Electronic Supplementary Information for:

PNacPNacE: (E = Ga, In, Tl) - monomeric group 13 metal(I) heterocycles stabilized by a sterically demanding bis(iminophosphoranyl)methanide

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1. Experimental Section

1.1 General considerations

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Toluene, tetrahydrofuran and *n*-hexane were dried and distilled over molten potassium or taken from an MBraun solvent purification system and degassed prior to use. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker DPX 300, Bruker Avance 400 or Bruker Avance III 500 spectrometer in deuterated benzene and were referenced to the residual ^{1}H or ^{13}C{^{1}H} resonances of the solvent used, or external aqueous H_3PO_4 solutions, respectively. IR spectra were recorded using a Perkin Elmer RXI FT-IR spectrometer as Nujol mulls between NaCl plates, or on neat solids using an Agilent Cary 630 ATR FTIR or a Perkin Elmer Spectrum GX IR (ATR) spectrometer. Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected. Elemental analyses were performed by Stephen Boyer from the Elemental Analysis Service at London Metropolitan University. The syntheses of LH,[S1] $LAlMe_2$[S2] and "GaI"[S3] were performed as previously described. The alkali metal complexes LM (M = Li, Na, K) and solvates were reported previously;[S4] further information on obtaining LNa is given below. All other reagents were used as received from commercial sources. Abbreviations: br = broad, vbr = very broad, m = multiplet.

1.2 Syntheses

LNa: A mixture of LH ($H_2C(Ph_2PNDip)_2$) (3.94 g, 5.37 mmol, 1.0 eq) and [Na{$N(SiMe_3)_2$}] (0.984 g, 5.37 mmol, 1.0 eq) was cooled to 0°C and toluene (50 mL) was added. The reaction mixture was left to warm to room temperature over the course of 4 h and stirred at this temperature for a further 12 h. All volatiles were removed and *n*-hexane (30 mL) was added to the residue, stirred briefly, and solid LNa was collected by filtration and dried under vacuum. Yield: 3.67 g (90%); mp: 278-280°C (melts); ^{1}H NMR (400.3 MHz, C_6D_6, 296 K): δ 1.01 (d, $J_{H\text{-}H}$ = 6.8 Hz, 24H, $CH(CH_3)_2$), 2.07 (s, 1H, P_2CH), 3.90 (sept, $J_{H\text{-}H}$ = 6.8 Hz, 4H, $CH(CH_3)_2$), 6.94-7.14 (m, 18H, Ar-*H*), 7.63-7.82 (m, 8H, Ar-*H*); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 296 K): δ 24.4 ($CH(CH_3)_2$), 25.3 (tr, $J_{C\text{-}P}$ = 145 Hz, P_2CH), 27.9 ($CH(CH_3)_2$), 120.0 (Ar-*C*), 123.6 (Ar-*C*), 127.2 (vtr, $J_{C\text{-}P}$ = 5.0 Hz), 129.0 (Ar-*C*), 132.0 (vtr, $J_{C\text{-}P}$ = 4.5 Hz), 139.8 (d, $J_{C\text{-}P}$ = 97.7 Hz), 143.3 (vtr, $J_{C\text{-}P}$ = 2.6 Hz), 147.2 (vtr, $J_{C\text{-}P}$ = 3.7 Hz); ^{31}P{^{1}H} NMR (162.0 MHz, C_6D_6, 296 K) δ 7.8 (s); IR (ATR), ν~/cm^{-1}: 3053w, 2957m, 2866w, 1585w, 1422m, 1429s, 1418s, 1343m, 1323s, 1273s, 1215m, 1101s, 1047m, 995s, 976m, 772m, 760s, 745s, 731s, 693s, 517s, 500s; elemental analysis (%) for $C_{49}H_{55}N_2NaP_2$ (756.91 g·mol^{-1}): calcd: C 77.75, H 7.32, N 3.70; found: C 77.49, H 7.18, N 3.86.

LGa: (1): Toluene (40 mL) was added to a mixture of LNa (0.500 g, 0.661 mmol, 1.0 eq) and "GaI" (0.136 g, 0.694 mmol, 1.05 eq) at -60°C. The slurry was vigorously stirred with slow warming to room temperature for 16 h, further stirred for 24 h at room temperature and filtered. Concentrating the yellow solution to *ca.* 4 mL caused white $LGaI_2$ **4** to precipitate (*ca.* 30 mg, 4%, based on LNa. Please see below for data of **4**) which was collected using filtration. White/colourless LGa: **1** precipitated upon the addition of *n*-hexane (*ca*. 15 mL) to the filtrate. The solid was collected, washed with *n*-hexane (5 mL) and the residue was dried under vacuum. Yield: 0.197 g (37%). The isolated yields often varied between 20-30%. The crude product and some crystalline crops from other preparations typically contained small quantities of $LGaI_2$ **4** and LH as impurities. The NMR spectra for LGa: **1** show some broad features that sharpen at elevated temperature and ^{1}H NMR spectroscopic data is given for two temperatures. Mainly, the very broad resonance at *ca.* 1.0 ppm sharpens to a resolved doublet whereas the septet is sharp over the whole investigated range (30-65°C). Mp: 233-237°C (decomp., then black at 251-253°C); ^{1}H NMR (C_6D_6, 300.1 MHz, 303 K): δ 1.03 (vbr, 24H, CH(CH_3)$_2$), 1.66 (s, 1H, P_2CH), 3.85 (sept, $J_{H\text{-}H}$ = 6.8 Hz, 4H, CH(CH_3)$_2$), 6.85-7.17 (m, 18H, Ar-H), 7.56-7.70 (m, 8H, Ar-H); ^{1}H NMR (C_6D_6, 300.1 MHz, 338 K): δ 1.02 (d, br, $J_{H\text{-}H} \approx$ 6.3 Hz, 24H, CH(CH_3)$_2$), 1.65 (s, 1H, P_2CH), 3.86 (sept, $J_{H\text{-}H}$ = 6.8 Hz, 4H, CH(CH_3)$_2$), 6.80-7.18 (m, 18H, Ar-H), 7.55-7.69 (m, 8H, Ar-H); ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 338 K): δ 17.2 (tr, $J_{C\text{-}P}$ = 145 Hz, P_2CH), 25.2 (br, CH(CH_3)$_2$), 29.0 (CH(CH_3)$_2$), 124.1 (vtr, not resolved, Ar-C), 124.9 (tr, $J_{C\text{-}P}$ = 1.5 Hz, Ar-C), 127.8 (partially hidden by solvent resonance, Ar-C), 130.3 (Ar-C), 133.0 (vtr, $J_{C\text{-}P$ = 4.9 Hz, Ar-C), 136.8 (dd, $J_{C\text{-}P$ = 94.7, 1.8 Hz, Ar-C), 141.7 (vtr, $J_{C\text{-}P$ = 3.9 Hz, Ar-C), 148.3 (vtr, $J_{C\text{-}P$ = 2.7 Hz, Ar-C); ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz, 303 K): δ 20.4 (s); IR (nujol), ν~/cm^{-1}: 1586w, 1477m, 1461s, 1431s, 1388m, 1379m, 1366s, 1313m, 1231s, 1196m, 1101m, 1097m, 1005m, 990s, 983s, 955m, 798m, 777s, 746m, 703m, 692s, 590m.

LIn: (2): THF (*ca.* 40 mL) was added to a mixture of finely powdered InBr (0.135 g, 0.693 mmol, 1.05 eq) and LNa (0.500 g, 0.661 mmol, 1.0 eq) at -60°C. The mixture was vigorously stirred with slow warming to room temperature and stirred for a further 3 h. The yellow solution was filtered and concentrated under reduced pressure to *ca.* 5 mL followed by the addition of *n*-hexane (25 mL). Upon standing, LIn: **2** precipitated, was collected by filtration and washed with *n*-hexane (2 × 5 mL). The filtrate was concentrated to *ca.* 10 mL and stored at -40°C, giving a second crop of colourless to off-white crystalline LIn: **2**. Yield: 0.322 g (57%). The isolated yields often varied between 30-40%. The crude product and some crystalline crops typically contained small quantities of LH and in some cases LM as impurities. Compound **2** is highly sensitive to air and moisture and decomposes in solution to In metal (dark brown precipitate) and LH. In crystalline form, especially

as large crystals, it is significantly more stable. It is recommended to store the compound in a glove box freezer. Mp: 170-175°C (decomp., dark-brown); ^{1}H NMR (C_6D_6, 300.1 MHz, 303 K): δ 1.03 (d, $J_{H\text{-}H}$ = 6.8 Hz, 24H, CH(CH_3)$_2$), 2.20 (s, 1H, P_2CH), 3.88 (sept, $J_{H\text{-}H}$ = 6.8 Hz, 4H, CH(CH_3)$_2$), 6.92-7.16 (m, 18H, Ar-*H*), 7.55-7.78 (m, 8H, Ar-*H*); ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 303 K): δ 21.2 (tr, $J_{C\text{-}P}$ = 142 Hz, P_2*C*H), 25.6 (CH(*C*H_3)$_2$), 28.9 (*C*H(CH_3)$_2$), 123.9 (tr, not resolved, Ar-*C*), 124.2 (tr, not resolved, Ar-*C*), 127.9 (partially hidden by solvent resonance, Ar-*C*), 130.2 (Ar-*C*), 133.0 (vtr, $J_{C\text{-}P}$ = 4.8 Hz, Ar-*C*), 137.1 (dd, $J_{C\text{-}P}$ = 96.0, 2.6 Hz, Ar-*C*), 142.9 (vtr, $J_{C\text{-}P}$ = 4.5 Hz, Ar-*C*), 146.9 (vtr, $J_{C\text{-}P}$ = 2.9 Hz, Ar-*C*); ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz, 303 K): δ 17.0 (s); IR (nujol), ν~/cm^{-1}: 1587w, 1479m, 1461s, 1455s, 1433s, 1378s, 1366s, 1319m, 1305m, 1259m, 1234m, 1208m, 1191m, 1178m, 1098m, 980s, 974s, 950s, 811m, 779m, 770m, 743m, 715m, 694s, 661m, 597m, 581m.

LTl: (3): THF (*ca.* 50 mL) was added to a mixture of finely powdered TlBr (0.165 g, 0.580 mmol, 1.12 eq) and LNa (0.392 g, 0.517 mmol, 1.0 eq) at -80°C. The mixture was vigorously stirred with slow warming to room temperature and further stirred for one day. The reaction mixture was filtered and concentrated to *ca.* 10 mL affording a white precipitate of LTl: **3**. The filtrate was concentrated to *ca.* 5mL and stored at -40°C overnight to yield a second crop of crystalline LTl: **3**. Yield: 0.091g (19%). More LTl: **3** was formed though further crops contained significant quantities of the free iminophosphorane LH. Mp: 200-204°C (decomp., black); ^{1}H NMR (C_6D_6, 300.1 MHz, 303 K): δ 1.04 (d, $J_{H\text{-}H}$ = 6.8 Hz, 24H, CH(CH_3)$_2$), 2.34 (br, 1H, P_2CH), 3.86 (sept, br, $J_{H\text{-}H}$ ≈ 6.3 Hz, 4H, CH(CH_3)$_2$), 6.90-7.19 (m, 18H, Ar-*H*), 7.60-7.72 (m, 8H, Ar-*H*); ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 303 K): δ 25.8 (d, br, $J_{Tl\text{-}C?}$ ≈ 81.7 Hz, CH(*C*H_3)$_2$), 28.6 (d, br, $J_{Tl\text{-}C?}$ ≈ 21.6 Hz, *C*H(CH_3)$_2$), 122.7 (Ar-*C*), 124.0 (Ar-*C*), 127.6 (partially hidden by solvent resonance, Ar-*C*), 130.0 (Ar-*C*), 132.7 (vtr, $J_{C\text{-}P}$ ≈ 4 Hz, Ar-*C*), 138.8 (d, br, $J_{C\text{-}P}$ = 19.9 Hz, Ar-*C*), *ca.* 144 (vbr, weak, Ar-*C* ?), 145.8 (vtr, $J_{C\text{-}P}$ = 3.1 Hz, Ar-*C*). A ^{13}C{^{1}H} NMR spectrum at 125.7 MHz and 295 K shows the methyl and methine ^{13}C NMR resonances as a very broad resonance (*ca.* 25.5 ppm, ranging from *ca.* 24.8-26.2, CH(*C*H_3)$_2$) and a broad resonance (28.2 ppm, *C*H(CH_3)$_2$), respectively. The P_2*C*H resonance was observed here as a broad triplet at 23.7 ppm (tr, br, $J_{C\text{-}P}$ = 140 Hz, P_2*C*H). We were unable to obtain a ^{205}Tl NMR resonance for the complex; likely hindered by coupling and line broadening, similar to attempts for $Ph_2P(NDip)_2Tl$.[S5] ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz, 303 K): δ 11.0 (d, $J_{Tl\text{-}P}$ = 109 Hz); IR (nujol), ν~/cm^{-1}: 1587w, 1481m, 1460s, 1432s, 1378s, 1357s, 1321s, 1307m, 1263s, 1239s, 1213s, 1196s, 1179s, 1098s, 953s, 809m, 802m, 776s, 767s, 741m, 713m, 693s, 658m, 594m, 579m; elemental analysis (%) for $C_{49}H_{55}N_2P_2Tl$ (938.31 g·mol^{-1}): calcd: C 62.72, H 5.91, N 2.99; found: C 62.57, H 5.79, N 3.08.

$LGaI_2$ (4): This product was obtained as a by-product from the above reaction of LM (M = Li, Na, K) with "GaI". In addition, $LGaI_2$ **4** was rapidly formed when one equivalent of LGa: **1** was treated with one equivalent of I_2 in deuterated benzene in a J.Young NMR tube at room temperature. Once crystallised, the complex shows a relatively poor solubility. Selected data for $LGaI_2$ **4**: ^{1}H NMR (C_6D_6, 300.1 MHz, 303 K): δ 0.41 (vbr, 12H, CH(CH_3)$_2$), 1.39 (tr, $J_{H\text{-}P}$ = 2.1 Hz, 1H, P_2C*H*), 1.48 (vbr, 12H, CH(CH_3)$_2$), 4.01 (sept, $J_{H\text{-}H}$ = 6.8 Hz, 4H, C*H*(CH_3)$_2$), 6.85-7.21 (m, 18H, Ar-*H*), 7.60-7.71 (m, 8H, Ar-*H*). At elevated temperature, both isopropyl-CH_3 ^{1}H NMR spectroscopic resonances merge to one very broad resonance: ^{1}H NMR (C_6D_6, 300.1 MHz, 338 K): δ 0.95 (vbr, 24H, CH(CH_3)$_2$), 1.42 (tr, not resolved, 1H, P_2C*H*), 4.00 (sept, $J_{H\text{-}H}$ = 6.8 Hz, 4H, C*H*(CH_3)$_2$), 6.80-7.20 (m, 18H, Ar-*H*), 7.58-7.75 (m, 8H, Ar-*H*); ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 303 K): δ 17.5 (tr, $J_{C\text{-}P}$ = 139 Hz, P_2*C*H), 22.8 (vbr, CH(*C*H_3)$_2$), 29.6 (*C*H(CH_3)$_2$), 30.7 (vbr, CH(*C*H_3)$_2$), 125.5 (tr, not resolved, Ar-*C*), 127.2 (tr, not resolved, Ar-*C*), 128.2 (partially hidden by solvent resonance, Ar-*C*), 131.7 (Ar-*C*), 133.8 (dd, $J_{C\text{-}P}$ = 99.3, 3.1 Hz, Ar-*C*), 135.0 (vtr, $J_{C\text{-}P}$ = 5.1 Hz, Ar-*C*), 138.4 (vtr, $J_{C\text{-}P}$ = 4.2 Hz, Ar-*C*), 150.1 (vtr, $J_{C\text{-}P}$ = 2.4 Hz, Ar-*C*); ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz, 303 K): δ 35.0 (s); IR (nujol), ν~/cm^{-1}: 1588w, 1461s, 1454s, 1434s, 1379s, 1223m, 1178m, 1104s, 1097s, 1010m, 994m, 954s, 934m, 838m, 800m, 794s, 734m, 703m, 692m.

$LAlI_2$ (5): A solution of I_2 (0.80 g, 3.13 mmol, 2.1 eq) in toluene (25 mL) was added dropwise (titration) to a slurry of $LAlMe_2$ (1.18 g, 1.49 mmol, 1.0 eq) in toluene (45 mL) and the decolourization of the iodine can be observed. The decolourization somewhat slows down when approximately half of the solution was added. After all I_2 solution was added, a slight orange-red colour remained and the mixture was vigorously stirred overnight; some precipitate started to form. The reaction mixture was concentrated (*ca.* 20 mL of toluene were removed) and the precipitated product was filtered off and dried under vacuum. (Smaller crops can be obtained from the supernatant toluene solution after some concentration and storing at 4°C, though concentration to small volumes will also result in the precipitation of by-products). Yield: 1.02 g (67%). Once precipitated, the compound shows a low solubility in aromatic solvents. The ^{13}C{^{1}H} NMR spectrum was recorded at elevated temperature to aid dissolution of the complex. Mp: no visible melting or decomposition observed up to 280°C (limit); ^{1}H NMR (C_6D_6, 300.1 MHz, 303 K): δ 0.49 (d, $J_{H\text{-}H}$ = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.54 (d, $J_{H\text{-}H}$ = 6.9 Hz, 12H, CH(CH_3)$_2$), 2.14 (tr, $J_{P\text{-}H}$ = 3.0 Hz, 1H, P_2C*H*), 4.13 (sept, $J_{H\text{-}H}$ = 6.8 Hz, 4H, C*H*(CH_3)$_2$), 6.79-7.23 (m, 18H, Ar-*H*), 7.47-7.58 (m, 8H, Ar-*H*); ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 338 K): δ 18.0 (tr, $J_{C\text{-}P}$ = 130 Hz, P_2*C*H), 22.9 (CH(*C*H_3)$_2$), 29.8 (CH(*C*H_3)$_2$), 30.4 (*C*H(CH_3)$_2$), 125.4 (tr, not resolved, Ar-*C*), 126.9 (tr, not resolved, Ar-*C*), 128.2 (partially hidden by solvent resonance, Ar-*C*), 131.7 (Ar-*C*), 132.4 (dd, $J_{C\text{-}P}$ = 97.2, 2.7 Hz, Ar-*C*), 134.7 (vtr, $J_{C\text{-}P}$ = 5.1 Hz, Ar-*C*), 138.0 (vtr, $J_{C\text{-}P}$ = 4.3 Hz, Ar-*C*), 149.4 (vtr,

$J_{C\text{-}P}$ = 2.6 Hz, Ar-*C*); $^{31}P\{^{1}H\}$ NMR (C_6D_6, 121.5 MHz, 303 K): δ 30.3 (s); IR (ATR), ν~/cm^{-1}: 1462w, 1435m, 1381m, 1312m, 1221m, 1180m, 1161m, 1105s, 1038m, 1011m, 993m, 947s, 849s, 795s, 737s, 708s, 691m, 685s, 563m, 550s; elemental analysis (%) for $C_{49}H_{55}AlI_2N_2P_2$ (1014.71 g·mol^{-1}): calcd: C 58.00, H 5.46, N 2.76; found: C 57.87, H 5.30, N 2.91.

2. X-ray crystallography

Suitable crystals were mounted in silicone oil and were either measured using an Oxford Xcalibur Gemini Ultra diffractometer (**1**, **2**) with $Mo_{K\alpha}$ radiation, or at the MX1 beamline at the Australian Synchrotron[S6] (**3**, **4**) using synchrotron radiation with a wavelength close to $Mo_{K\alpha}$ radiation. Data collection at the synchrotron was performed using the Blu-Ice software package,[S7] and data reduction was performed using XDS.[S8] All structures were refined using SHELX,[S9] and all non-hydrogen atoms were refined anisotropically.

Selected bond lengths and angles of all crystal structures are collected in the main text in Table 1. Crystal data and refinement details are summarized in Table S1. CCDC 1580479-1580482 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/.

The two crystal structure determinations from the synchrotron (**3**, **4**) show a relatively low data completeness due to the experimental constraint that only one phi scan could be collected on the day. High angle diffraction data up to *ca.* theta = 28.5° is available for both structures and was used for the refinement of the structures.

A crystal structure determination of $LAlI_2$ **5** shows it to be isostructural and isomorphous to $LGaI_2$ **4**. Due to poor data quality, only an image is given below in Figure S1.

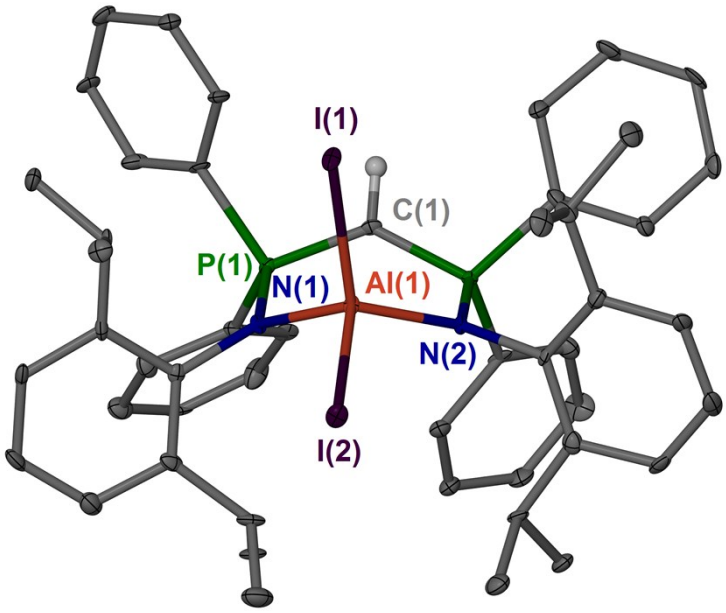

Figure S1. Molecular structure of $LAlI_2$ **5**.

Table S1 Crystallographic data.

Compound reference	LGa: **1**	LIn: **2**	LTl: **3**	$LGaI_2$ **4**
Chemical formula	$C_{49}H_{55}GaN_2P_2$	$C_{49}H_{55}InN_2P_2$	$C_{49}H_{55}N_2P_2Tl$	$C_{49}H_{55}GaI_2N_2P_2$
Formula Mass	803.61	848.71	938.26	1057.41
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	*P*-1	*P*21/n	*P*21/n	*P*-1
a/Å	8.9222(8)	13.3207(7)	13.367(3)	9.4770(19)
b/Å	10.7694(10)	19.7596(11)	19.711(4)	10.759(2)
c/Å	22.723(3)	16.5158(11)	16.535(3)	23.466(5)
α/°	82.923(10)	90	90	89.37(3)
β/°	82.048(10)	107.704(6)	107.83(3)	88.94(3)
γ/°	78.025(8)	90	90	70.95(3)
Unit cell volume/Å^3	2105.3(4)	4141.3(4)	4147.3(16)	2261.2(9)
Temperature/K	123(2)	123(2)	100(2)	100(2)
No. of formula units per unit cell, *Z*	2	4	4	2
Radiation type	$Mo_{K\alpha}$	$Mo_{K\alpha}$	Synchrotron	Synchrotron
Wavelength/Å	0.71073	0.71073	0.7107	0.7107
Density (calc)/ Mg/m^3	1.268	1.361	1.503	1.553
Absorption coefficient, μ/mm^{-1}	0.765	0.685	4.008	2.080
F(000)	848	1768	1896	1060
Reflections collected	14768	22227	54404	20076
Independent reflections	7604	9018	9815	9981
Theta range/°	1.942 to 25.242	2.012 to 26.999	1.656 to 28.610	0.868 to 28.575
Completeness (to theta)/%	99.9 (at 25.24°)	99.9 (at 25.24°)	95.4 (at 25.24°)	90.5 (at 25.24°)
R_{int}	0.0349	0.0246	0.0302	0.0388
Data / restraints / parameter	7604 / 0 / 495	9018 / 0 / 495	9815 / 0 / 495	9981 / 0 / 513
Final R_1 values ($I > 2\sigma(I)$)	0.0730	0.0319	0.0283	0.0618
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.2043	0.0760	0.0798	0.1480
Final R_1 values (all data)	0.0964	0.0417	0.0292	0.0650
Final $wR(F^2)$ values (all data)	0.2241	0.0816	0.0805	0.1496
Goodness of fit on F^2	1.032	1.052	1.047	1.089
Largest diff. peak and hole/e·Å^{-3}	1.247 and -1.500	0.617, -0.494	0.588, -3.196	2.176, -1.843
CCDC number	1580479	1580482	1580481	1580480

3. Computational studies

Computations using density functional theory were carried out at the pbe0[S10]/def2-tzvp (E,N,P, C(1)) + def2-svp[S11] (all other atoms) level of theory using G09 D.01.[S12] Basis sets were obtained from the Basis Set Exchange.[S13] All computations were carried out on the full molecules LE: (E = Al, Ga, In, Tl) with their solid state structures as starting points. The molecules were optimized in their singlet states. That a local minimum had been obtained was tested using normal mode analysis. Natural bond order analyses were carried out using NBO6.[S14] Results are summarised in Table 2 in the main text. All energies are in Hartree/particle (section 3.2).

3.1 Selected molecular orbitals for LE: (E = Al, Ga, In, Tl) at pbe0/def2-tzvp+def2-svp level of theory (isovalue = 0.04 e/Å^3)

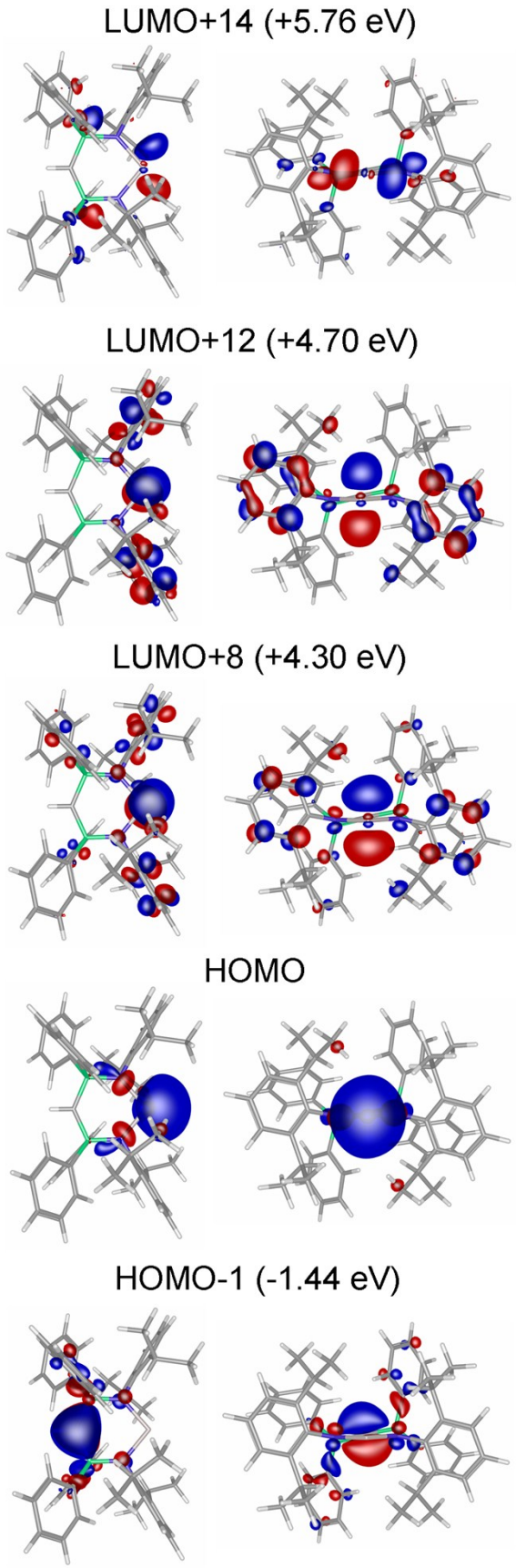

Figure S2. LAl:, two views (*cf.* Fig. 3 in the main text).

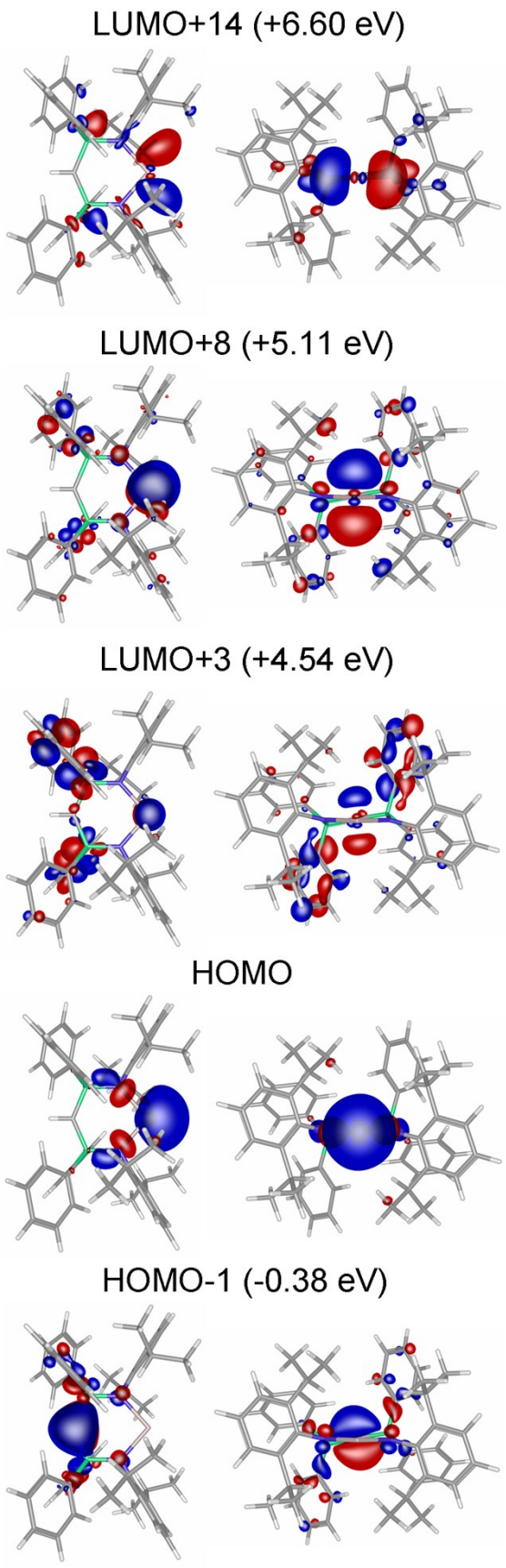

Figure S3. LGa: **1**, two views (*cf.* Fig. 3 in the main text).

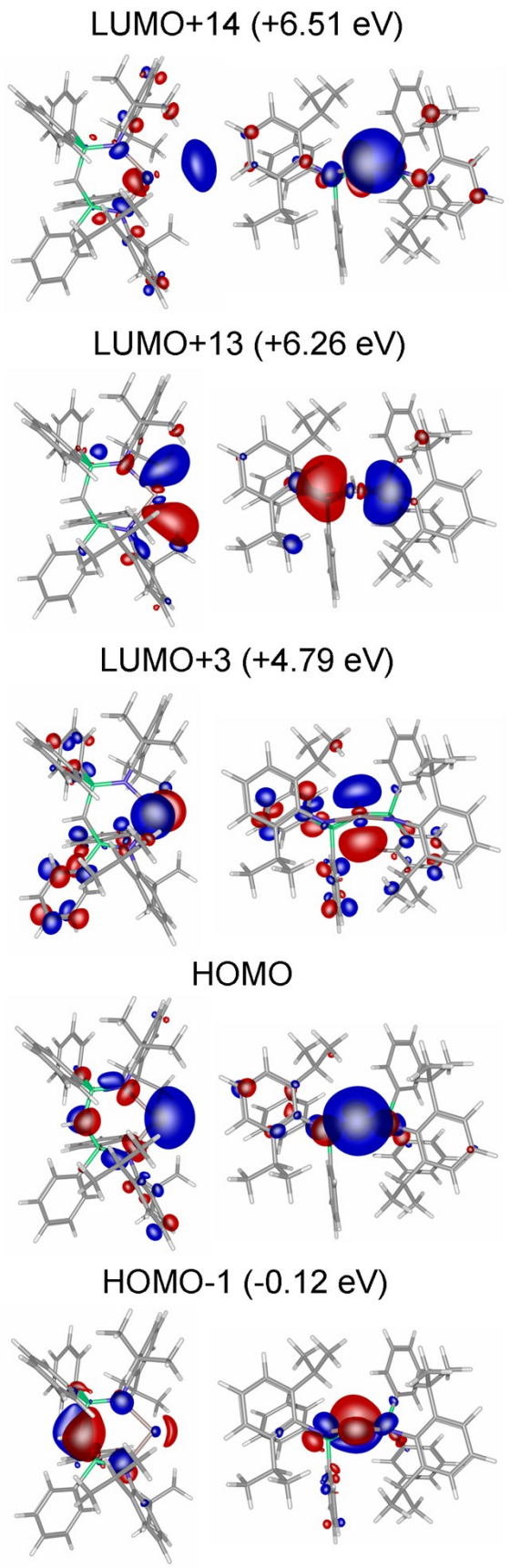

Figure S4. LIn: **2**, two views (*cf.* Fig. 3 in the main text).

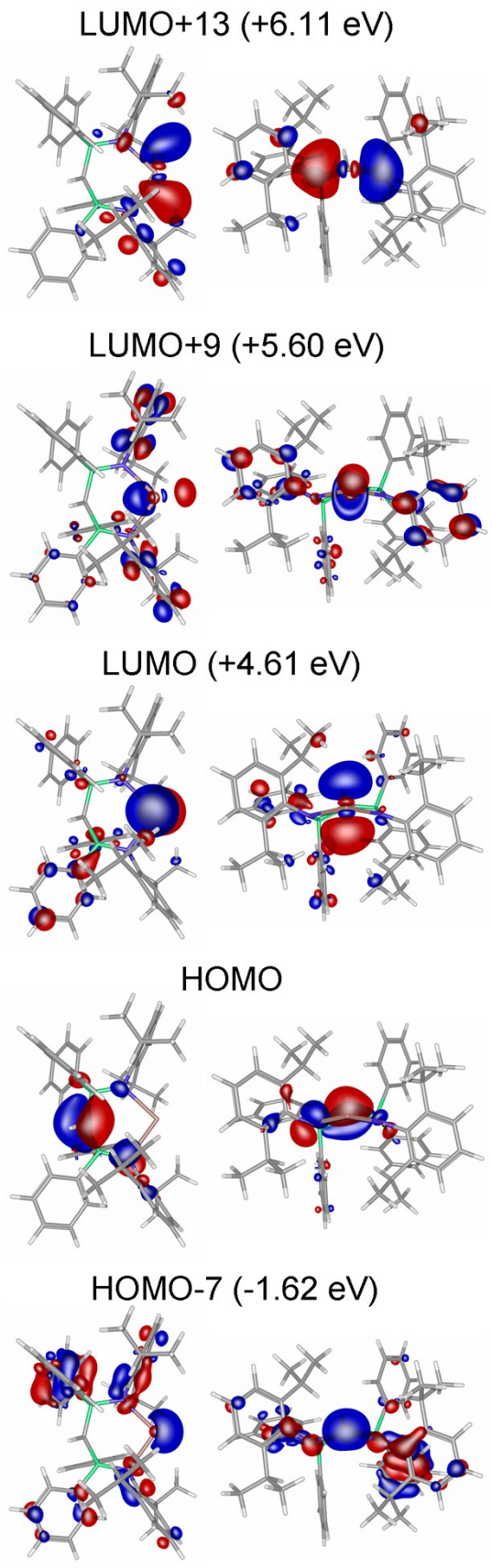

Figure S5. LTl: **3**, two views (*cf.* Fig. 3 in the main text).

3.2 Atomic coordinates for optimized geometries

LAl:

109, -2931.05476563 Hartree

Al	0.00006	-0.00000	1.99309
P	1.52487	0.28643	-0.89604
N	1.50944	0.01204	0.71637
C	-0.00003	0.00010	-1.58506
H	-0.00006	0.00017	-2.67124
P	-1.52487	-0.28635	-0.89597
N	-1.50938	-0.01202	0.71645
C	1.99839	2.00887	-1.30149
C	1.24183	3.02563	-0.69984
H	0.46740	2.76344	0.02539
C	1.45738	4.36105	-1.01870
H	0.86261	5.13814	-0.53198
C	2.42813	4.70622	-1.96238
H	2.59878	5.75534	-2.21611
C	3.17043	3.70581	-2.58282
H	3.92390	3.96537	-3.33065
C	2.95708	2.36418	-2.25689
H	3.54092	1.59438	-2.76370
C	2.78570	-0.70404	-1.75634
C	2.39555	-1.67139	-2.68919
H	1.33112	-1.83922	-2.86856
C	3.35232	-2.42096	-3.37274
H	3.03470	-3.16980	-4.10232
C	4.70819	-2.21743	-3.12267
H	5.45845	-2.80431	-3.65848
C	5.10634	-1.26944	-2.17875
H	6.16725	-1.11631	-1.96747
C	4.15285	-0.51616	-1.49813
H	4.47647	0.22107	-0.75987
C	-1.99838	-2.00880	-1.30142
C	-1.24186	-3.02557	-0.69974
H	-0.46745	-2.76339	0.02553
C	-1.45742	-4.36099	-1.01860
H	-0.86267	-5.13808	-0.53186
C	-2.42814	-4.70614	-1.96231
H	-2.59879	-5.75527	-2.21604
C	-3.17041	-3.70573	-2.58276
H	-3.92387	-3.96529	-3.33061
C	-2.95706	-2.36410	-2.25683
H	-3.54088	-1.59430	-2.76365
C	-2.78579	0.70409	-1.75618
C	-4.15292	0.51610	-1.49794
H	-4.47646	-0.22122	-0.75972
C	-5.10649	1.26936	-2.17846
H	-6.16738	1.11615	-1.96715
C	-4.70844	2.21745	-3.12232
H	-5.45876	2.80432	-3.65806
C	-3.35259	2.42108	-3.37243
H	-3.03505	3.17001	-4.10197
C	-2.39574	1.67153	-2.68898
H	-1.33134	1.83946	-2.86836
C	2.74444	-0.27734	1.39689
C	3.19349	-1.62263	1.47208
C	4.39025	-1.90181	2.13668
H	4.74118	-2.93480	2.19287
C	5.13954	-0.89559	2.73451
H	6.07619	-1.13345	3.24495
C	4.67132	0.40964	2.69854
H	5.24054	1.19769	3.19858
C	3.47495	0.74367	2.05173
C	2.38056	-2.77902	0.91541
H	1.67837	-2.35708	0.18162
C	1.55275	-3.42614	2.02988
H	0.93563	-4.25084	1.63647
H	0.88436	-2.69476	2.51609
H	2.20695	-3.84003	2.81405
C	3.22022	-3.82647	0.18705
H	3.87158	-4.38639	0.87686
H	3.85438	-3.37126	-0.58700
H	2.56361	-4.56330	-0.30212
C	2.99892	2.18213	2.13753
H	2.06026	2.24625	1.57196
C	2.67910	2.56977	3.58343
H	1.92929	1.88969	4.01577
H	2.27713	3.59495	3.62699
H	3.57748	2.53693	4.22090
C	3.98979	3.16201	1.50854
H	4.95054	3.16857	2.04858
H	3.58886	4.18734	1.53694
H	4.19500	2.91396	0.45621
C	-2.74435	0.27731	1.39703
C	-3.47483	-0.74374	2.05182
C	-4.67121	-0.40977	2.69865
H	-5.24041	-1.19785	3.19864
C	-5.13945	0.89546	2.73468
H	-6.07610	1.13327	3.24514
C	-4.39018	1.90172	2.13689
H	-4.74114	2.93470	2.19312
C	-3.19342	1.62259	1.47227
C	-2.99879	-2.18221	2.13749
H	-2.06013	-2.24626	1.57194
C	-2.67902	-2.57000	3.58336
H	-1.92923	-1.88994	4.01579
H	-2.27703	-3.59517	3.62683
H	-3.57741	-2.53723	4.22081
C	-3.98965	-3.16203	1.50837
H	-4.95041	-3.16865	2.04838
H	-3.58871	-4.18736	1.53667
H	-4.19482	-2.91387	0.45606
C	-2.38052	2.77901	0.91562
H	-1.67827	2.35709	0.18187
C	-1.55279	3.42619	2.03012
H	-2.20704	3.84006	2.81425
H	-0.93571	4.25092	1.63671
H	-0.88438	2.69486	2.51636
C	-3.22020	3.82640	0.18719
H	-3.85430	3.37114	-0.58687
H	-2.56360	4.56325	-0.30197
H	-3.87161	4.38632	0.87696

LGa: 1

109, -4613.33508837 Hartree

Ga	-0.00006	-0.00005	-2.00828
P	-1.53567	0.28461	0.97555
N	-1.56666	0.01770	-0.62726
C	0.00001	-0.00015	1.64348
H	0.00001	-0.00030	2.73044
P	1.53570	-0.28468	0.97549
N	1.56660	-0.01771	-0.62731
C	-2.00003	2.00648	1.40427
C	-1.24394	3.02422	0.80329
H	-0.46940	2.76137	0.07819
C	-1.45830	4.35931	1.12447
H	-0.86351	5.13720	0.63891
C	-2.42683	4.70336	2.07109
H	-2.59582	5.75208	2.32768
C	-3.16811	3.70220	2.69129
H	-3.91944	3.96086	3.44165
C	-2.95656	2.36089	2.36178
H	-3.54013	1.59028	2.86785
C	-2.78207	-0.70948	1.85686
C	-2.38066	-1.67829	2.78313
H	-1.31405	-1.84135	2.95409
C	-3.32869	-2.43604	3.46993
H	-3.00213	-3.18583	4.19464
C	-4.68742	-2.23950	3.22942
H	-5.43078	-2.83271	3.76790
C	-5.09702	-1.29033	2.29186
H	-6.16018	-1.14247	2.08807
C	-4.15181	-0.52895	1.60821
H	-4.48479	0.20930	0.87514
C	2.00021	-2.00651	1.40420
C	1.24411	-3.02429	0.80331
H	0.46947	-2.76148	0.07831
C	1.45859	-4.35937	1.12446
H	0.86379	-5.13730	0.63898
C	2.42726	-4.70336	2.07097
H	2.59634	-5.75206	2.32755
C	3.16854	-3.70215	2.69109
H	3.91998	-3.96077	3.44136
C	2.95688	-2.36085	2.36159
H	3.54045	-1.59020	2.86759
C	2.78206	0.70952	1.85674
C	4.15180	0.52915	1.60803
H	4.48484	-0.20906	0.87495
C	5.09696	1.29064	2.29164
H	6.16012	1.14290	2.08781
C	4.68729	2.23976	3.22922
H	5.43060	2.83306	3.76767
C	3.32855	2.43614	3.46978
H	3.00193	3.18590	4.19451
C	2.38057	1.67828	2.78303
H	1.31395	1.84120	2.95403
C	-2.78929	-0.27699	-1.30680
C	-3.22335	-1.62683	-1.40225
C	-4.40734	-1.91375	-2.08619
H	-4.74561	-2.95034	-2.15627
C	-5.16000	-0.91099	-2.68630
H	-6.08647	-1.15498	-3.21213
C	-4.70712	0.39954	-2.63162
H	-5.27886	1.18593	-3.13183
C	-3.52452	0.74043	-1.96426
C	-2.40174	-2.77546	-0.84271
H	-1.70722	-2.34571	-0.10635
C	-1.56140	-3.41611	-1.95169
H	-0.94002	-4.23586	-1.55489
H	-0.89386	-2.68289	-2.43438
H	-2.20592	-3.83500	-2.74119
C	-3.23510	-3.83048	-0.11821
H	-3.88519	-4.39038	-0.80935
H	-3.87016	-3.37982	0.65780
H	-2.57513	-4.56601	0.36849
C	-3.06013	2.18403	-2.02182
H	-2.12870	2.24492	-1.44433
C	-2.73149	2.60274	-3.45705
H	-1.97783	1.93565	-3.90278
H	-2.33385	3.63031	-3.47817
H	-3.62480	2.57894	-4.10203
C	-4.06275	3.14489	-1.38234
H	-5.02309	3.14755	-1.92320
H	-3.67314	4.17498	-1.39499
H	-4.26526	2.87963	-0.33372
C	2.78921	0.27698	-1.30690
C	3.52440	-0.74046	-1.96437
C	4.70700	-0.39959	-2.63175
H	5.27872	-1.18599	-3.13197
C	5.15990	0.91093	-2.68645
H	6.08636	1.15491	-3.21230
C	4.40726	1.91370	-2.08633
H	4.74555	2.95029	-2.15641
C	3.22328	1.62681	-1.40236
C	3.06000	-2.18405	-2.02191
H	2.12860	-2.24494	-1.44437
C	2.73127	-2.60274	-3.45713
H	1.97760	-1.93564	-3.90281
H	2.33362	-3.63031	-3.47824
H	3.62455	-2.57894	-4.10215
C	4.06265	-3.14493	-1.38250
H	5.02295	-3.14761	-1.92342
H	3.67302	-4.17501	-1.39512
H	4.26523	-2.87967	-0.33389
C	2.40171	2.77546	-0.84280
H	1.70721	2.34572	-0.10643
C	1.56137	3.41613	-1.95177
H	2.20589	3.83500	-2.74128
H	0.94003	4.23591	-1.55495
H	0.89379	2.68294	-2.43444
C	3.23511	3.83045	-0.11830
H	3.87016	3.37976	0.65770
H	2.57517	4.56600	0.36840
H	3.88522	4.39033	-0.80944

LIn: 2

109, -2878.87912271 Hartree

In	-0.14479	-0.60326	-2.09221
P	1.53946	-0.18720	1.04363
N	1.58918	-0.18891	-0.57662
C	-0.06220	-0.13574	1.62116
H	-0.16706	-0.57305	2.60524
P	-1.49918	0.46088	0.90799
N	-1.85445	-0.09753	-0.56658
C	2.20767	-1.68741	1.86465
C	1.59393	-2.90953	1.55263
H	0.77926	-2.92824	0.82508
C	2.00057	-4.09050	2.16446
H	1.51417	-5.03392	1.90358
C	3.02356	-4.06732	3.11488
H	3.34310	-4.99316	3.59977
C	3.62802	-2.85835	3.44755
H	4.42044	-2.82986	4.19959
C	3.22309	-1.67430	2.82699
H	3.69903	-0.73401	3.10854
C	2.62440	1.12995	1.69361
C	2.07063	2.13677	2.49021
H	0.99693	2.11799	2.68985
C	2.87458	3.14565	3.02056
H	2.42652	3.92837	3.63768
C	4.24480	3.15135	2.76674
H	4.87746	3.93757	3.18649
C	4.80776	2.15181	1.97138
H	5.88044	2.15515	1.76318
C	4.00442	1.14912	1.43262
H	4.45919	0.37689	0.80827
C	-1.43965	2.28713	0.83794
C	-1.26286	2.97968	-0.36236
H	-1.21165	2.42318	-1.30037
C	-1.16633	4.37272	-0.37142
H	-1.03082	4.90007	-1.31892
C	-1.25430	5.08859	0.81966
H	-1.18832	6.17933	0.81114
C	-1.43274	4.40604	2.02486
H	-1.50855	4.96129	2.96320
C	-1.51782	3.01727	2.03371
H	-1.65565	2.49052	2.98212
C	-2.85053	0.13763	2.07860
C	-4.07498	0.78255	1.85283
H	-4.17293	1.48810	1.02509
C	-5.16689	0.54146	2.68157
H	-6.11458	1.05047	2.49077
C	-5.04977	-0.34621	3.75073
H	-5.90557	-0.53428	4.40371
C	-3.83760	-0.99281	3.98319
H	-3.73858	-1.69017	4.81854
C	-2.74537	-0.75660	3.14907
H	-1.81000	-1.28635	3.33571
C	2.78101	0.06906	-1.31175
C	3.08349	1.39068	-1.74009
C	4.26148	1.62474	-2.45582
H	4.49611	2.64437	-2.77272
C	5.13464	0.59420	-2.77968
H	6.05477	0.79968	-3.33232
C	4.80466	-0.70554	-2.41851
H	5.46671	-1.52643	-2.70831
C	3.63692	-0.99495	-1.70462
C	2.13442	2.55486	-1.51792
H	1.36341	2.21905	-0.81006
C	1.43817	2.91621	-2.83430
H	2.17048	3.23539	-3.59330
H	0.72424	3.74264	-2.69062
H	0.88970	2.05863	-3.25805
C	2.80326	3.78714	-0.91101
H	3.32496	3.54386	0.02490
H	2.04664	4.55550	-0.68652
H	3.53467	4.23944	-1.60029
C	3.30555	-2.45152	-1.43513
H	2.38488	-2.46485	-0.83757
C	3.01181	-3.19692	-2.74013
H	2.20463	-2.70864	-3.30834
H	2.70428	-4.23502	-2.53404
H	3.89923	-3.23603	-3.39231
C	4.39098	-3.16503	-0.62961
H	5.34387	-3.20740	-1.18170
H	4.09127	-4.20169	-0.40936
H	4.57904	-2.66178	0.33049
C	-3.03369	-0.78820	-0.94885
C	-4.07425	-0.10000	-1.63099
C	-5.18659	-0.81158	-2.08594
H	-5.98290	-0.27872	-2.61047
C	-5.30269	-2.18283	-1.88864
H	-6.17992	-2.72253	-2.25368
C	-4.28976	-2.85524	-1.22054
H	-4.37816	-3.93349	-1.06122
C	-3.15539	-2.18860	-0.74307
C	-3.97689	1.38825	-1.90525
H	-3.32526	1.80853	-1.12664
C	-3.29949	1.65298	-3.25171
H	-2.31123	1.16958	-3.30893
H	-3.16310	2.73336	-3.42270
H	-3.90577	1.25172	-4.07988
C	-5.31336	2.12389	-1.82328
H	-5.15123	3.21188	-1.87726
H	-5.84398	1.90567	-0.88330
H	-5.98709	1.85901	-2.65367
C	-2.09280	-3.00816	-0.03003
H	-1.34357	-2.30036	0.36118
C	-1.38476	-3.96944	-0.98972
H	-0.59935	-4.54249	-0.46966
H	-0.91489	-3.43936	-1.83441
H	-2.09315	-4.69539	-1.42008
C	-2.65889	-3.77915	1.16475
H	-3.21166	-3.11755	1.84632
H	-1.84655	-4.25857	1.73505
H	-3.34746	-4.57712	0.84354

LTl: 3

109, -2861.255151 Hartree

Tl	-0.16105	-1.10472	-1.78963
P	1.56597	0.05440	1.15119
N	1.69481	-0.24291	-0.43159
C	-0.05477	0.16043	1.67663
H	-0.23340	-0.46776	2.54074
P	-1.49903	0.69902	0.92046
N	-1.97209	-0.07186	-0.40856
C	2.21758	-1.26346	2.25205
C	1.63750	-2.53602	2.14431
H	0.84834	-2.70621	1.40722
C	2.04379	-3.57955	2.96985
H	1.58058	-4.56454	2.87015
C	3.03973	-3.36582	3.92477
H	3.36098	-4.18338	4.57499
C	3.61712	-2.10491	4.04805
H	4.39066	-1.92713	4.79932
C	3.20828	-1.05874	3.21815
H	3.66140	-0.07319	3.33626
C	2.60689	1.48937	1.58156
C	2.03256	2.59469	2.21579
H	0.96419	2.57350	2.43923
C	2.81041	3.70006	2.55973
H	2.34509	4.55958	3.04866
C	4.17700	3.70386	2.28628
H	4.78968	4.56614	2.56152
C	4.76208	2.60231	1.65976
H	5.83279	2.59950	1.44146
C	3.98345	1.50343	1.30260
H	4.45615	0.65163	0.80904
C	-1.36321	2.47712	0.52459
C	-1.18023	2.92377	-0.78668
H	-1.13213	2.19564	-1.59815
C	-1.07886	4.28789	-1.06471
H	-0.93956	4.62243	-2.09576
C	-1.16871	5.22154	-0.03516
H	-1.09919	6.28980	-0.25464
C	-1.35630	4.78581	1.27760
H	-1.43725	5.51216	2.09022
C	-1.44918	3.42509	1.55462
H	-1.60509	3.09406	2.58447
C	-2.78302	0.66763	2.21110
C	-4.11590	0.86851	1.82410
H	-4.36129	1.02951	0.77347
C	-5.13689	0.85682	2.77123
H	-6.17102	1.00724	2.45251
C	-4.84076	0.65026	4.11815
H	-5.64264	0.63875	4.86059
C	-3.51753	0.46434	4.51478
H	-3.27664	0.31171	5.56966
C	-2.49424	0.47508	3.56778
H	-1.46024	0.34389	3.89058
C	2.87287	-0.10889	-1.20318
C	3.14491	1.10939	-1.88596
C	4.31394	1.22626	-2.64301
H	4.52202	2.16955	-3.15513
C	5.21202	0.17316	-2.76582
H	6.12527	0.28806	-3.35482
C	4.91497	-1.03696	-2.15228
H	5.59606	-1.88345	-2.27696
C	3.75716	-1.20733	-1.38629
C	2.16249	2.26551	-1.88440
H	1.42169	2.06251	-1.09810
C	1.42234	2.31226	-3.22495
H	2.12377	2.47789	-4.05851
H	0.68144	3.12690	-3.24426
H	0.89524	1.36639	-3.43351
C	2.79997	3.61732	-1.56926
H	3.34237	3.59029	-0.61342
H	2.02298	4.39438	-1.49474
H	3.50679	3.93488	-2.35306
C	3.46553	-2.58632	-0.82378
H	2.53992	-2.50210	-0.23977
C	3.20839	-3.59650	-1.94592
H	2.39505	-3.26437	-2.61024
H	2.92935	-4.57848	-1.53034
H	4.10338	-3.74334	-2.57187
C	4.56141	-3.08394	0.11829
H	5.52196	-3.20904	-0.40747
H	4.28961	-4.06078	0.54846
H	4.72221	-2.38587	0.95324
C	-3.13913	-0.80461	-0.68903
C	-4.09608	-0.27854	-1.60361
C	-5.20579	-1.04733	-1.95902
H	-5.93629	-0.63924	-2.66181
C	-5.40676	-2.31985	-1.43358
H	-6.28223	-2.90652	-1.72237
C	-4.48105	-2.83096	-0.53480
H	-4.63815	-3.82909	-0.11560
C	-3.34897	-2.10339	-0.15039
C	-3.90971	1.10351	-2.19938
H	-3.28739	1.66457	-1.48707
C	-3.13798	1.03563	-3.51899
H	-2.17147	0.52239	-3.39511
H	-2.93828	2.04391	-3.91707
H	-3.70829	0.47740	-4.27912
C	-5.21179	1.88192	-2.37842
H	-4.99538	2.91981	-2.67644
H	-5.79857	1.91453	-1.44726
H	-5.85370	1.44961	-3.16257
C	-2.38417	-2.74079	0.83381
H	-1.57946	-2.01195	1.02025
C	-1.73832	-4.00491	0.25976
H	-1.01373	-4.43514	0.97045
H	-1.20935	-3.80348	-0.68621
H	-2.49042	-4.78134	0.04705
C	-3.05043	-3.03984	2.17871
H	-3.51819	-2.13986	2.60319
H	-2.31028	-3.41447	2.90432
H	-3.83340	-3.80901	2.07814

4. References

S1 S. Al-Benna, M. J. Sarsfield, M. Thornton-Pett, D. L. Ormsby, P. J. Maddox, P. Brès and M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 2000, 4247–4257.

S2 C. P. Sindlinger and A. Stasch, *Aus. J. Chem.* 2012, **66**, 1219–1225.

S3 M. L. H. Green, P. Mountford, G. J. Smout and S. R. Speel, *Polyhedron*, 1990, **9**, 2763–2765.

S4 (a) C. P. Sindlinger, A. Stasch and L. Wesemann, *Organometallics*, 2014, **33**, 322−328; (b) A. J. Wooles, M. Gregson, S. Robinson, O. J. Cooper, D. P. Mills, W. Lewis, A. J. Blake and S. T. Liddle, *Organometallics*, 2011, **30**, 5326–5337; (c) O. J. Cooper, A. J. Wooles, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Angew. Chem. Int. Ed.*, 2010, **49**, 5570–5573.

S5 A. L. Hawley, C. A. Ohlin, L. Fohlmeister and A. Stasch, *Chem. Eur. J.*, 2017, **23**, 447–455.

S6 N. P. Cowieson, D. Aragao, M. Clift, D. J. Ericsson, C. Gee, S. J. Harrop, N. Mudie, S. Panjikar, J. R. Price, A. Riboldi-Tunnicliffe, R. Williamson and T. Caradoc-Davies, *J. Synchrotron Rad.*, 2015, **22**, 187–190.

S7 T. M. McPhillips, S. E. McPhillips, H. J. Chiu, A. E. Cohen, A. M. Deacon, P. J. Ellis, E. Garman, A. Gonzalez, N. K. Sauter, R. P. Phizackerley, S. M. Soltis and P. Kuhn, *J. Synchrotron Radiat.*, 2002, **9**, 401–406.

S8 W. Kabsch, *J. Appl. Crystallogr.*, 1993, **26**, 795–800.

S9 G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3–8.

S10 C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158–6159.

S11 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.

S12 Gaussian 09, Revision D.01: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz and J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

S13 (a) K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li and T. L. Windus, *J. Chem. Inf. Model.*, 2007, **47**, 1045–1052; (b) D. Feller, *J. Comp. Chem.*, 1996, **17**, 1571–1586.

S14 NBO 6.0: E. D. Glendening, J, K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis and F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison (2013); http://nbo6.chem.wisc.edu/.