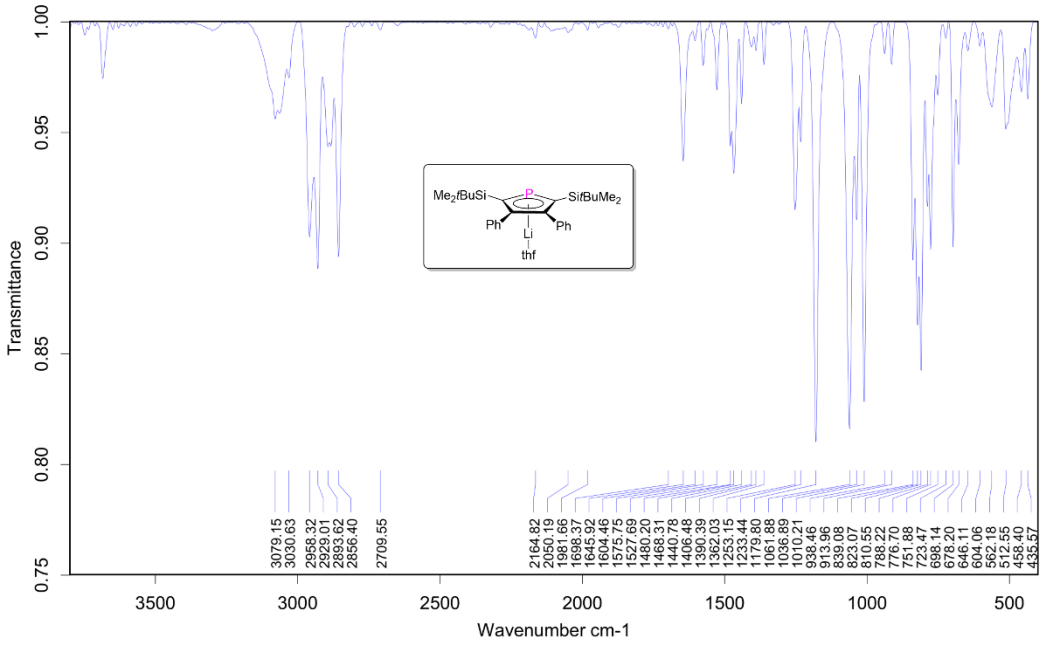


Figure S18. IR spectrum of complex **1**.

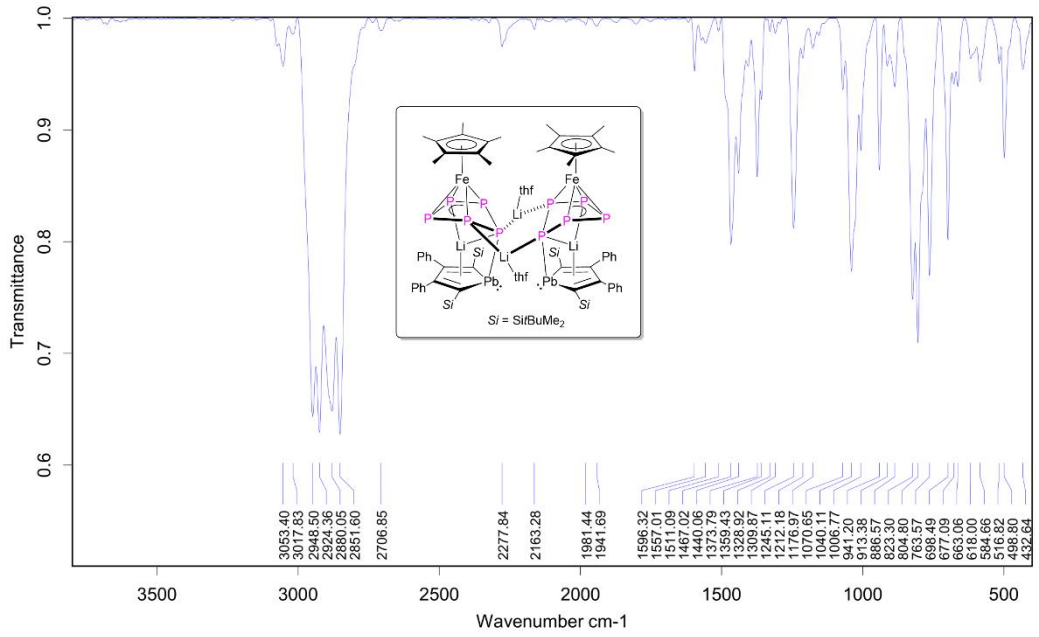


Figure S19. IR spectrum of complex **2**.

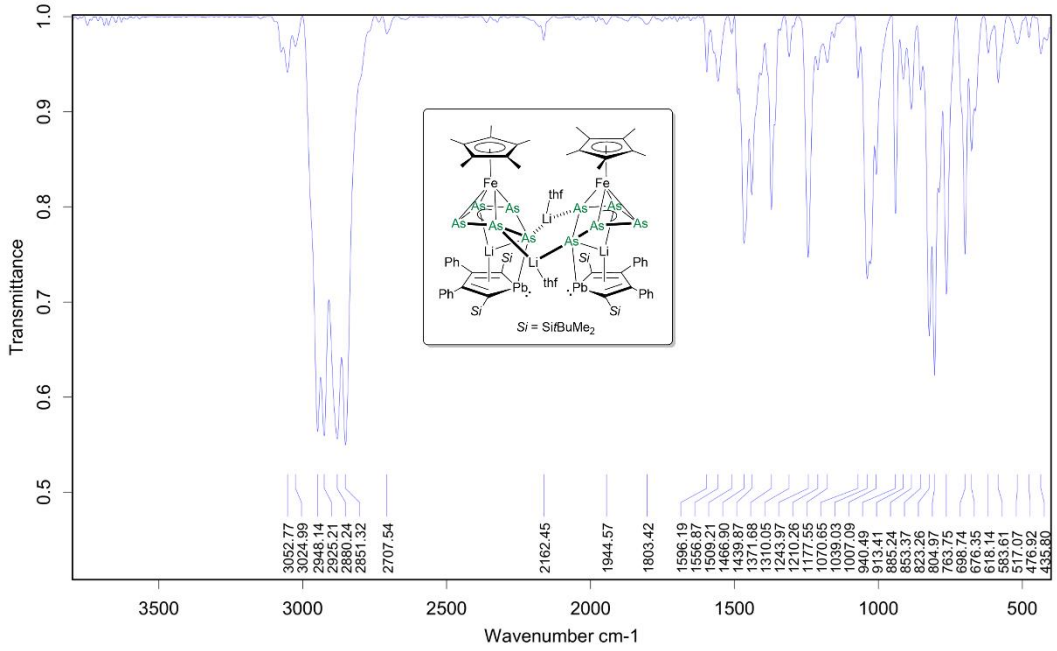


Figure S20. IR spectrum of complex **3**.

IV. X-ray crystallography

IV.1 General methods

Suitable crystals for the X-ray analysis of all compounds were obtained as described above. A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fibre. The crystal was transferred directly to the cold stream of a STOE StadiVari (100 K or 150 K) diffractometer. All structures were solved by using the program SHELXS/T[4,5] and Olex2.[6] The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F^2 by using the program SHELXL.[5,6] The H-atoms were introduced into the geometrically calculated positions (SHELXL procedures) unless otherwise stated and refined riding on the corresponding parent atoms. In each case, the locations of the largest peaks in the final difference Fourier map calculations, as well as the magnitude of the residual electron densities, were of no chemical significance. Specific comments for each data set are given below. Summary of the crystal data, data collection and refinement for compounds are given in Table S1.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC 2119835-2119837. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

<u>The following special comments apply to the models of the structures:</u>

- In the crystal structure of **1**, the coordinated thf molecules (O1, C29-C32 and O2, C61-C64) are disordered over two positions with an occupancy of 0.63/0.37 and 0.71/0.29, respectively.
- In the crystal structure of **3**, two co-crystallized benzene molecules (C91-C96 and C97-C102) are disordered over two positions with an occupancy of 0.60/0.40 and 0.55/0.45, respectively.

IV.2. Summary of crystal data

Compounds	**1**	**2**	**3**
Chemical formula	$C_{32}H_{48}LiOPSi_2$	$C_{102}H_{144}Fe_2Li_4O_2P_{10}Pb_2Si_4$	$C_{102}H_{144}Fe_2Li_4O_2As_{10}Pb_2Si_4$
CCDC Number	2119835	2119836	2119837
Formula Mass	542.79	2378.06	2817.56
Radiation type	MoKα	GaKα	GaKα
Wavelength/Å	0.71073	1.34143	1.34143
Crystal system	monoclinic	monoclinic	monoclinic
a/Å	21.8956(12)	29.2638(11)	26.1239(5)
b/Å	23.8229(9)	13.1463(3)	19.7028(2)
c/Å	12.4303(7)	30.0306(11)	24.2819(5)
α/°			
β/°	99.295(4)	103.390(3)	113.349(2)
γ/°			
Unit cell volume/Å^3	6398.7(6)	11239.0(8)	11474.7(4)
Temperature/K	100	150	150
Space group	$P2_1/c$	$C2/c$	$P2_1/c$
Z	8	4	4
Absorption coefficient μ/mm^{-1}	0.183	6.727	7.736
No. of reflections measured	33188	70727	70573
No. of independent reflections	15740	13492	26475
R_{int}	0.0489	0.0686	0.0257
Final R_1 values ($I > 2\,\sigma(I)$)	0.0639	0.0304	0.0347
Final $wR(F^2)$ values ($I > 2\,\sigma(I)$)	0.1652	0.0487	0.0856
Final R_1 values (all data)	0.0998	0.0684	0.0490
Final $wR(F^2)$ values (all data)	0.1848	0.0533	0.0891
Goodness of fit on F^2	1.025	0.770	1.050

IV.3 Crystal structures

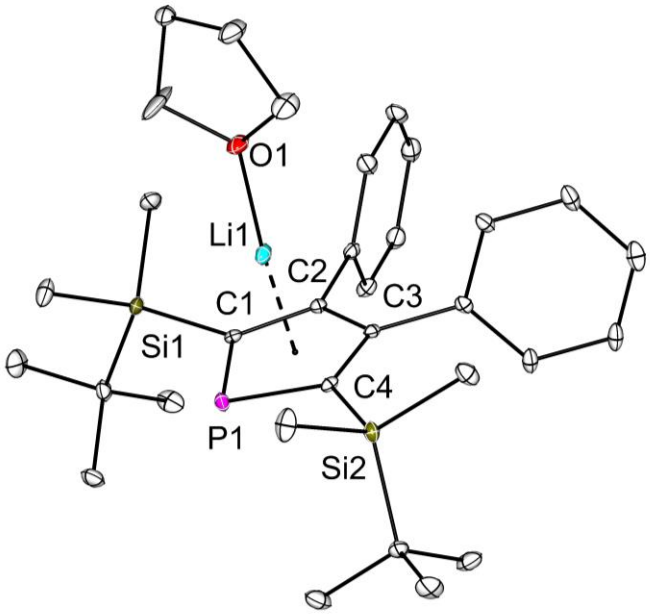


Figure S21. Molecular structure of the complex **1** in the solid state with thermal ellipsoids at the 25% probability level. Non-coordinating solvent molecules and H atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: P1-C1 1.775(2), P1-C4 1.774(2), P1-Li1 2.425(4), C1-Li1 2.235(5), C2-Li1 2.207(5), C3-Li1 2.228(5), C4-Li1 2.294(5), C1-C2 1.423(3), C2-C3 1.418(3), C3-C4 1.425(3); C1-P1-C4 92.63(11), C1-C2-C3 114.3(2), C2-C3-C4 113.3(2), C3-C4-P1 110.1(2), P1-C1-C2 109.6(2). The asymmetric unit of **1** contains two molecules with similar metrical data, only one molecule is displayed here.

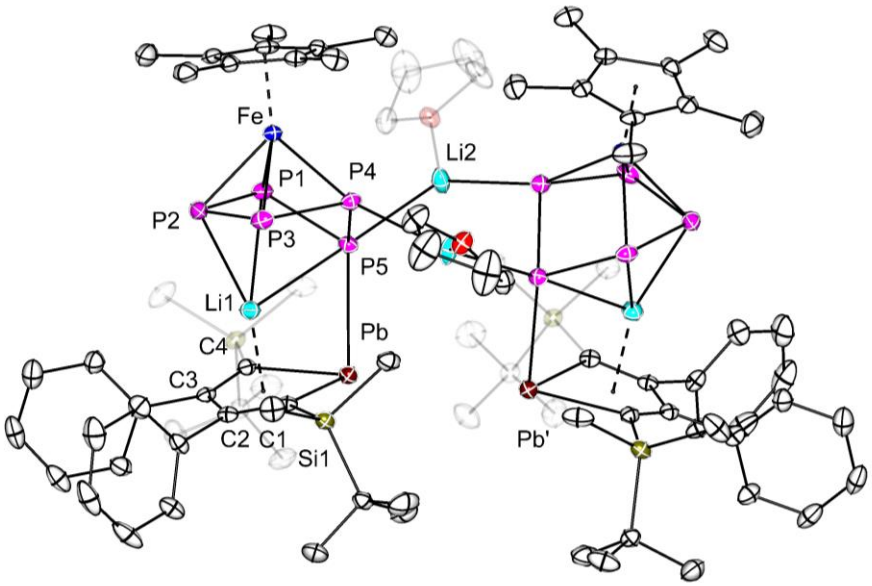


Figure S22. Molecular structure of the complex **2** in the solid state with thermal ellipsoids at the 30% probability level. Non-coordinating solvent molecules and H atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Pb-P5 2.8357(9), Pb-C1 2.345(3), Pb-C4 2.334(3), Pb-Li1 2.794(6), Fe-P1 2.2769(10), Fe-P2 2.3038(10), Fe-P3 2.3363(10), Fe-P4 2.2683(10), P1-P2 2.1950(13), P1-P5 2.1968(12), P2-P3 2.1489(14), P3-P4 2.1788(12), P4-P5 2.1763(12), P2-Li1 2.484(6), P4-Li2 2.592(6), P5-Li1 2.631(6), P5-Li2 2.577(6), C1-C2 1.355(4), C2-C3 1.515(4), C3-C4 1.364(4), C1-Li1 2.261(7), C2-Li1 2.300(6), C3-Li1 2.333(6), C4-Li1 2.337(6); C1-Pb-P5 97.37(9), C4-Pb-P5 89.10(7), C1-Pb-C4 76.51(10), P1-P2-P3 101.35(5), P2-P3-P4 101.35(5), P3-P4-P5 107.93(5), P1-P5-P4 87.01(4), P2-P1-P5 107.90(5).

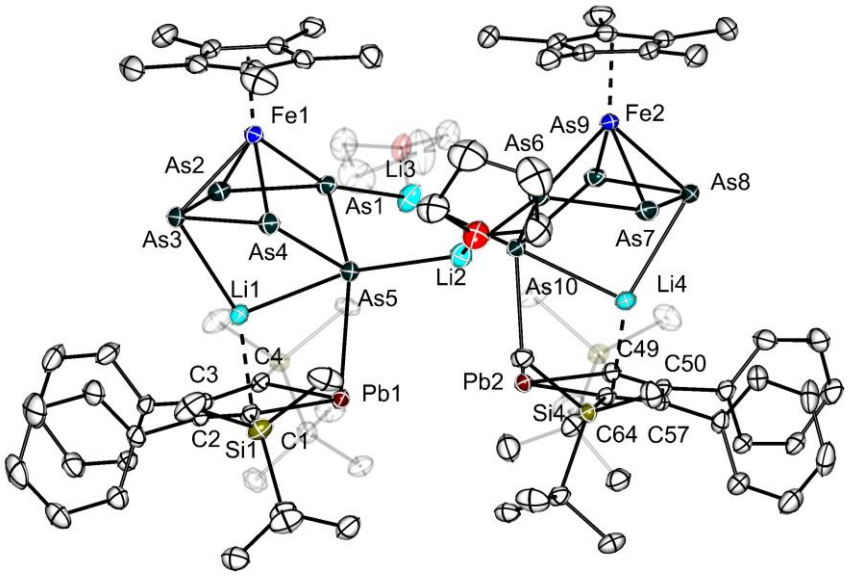


Figure S23. Molecular structure of the complex **3** in the solid state with thermal ellipsoids at the 30% probability level. Non-coordinating solvent molecules and H atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Pb1-As5 2.9171(5), Pb1-C1 2.341(4), Pb1-C4 2.334(4), Pb1-Li1 2.842(6), Pb2-As10 2.9132(4), Pb2-C49 2.334(4), Pb2-C64 2.338(4), Pb2-Li4 2.866(7), Fe1-As1 2.3686(7), Fe1-As2 2.4651(8), Fe1-As3 2.4385(7), Fe1-As4 2.4049(7), Fe2-As6 2.3690(7), Fe2-As7 2.4708(7), Fe2-As8 2.4414(7), Fe2-As9 2.3989(8), As1-As2 2.3983(7), As1-As5 2.3981(6), As2-As3 2.3756(7), As3-As4 2.4037(7), As4-As5 2.4421(6), As6-As7 2.4005(7), As6-As10 2.3952(7), As7-As8 2.3663(8), As8-As9 2.4100(7), As9-As10 2.4326(6), As3-Li1 2.630(6), As5-Li1 2.663(7), As1-Li3 2.632(8), As5-Li2 2.605(8), As6-Li2 2.696(8), As10-Li3 2.582(8), As10-Li4 2.632(7), As8-Li4 2.675(7), C1-C2 1.344(6), C2-C3 1.524(5), C3-C4 1.364(5), C49-C50 1.340(5), C50-C57 1.519(5), C57-C64 1.360(5); C1-Pb1-C4 76.73(13), As1-As2-As3 99.60(2), As2-As3-As4 100.23(2), As3-As4-As5 107.67(2), As1-As5-As4 82.88(2), As2-As1-As5 107.82(2), C49-Pb-C64 76.67(13), As6-As7-As8 100.00(3), As7-As8-As9 100.18(2), As8-As9-As10 108.22(2), As6-As10-As9 83.36(2), As7-As6-As10 108.04(2).

V. Quantum Chemical Calculations

The geometry optimizations were initiated from the coordinates taken from the crystal structure coordinates of complex **2** and complex **3**. All structure optimizations were carried out using the *Gaussian 16, revision C.01*, *package*.[7] The geometry optimizations have been done without any constraints and frequency calculations were also performed on all the optimized geometries to ensure that the optimized geometries did not have any imaginary frequencies.

Geometry optimizations have been carried out using the unrestricted density functional method with dispersion corrected B97D[8] functional. The basis set was DEF2SVP for the arsenic, iron and lead atom and 6-31G** for C, N, O, P, Si, Li and H atoms. The complexes were optimized as a charge neutral species with a spin multiplicity of singlet. NBO calculation were performed to get Wiberg bond order. The QTAIM analysis were performed with the Multiwfn[9] software on wave functions generated with the Gaussian 16 program. NMR shielding tensors were also calculated with the Gauge-Independent Atomic Orbital (GIAO) method at B3LYP level with DEF2TZVP basis set. Calculations revealed the same trend as obtained experimentally. Visualization of the molecular orbitals and the corresponding diagrams were done employing the Chemcraft software.[10]

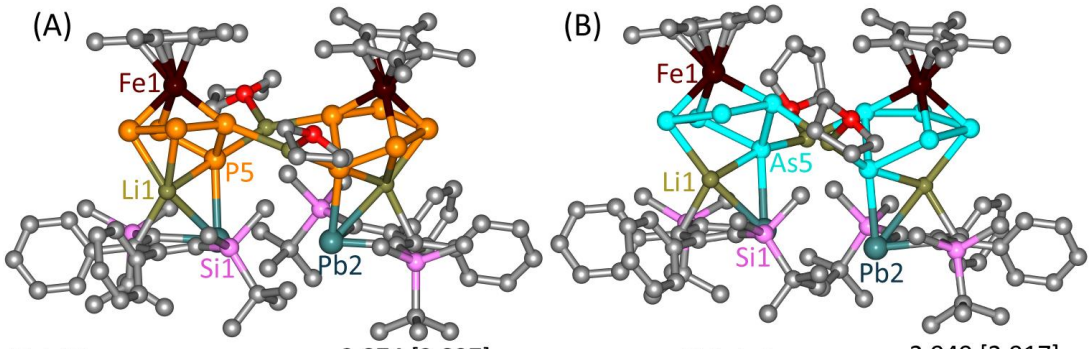


Figure S24. UB97D optimized geometries of (A) complex **2** and (B) complex **3** with bond lengths in Å as calculated using DEF2SVP basis set for arsenic, iron and lead atom and 6-31G** for all other atoms. Parentheses contain the experimental value obtained from the respective X-ray structures. [ΔP_4-P5=Displacement of the P5 atom from the mean plane of P_4 core, P_4-Li1= Displacement of Li1 atom from the mean plane of P_4 core, Displacement of Li1 atom from the mean plane of C_4Pb_1 core].

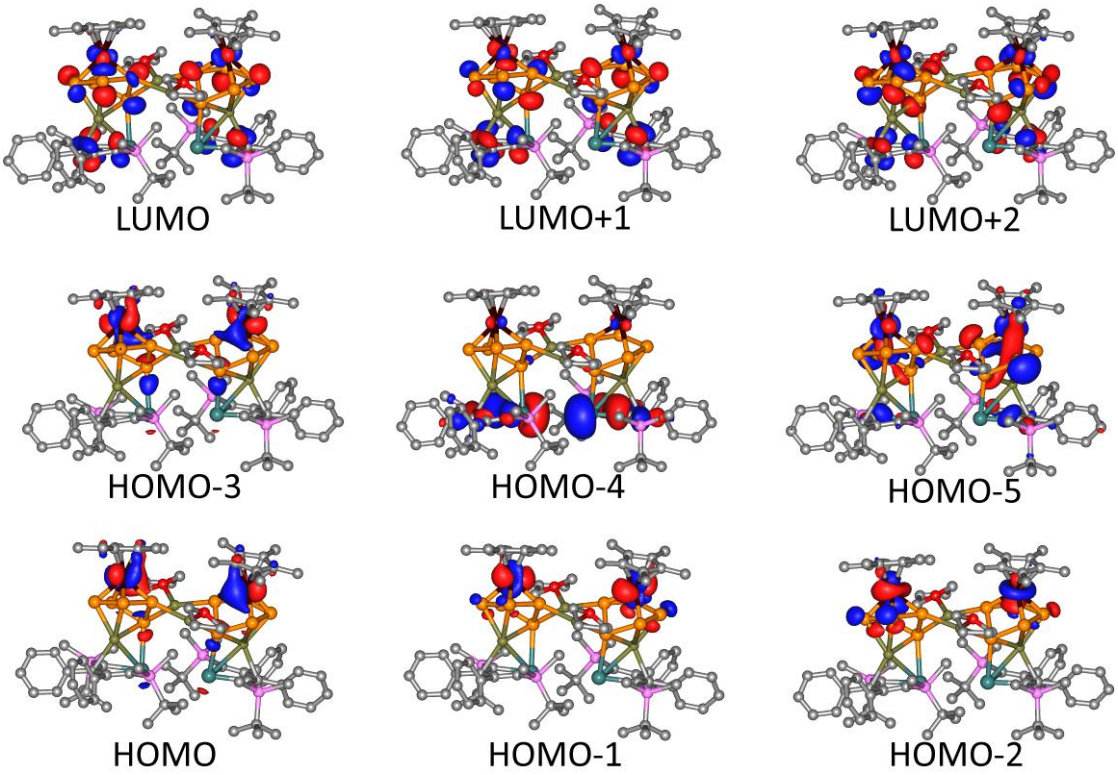


Figure S25. Selected Kohn-Sham orbitals (side view) of B97D/6-31G**/DEF2SVP optimized geometry of complex **2**.

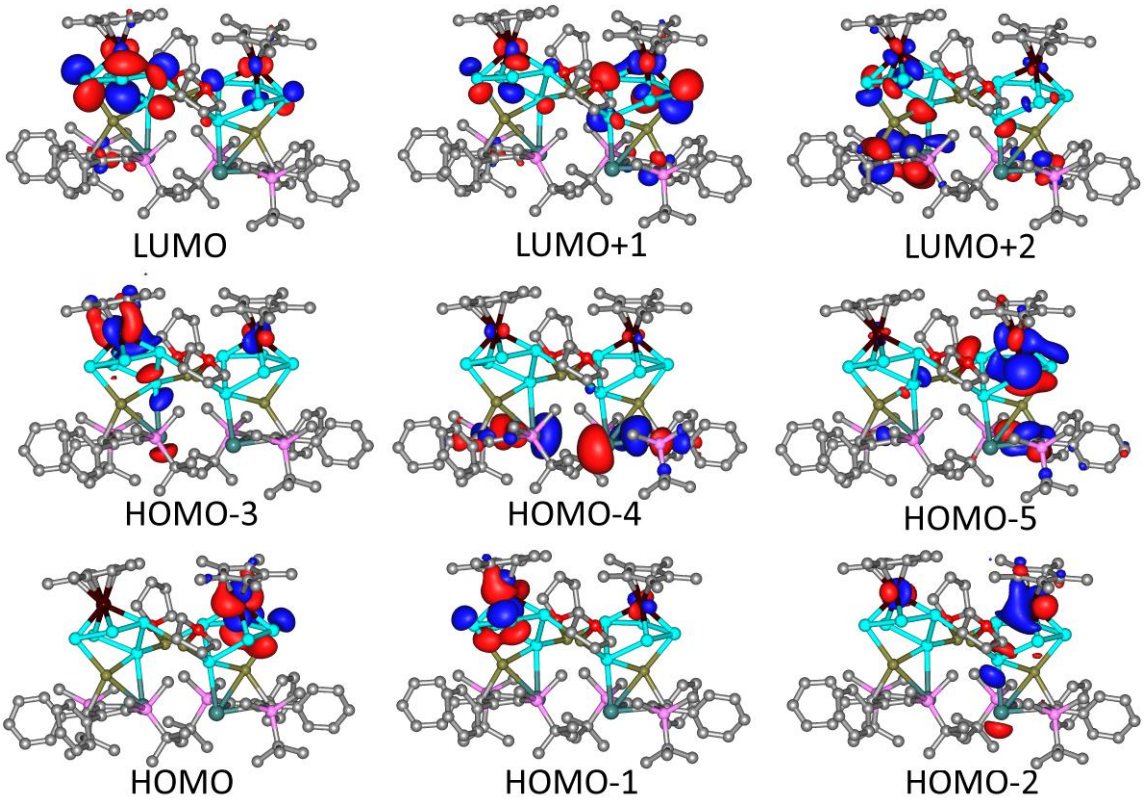


Figure S26. Selected Kohn-Sham orbitals (side view) of B97D/6-31G**/DEF2SVP optimized geometry of complex **3**.

VI. Cartesian Coordinates of the Optimized Structures

Complex **2** (UB97D/DEF2SVP/6-31G**)

6	3.281649000	-1.762120000	-1.684830000
6	4.615095000	-2.002995000	-1.434463000
6	5.117709000	-2.095008000	-0.006120000
6	4.227492000	-1.964243000	1.036196000
6	1.136604000	-0.140993000	-3.035767000
6	3.577857000	-0.773587000	-4.736666000
6	1.517423000	-3.045717000	-4.001307000
6	0.507574000	-3.533553000	-2.943292000
6	0.744910000	-2.655840000	-5.282909000
6	2.491804000	-4.196448000	-4.326069000
6	5.636085000	-2.038758000	-2.531729000
6	5.736108000	-3.136090000	-3.405437000
6	6.660164000	-3.126537000	-4.461002000
6	7.496786000	-2.015638000	-4.654325000
6	7.413183000	-0.921457000	-3.776964000
6	6.496111000	-0.937721000	-2.718278000
6	6.591549000	-2.283174000	0.182935000
6	7.236311000	-3.451644000	-0.274622000
6	8.615570000	-3.622432000	-0.098734000
6	9.378008000	-2.617853000	0.521540000
6	8.748621000	-1.444529000	0.965779000
6	7.365532000	-1.279911000	0.797009000
6	2.976940000	-1.466282000	3.781997000
6	6.040794000	-1.449010000	3.709034000
6	4.474255000	-4.129101000	3.238953000
6	3.350089000	-4.805627000	2.425008000
6	5.828600000	-4.757411000	2.847637000
6	4.218300000	-4.366896000	4.743753000
6	3.192846000	5.541448000	-0.096842000
6	4.629971000	5.459083000	0.004497000
6	4.959506000	5.131451000	1.366116000
6	3.735024000	5.008009000	2.104891000
6	2.639827000	5.251620000	1.208730000
6	2.411620000	5.900165000	-1.327004000
6	5.619457000	5.701391000	-1.098098000
6	6.336076000	4.964572000	1.940892000
6	3.633626000	4.746172000	3.579007000
6	1.189324000	5.281541000	1.584540000
6	-1.322135000	1.959232000	-4.639697000
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6	0.693642000	2.297000000	-5.883626000
6	0.821320000	3.027900000	-4.540620000
26	3.722226000	3.635695000	0.481215000
3	4.082096000	-0.016632000	-0.363267000
3	0.064531000	1.750480000	-2.097035000
8	-0.363597000	2.648004000	-3.773488000
15	2.106246000	2.436049000	-0.590657000
15	4.120665000	2.475670000	-1.538983000
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15	3.901187000	1.756973000	1.816552000
15	2.058380000	0.849241000	0.934847000
82	2.013475000	-1.949719000	0.284446000
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6	-5.729337000	-3.129289000	3.411861000
6	-6.647598000	-3.115927000	4.472935000
6	-7.479660000	-2.002218000	4.669877000
6	-7.396657000	-0.909080000	3.790933000
6	-6.484596000	-0.928593000	2.727919000
6	-6.598825000	-2.269584000	-0.175663000
6	-7.249236000	-3.432196000	0.288746000
6	-8.628851000	-3.598568000	0.111807000
6	-9.385657000	-2.595407000	-0.517066000
6	-8.750932000	-1.427118000	-0.966664000
6	-7.367669000	-1.266654000	-0.796064000
6	-2.996940000	-1.455367000	-3.788041000
6	-6.060346000	-1.428261000	-3.707044000
6	-4.505898000	-4.112895000	-3.247505000
6	-3.372479000	-4.794906000	-2.451074000
6	-5.857160000	-4.738269000	-2.839755000
6	-4.271460000	-4.346846000	-4.756800000
6	-3.178354000	5.542115000	0.109464000
6	-4.615830000	5.462443000	0.009803000
6	-4.947678000	5.137803000	-1.351928000
6	-3.724289000	5.013435000	-2.092470000
6	-2.627566000	5.253596000	-1.197297000
6	-2.395297000	5.896645000	1.339626000
6	-5.603102000	5.703936000	1.114441000
6	-6.325233000	4.974019000	-1.925140000
6	-3.625235000	4.753452000	-3.567100000
6	-1.177385000	5.280982000	-1.575236000
6	1.321145000	1.952971000	4.643147000
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6	-0.705080000	2.277607000	5.874649000
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26	-3.712265000	3.638373000	-0.471518000
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14	-2.456943000	-1.497686000	3.340977000
14	-4.517744000	-2.199128000	-2.888328000

v

Complex **3** (UB97D/DEF2SVP/6-31G**)

82	2.368391000	-2.423539000	0.357721000
82	-1.655022000	-2.285025000	-0.303365000
33	1.645204000	0.404405000	0.777203000
33	-1.979543000	0.544471000	-0.993753000
33	-2.154422000	2.390408000	0.668496000
33	-4.243800000	1.351033000	-1.816947000
33	-5.821971000	1.326122000	0.153252000
33	1.636145000	2.262239000	-0.909674000
33	3.466895000	1.794158000	1.885742000
33	-4.266828000	1.955837000	1.969210000
33	5.305074000	2.193454000	0.203977000
33	3.967274000	2.373897000	-1.867620000
26	-4.247388000	3.218185000	-0.218402000
26	3.263873000	3.606978000	0.242064000
14	2.840974000	-2.038661000	-3.278444000
14	-2.461876000	-2.060611000	3.286752000
14	4.700320000	-1.956597000	3.054827000
14	-3.864597000	-2.596105000	-3.145406000
8	0.045631000	2.430681000	3.881925000
6	-4.360868000	-2.716614000	1.155807000
6	4.975544000	-2.027022000	-1.271413000
6	3.633529000	-2.060318000	-1.577837000
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6	-3.092320000	-2.338257000	1.542131000
6	-5.440999000	-2.990665000	2.158152000
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6	2.998828000	-1.517763000	3.826979000
6	-3.764537000	-1.576880000	4.594772000
6	2.463265000	5.397784000	-0.369833000
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6	-6.158126000	-3.054759000	-0.654106000
6	1.264637000	-4.365353000	-2.646337000
6	-4.082522000	5.158237000	0.467919000
6	1.361256000	-0.835090000	-3.085740000
6	2.059526000	5.086593000	0.985592000
6	-3.501282000	5.065357000	-0.850118000
6	-0.200434000	-3.775862000	2.941515000
6	5.068470000	-3.802538000	3.558428000
6	9.082878000	-3.028577000	0.262532000
6	3.899188000	5.513945000	-0.391160000
6	6.032895000	-1.974321000	-2.332041000
6	-2.149969000	-4.817707000	4.129715000
6	-2.099191000	5.431075000	-1.238688000
6	-7.418265000	-3.445244000	4.122284000
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6	-5.384777000	-1.887117000	-4.057163000
6	3.251088000	5.046837000	1.793954000
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6	6.781110000	-0.796406000	-2.529821000
6	-6.733363000	-4.295034000	-0.305390000
6	0.656153000	4.935951000	1.491521000
6	6.554424000	-4.141773000	3.313210000
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6	4.748622000	5.857876000	-1.580007000
6	8.900971000	-0.860169000	1.337141000
6	4.379745000	5.309642000	0.947664000
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6	3.221128000	-4.756331000	-4.161655000
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6	-7.072620000	4.103154000	-1.612106000
6	-4.820875000	-5.304235000	-3.019660000
6	-6.959130000	-2.100567000	-1.309943000
6	9.686833000	-1.949023000	0.929230000
6	7.248965000	-3.020252000	-4.172884000
6	-6.482755000	4.792418000	1.472084000
6	-0.274557000	1.403444000	6.037563000
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6	4.748030000	-3.994477000	5.057376000
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6	3.299452000	4.865167000	3.283458000
6	-8.296836000	-2.382682000	-1.625405000
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6	-2.337112000	-1.696180000	-3.877100000
3	4.023119000	-0.086963000	-0.338258000
6	-1.274538000	2.839476000	-4.210635000
6	5.805905000	5.417874000	1.404941000
3	-3.991457000	-0.592559000	0.293635000
6	-1.596083000	2.046765000	5.528322000
6	0.629940000	3.713210000	-5.357968000
6	-0.464307000	4.131538000	-4.354719000
3	-0.284335000	1.373257000	2.289430000

VI. References

1. Scherer, O. J.; Brück, T., [(η^5-P_5)Fe(η^5-C_5Me_5)], a Pentaphosphaferrocene Derivative. *Angew. Chem. Int. Ed*. **1987**, *26*, 59-59.

2. Scherer, O. J.; Blath, C.; Wolmershäuser, G. Ferrocene mit einem Pentaarsacyclopentadienyl-Liganden. *J. Organomet. Chem*. **1990**, *C21,* 387.

3. Saito, M.; Nakada, M.; Kuwabara, T.;Minoura, M. A Reversible Two-Electron Redox System Involving a Divalent Lead Species. *Chem. Commun.* **2015**, *51*, 4674−4676.

4. Sheldrick, G. A short history of SHELX. *Acta Cryst. A* **2008**, *64*, 112-122.

5. Sheldrick, G. Crystal structure refinement with SHELXL. *Acta Cryst. C* **2015**, *71*, 3-8.

6. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr*. **2009**, *42*, 339-341.

7. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16 Rev. C.01*, Wallingford, CT, 2016.

8. S. Grimme, Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* **2006**, *27*, 1787-1799.

9. Lu, T.; Chen, F., Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012,** *33*, 580-592.

10. *http://www.chemcraftprog.com*.