Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for:

A transition metal-gallium cluster formed *via* insertion of "GaI"

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Contents

S1 – General Procedures

All reactions described were undertaken with rigorous exclusion of air and water using standard air-sensitive-handling techniques which included bench-top operations (Schlenk Line techniques) and glove-box techniques. Standard laboratory solvents were dried by distilling from potassium (toluene), sodium-benzophenone ketyl (THF), NaK (diethyl ether) or collected from the in-house dry-solvent towers (hexane) and were stored over a potassium mirror (toluene, diethyl ether, hexane) or 4 Å molecular sieves (THF). d_6-benzene was dried over potassium, while d_8-THF was dried over calcium hydride, before being vacuum-transferred into a Young's flask and stored in the glovebox prior to use. NMR samples of air and moisture sensitive compounds were prepared using glove box techniques and measured in Young's tap modified borosilicate glass NMR tubes. NMR data was collected on Bruker DPX400, AV400, AV(III)400 or AV(III)400HD spectrometers. Chemical shifts are quoted in ppm relative to TMS (^{1}H, ^{13}C). Air-sensitive mass spectrometry samples were prepared under an argon atmosphere by placing the sample inside glass capillaries. The spectra for the complexes described were recorded by the Dr Mick Cooper at the University of Nottingham and the EPSRC NMSF at Swansea University. Elemental microanalysis was performed by Mr. Stephen Boyer at the Microanalysis Service, London Metropolitan University, UK. ICP analysis was performed by MEDAC Ltd, UK. Air sensitive infrared spectroscopy samples were prepared as Nujol mulls between two KBr discs, while non air-sensitive samples were recorded using a Bruker ALPHA FTIR spectrometer over a frequency range of 4000-400 cm^{-1}. The magnetic moment for **1** was calculated using Evans' method.[1] $CoBr_2(DME)$,[2] $[2,6\text{-}Pmp_2C_6H_3Li]_2$[3] and "GaI"[4] were prepared according to the literature.

S2 – Synthesis of Compounds

S2.1 – Synthesis of $[2,6\text{-}Pmp_2C_6H_3]_2Co$ (**1**)

Toluene (40 mL) and THF (5 mL) were added to a mixture of $[2,6\text{-}Pmp_2C_6H_3Li]_2$ (1.00 g, 1.33 mmol) and $CoBr_2(DME)$ (0.41 g, 1.33 mmol) with vigorous stirring. The deep red/brown mixture was stirred overnight. The solvent was removed *in vacuo* and the resulting brown solid was extracted into hexane (3 × 20 mL). The supernatant was reduced to high concentration *in vacuo* followed by storage at –30 °C for 24 hours resulting in dark red crystals of pure product (220 mg, 21 %). ^{1}H NMR spectroscopy in C_6D_6 (400 MHz, 300 K) revealed a number of broad, paramagnetically shifted peaks that could not be assigned. μ_{eff} (Evans' method, C_6D_6, 300K) = 5.94 μ_B. Elemental analysis $C_{56}H_{66}Co$: calcd. C 84.28, H 8.34; found C 84.12, H 8.17. EI-MS: m/z = 797.5 $[M]^+$ (8%) fragment ion peaks at m/z 782.5 $[M - CH_3]^+$ (0.1%), 767.5 $[M - 2CH_3]^+$ (0.1%), 370.3 $[2,6\text{-}Pmp_2C_6H_3 + H]^+$ (100%); accurate mass $C_{56}H_{66}Co$: calc. 797.4493 found: 797.4491. IR (Nujol Mull) v/cm^{-1} = 2725 (w), 1958 (w), 1546 (m), 1305 (m, br), 1261 (s), 1239 (w), 1168 (w), 1151 (w), 1097 (s), 1063 (s), 1026 (s), 835 (w), 804 (m), 785 (m), 731 (s), 723 (s).

S2.2 – Reaction between **1** and 'GaI' in toluene (isolation of **2** and **3**)

A solution of **1** (100 mg, 0.12 mmol) in toluene (40 mL) was added drop wise to a freshly prepared suspension of 'GaI' (585 mg 1.49 mmol) in toluene (30 mL). The mixture turned black over 1 hour and was stirred at room temperature for 5 days. The supernatant solution was removed in *vacuo* resulting in a dark green/black solid. The solid was extracted into warm hexane (40 mL) resulting in a clear pale yellow solution which upon storage at room temperature for 24 hours resulted in bright orange/red crystals of pure [(2,6-Pmp$_2$C$_6$H$_3$)CoGa$_3$I$_5$] (12 mg, 8 %). (**note**: crystals are not stable in solution at –30 °C for longer than 2-3 days). [(2,6-Pmp$_2$C$_6$H$_3$)CoGa$_3$I$_5$] was characterised by single crystal XRD, XPS, and ICP analysis. ICP: $C_{28}H_{33}CoGa_3I_5$: calcd. Co 4.63, Ga 16.44; found Co 4.79, Ga 16.19.

Extraction of the remaining solid into diethyl ether (30 mL) resulted in a deep orange/red solution. Storage at 6 °C for 24 hours resulted in clear pale yellow crystals suitable for X-ray diffraction of (2,6-Pmp$_2$C$_6$H$_3$)$_2$GaI (**3**) (45 mg, 21 %). ^{1}H NMR (C$_6$D$_6$, 400 MHz, 300K) δ_H / ppm 1.85 (s, 12H, *p*-CH$_3$, **f**) 2.10 (s, 12H, *m*-CH$_3$, **g**), 2.20 (s, 6H, *p*-CH$_3$, **h**), 6.64 (d, 2H, $^3J_{HH}$ = 7.5 Hz, *m*-CH, **c**), 6.98 (t, 1H, $^3J_{HH}$ = 7.9 Hz, *p*-CH, **d**). ^{13}C NMR (C$_6$D$_6$, 100 MHz, 300K) δ_C / ppm 16.9 (*m*-CH$_3$, **g**), 17.0 (*p*-CH$_3$, **h**), 19.8 (*o*-CH$_3$, **f**), 129.4 (*p*-CH, **d**), 130.6 (*m*-CH), 132.4 (*m*-C, **g**), 133.4 (o-C, **f**), 134.5 (*p*-C, **h**), 141.3 (*ipso*-C, **e**), 147.1 (*o*-C, **b**, peak found by HMBC) 150.2 (*ipso*-C, **a**). Elemental analysis $C_{56}H_{66}GaI$: calcd. C 71.88, H 7.11; found C 71.68, H 6.95. EI-MS: m/z = 934.1 [M]$^+$ (0.1%), 807.5 [M-I]$^+$ (100%), 565.1 [2,6-Pmp$_2$C$_6$H$_3$GaI]$^+$ (26%), 437.1 [2,6-Pmp$_2$C$_6$H$_2$Ga]$^+$ (21%), 370.2 [2,6-Pmp$_2$C$_6$H$_4$]$^+$ (72%). IR (Nujol Mull) ν/cm^{-1} 1557 (w), 1304 (w, br), 1260 (s), 1188 (w, br), 1169 (w), 1151(w), 1108 (s, br), 1066 (s), 1042 (s), 902 (w), 861 (w), 840 (m, br), 795 (s), 740 (m), 722 (m), 655 (w), 588 (w), 484 (w).

S2.3 – Reaction between **1** and 'GaI' in toluene/THF (isolation of **2**·GaI$_3$(THF) and **4**)

A solution of **1** (424 mg, 0.531 mmol) in toluene (40 mL) and THF (5 mL) was added drop wise to a freshly prepared suspension of 'GaI' (591 mg, 3 mmol) in toluene (30 mL). The mixture turned black over 1 hour and was stirred at room temperature for 5 days. The supernatant solution was removed *in vacuo* resulting in a green/black solid. The solid was extracted into hexane where storage at room temperature for 24 hours resulted in deep red/orange crystals of **2**·GaI$_3$(THF) suitable for X-ray diffraction.

Extraction of the residual solid into toluene (30 mL) resulted in a deep red solution. Storage for 14 days at –30 °C resulted in a brown oil of **2**·GaI$_3$(THF) at which point the remaining supernatant was decanted and the solvent removed *in vacuo* to yield a black solid (385 mg). NMR spectroscopy revealed a mixture of **4** and another terphenyl-containing product that could not be separated. A small number of crystals of [(2,6-Pmp$_2$C$_6$H$_3$)$_2$Ga]$^+$[GaI$_4$]$^-$ (**4**) sufficient quality for X-ray diffraction studies were obtained from C$_6$D$_6$ at room temperature, but despite repeated attempts on these crystals elemental analysis did not yield reliable results, presumably due to impurities. ^{1}H NMR (C$_6$D$_6$/C$_4$D$_8$O 400 MHz, 300K) δ_H / ppm 1.83 (s, 12H, CH$_3$), 2.10 (s, 12H CH$_3$), 2.19 (s, 6H, *p*-CH$_3$), 6.63 (d, 2H, $^3J_{HH}$ = 7.6 Hz, *m*-CH), 6.99 (t, 1H, $^3J_{HH}$ = 7.7 Hz, *p*-CH). ^{13}C NMR (C$_6$D$_6$/C$_4$D$_8$O 400 MHz, 300K) δ_C / ppm 16.8 (CH$_3$), 16.9 (CH$_3$), 19.8 (CH$_3$), 129.4 (C$_{Ar}$-H), 131.0 (C$_{Ar}$-H), 131.9 (*quaternary*-C$_{Ar}$), 133.4 (*quaternary*-C$_{Ar}$), 134.9 (*quaternary*-C$_{Ar}$), 140.7 (*quaternary*-C$_{Ar}$, peak found through HMBC experiment), 143.1 (*quaternary*-C$_{Ar}$), 150.6 (*ipso*-C$_{Ar}$).

Extraction of the solid left over after the previous extractions into diethyl ether (30 mL) resulted in a clear orange solution. The solvent was removed *in vacuo* resulting in a red/brown oil, which upon trituration with dry hexane (20 mL), resulted in a fine grey powder of **2**·GaI$_3$(THF) (60 mg, 6 %). ^{1}H

NMR (d^8-THF, 400 MHz, 298K): δ_H / ppm 1.73 (s, CH_2-THF, underneath residual solvent peak) 2.03 (s, 6H, CH_3), 2.20 (s, 6H, CH_3), 2.26 (s, 3H, CH_3), 3.27 (s, 6H, CH_3), 3.36 (s, 3H, CH_3), 3.58 (s, CH_2-THF/CH_3 underneath residual solvent peak), 6.86 (br, 2H, *m*-CH), 7.39 (br, 1H, *p*-CH). ^{13}C NMR: the solubility of the sample was too low to allow for direct observation of signals by conventional ^{13}C{^{1}H} NMR spectroscopy. However, some ^{13}C signals could be identified and assigned from ^{1}H,^{13}C-HSQC and ^{1}H,^{13}C-HMBC experiments. In ring C (Figure S1), no quaternary aromatic carbons could be observed, possibly due to quadrupolar broadening arising from close contact with the Co atom. Two methyl groups on ring C were also not observed. The *ipso*-carbon of ring B and all quaternary carbons of ring A were unobservable due to the lack of nearby protons for magnetisation transfer.^{13}C NMR (d_8-THF, 101 MHz): δ = 16.6 (ring B, *o* + *p*-Me), 19.9 (ring B, *m*-Me), 58.8 (ring C, *o/m*-Me), 72.8 (ring C, *p*-Me), 129.3 (ring A, *m*-CH), 130.0 (ring A, *p*-CH), 133.0 (ring B, qC), 134.6 (ring B, qC), 141.3 (ring B, qC). Elemental analysis $C_{32}H_{43}CoGa_4I_8O$: calcd. C 21.39, H 2.41; found C 21.30, H 2.12. EI MS: M^+ not observed, fragment ion peaks at 691.9 [2,6-$Pmp_2C_6H_3GaI_2$]$^-$. CI-MS Cl^-(NH_3): M^+ not observed, fragment ion peaks at 821.8 [2,6-$Pmp_2C_6H_3CoGa_2I_2$]$^-$ 0.4%, 818.9 [2,6-$Pmp_2C_6H_3GaI_3$]$^-$ 4%, 691.9 [2,6-$Pmp_2C_6H_3GaI_2$]$^-$ 95%, 449.6 [GaI_3]$^-$ 19%, 322.7 [GaI_2]$^-$ 9%.

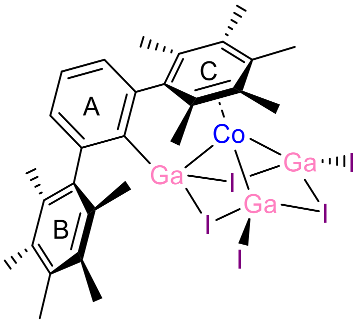


Figure S1: Naming scheme for the 3 aromatic rings (A, B, and C) of compound **2.**

S3 – NMR spectra

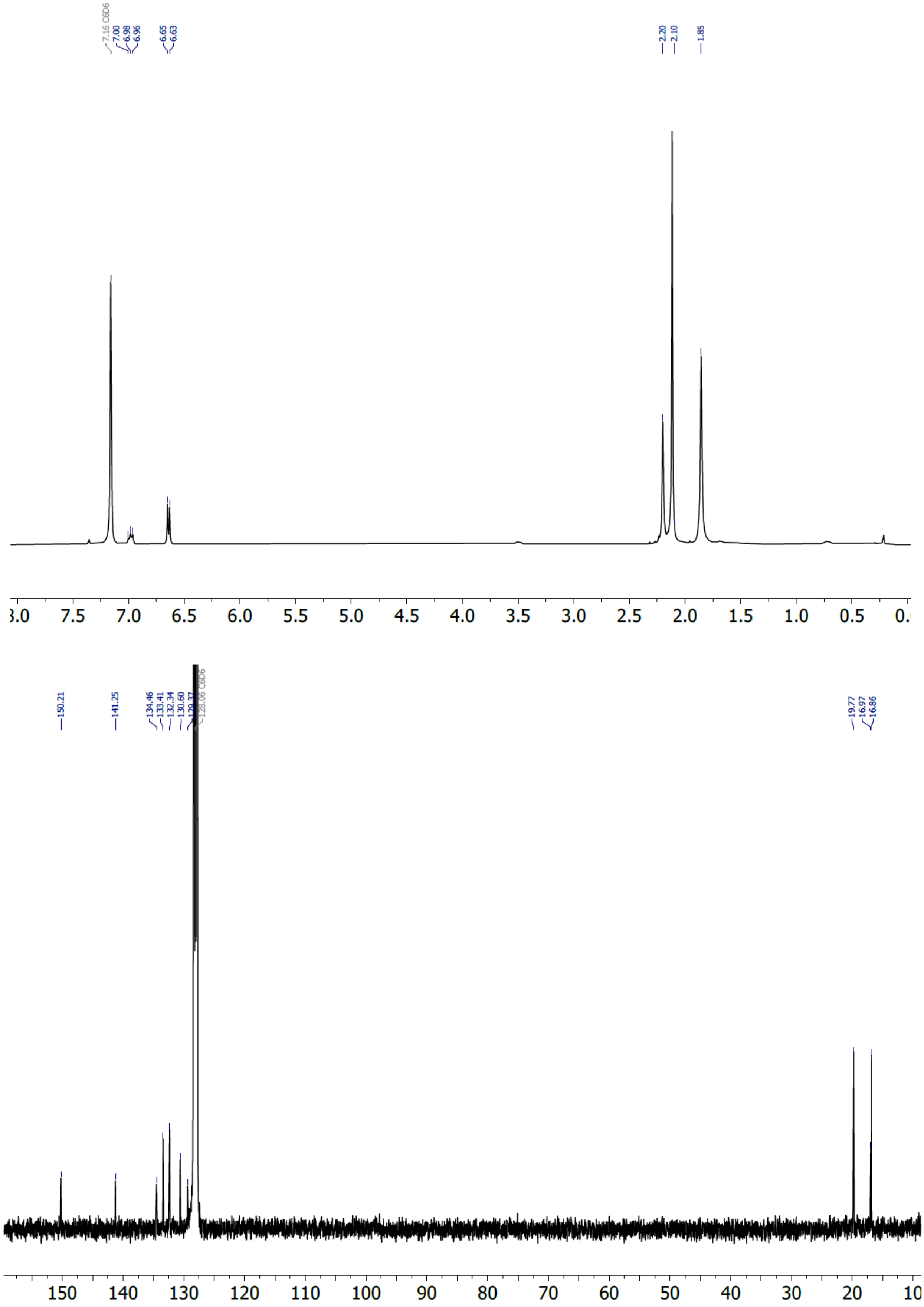


Figure S2: ^{1}H (top) and ^{13}C (bottom) NMR spectra for compound **3** in C_6D_6.

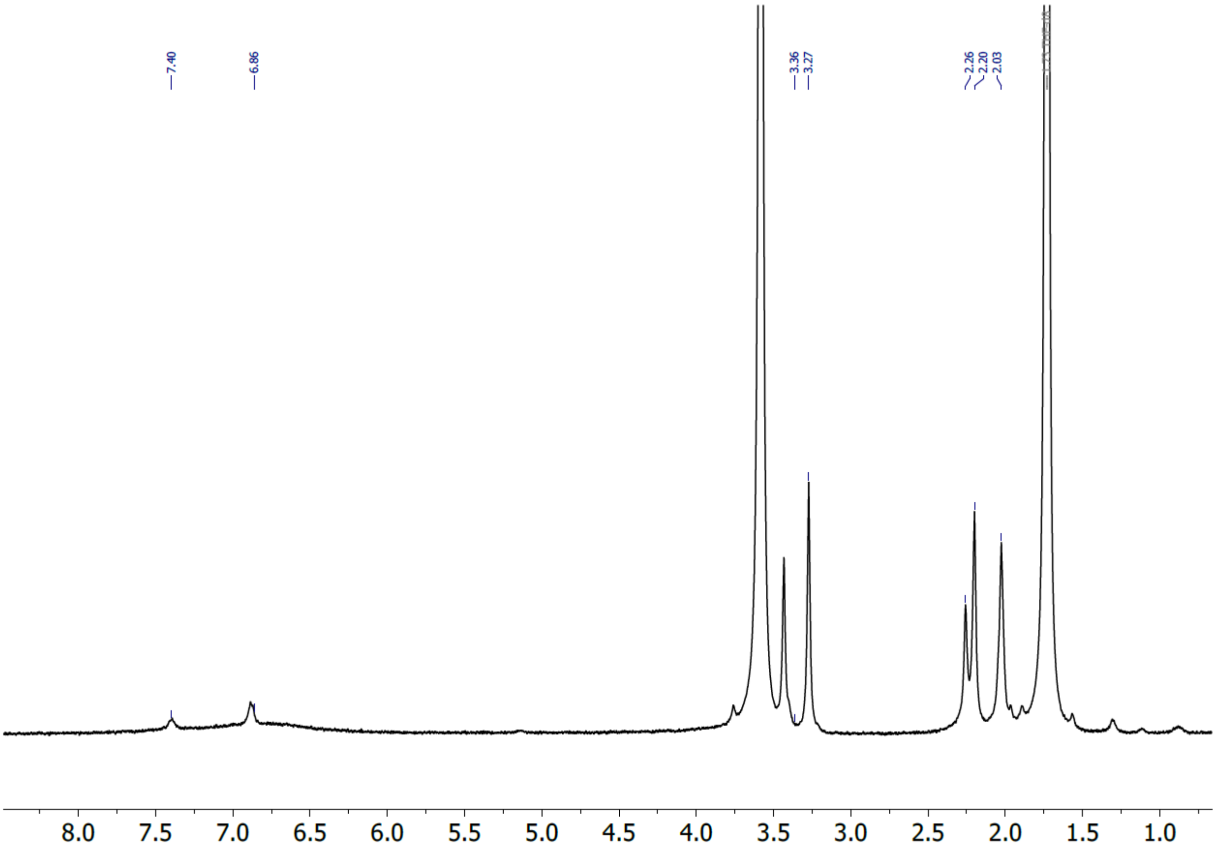


Figure S3: ^{1}H NMR spectrum of **2**·GaI$_3$(THF) in C_4D_8O.

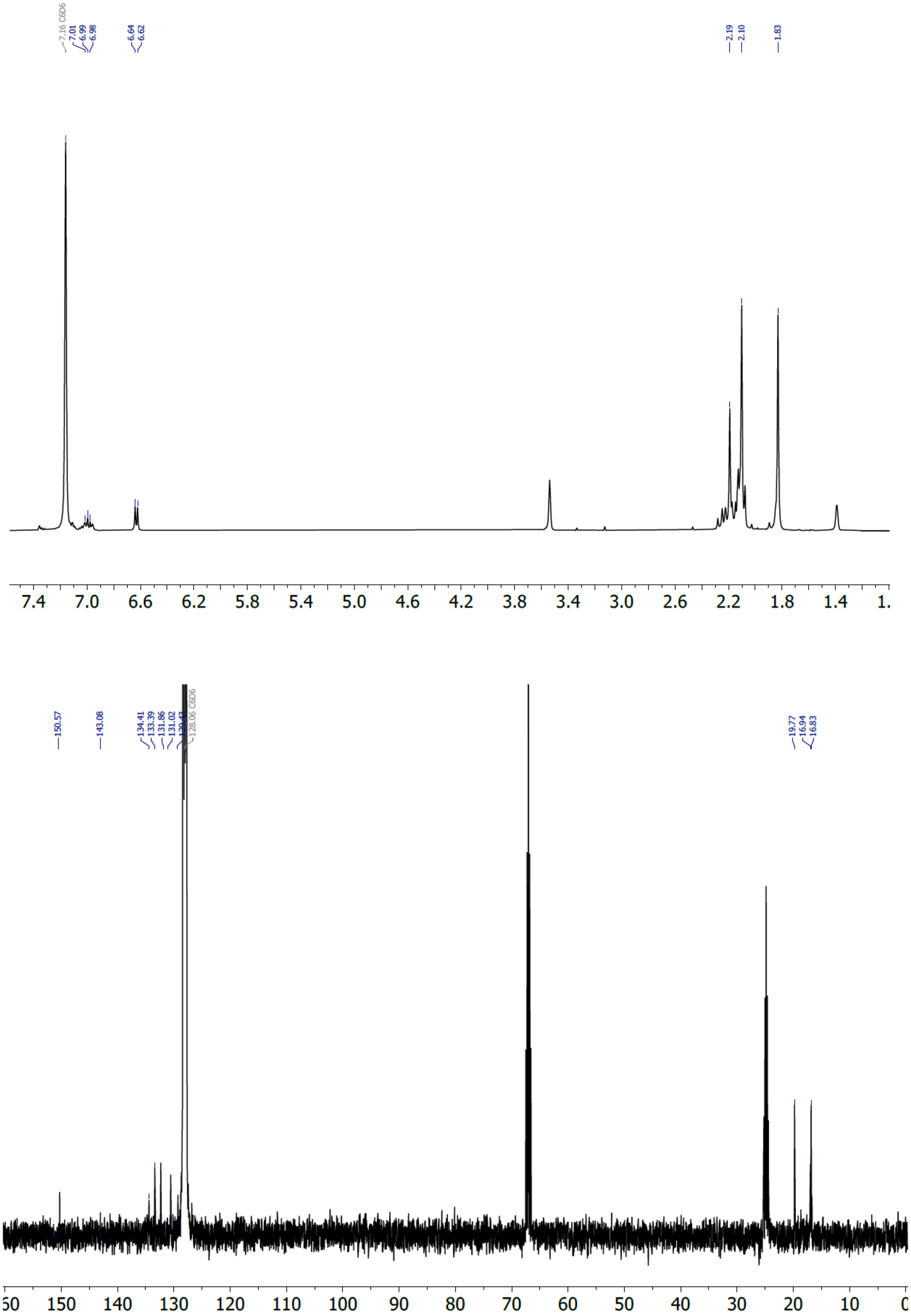


Figure S 4: ^{1}H (top) and ^{13}C (bottom) NMR spectra for **4** in C_6D_6/C_4D_8O**.**

S4 – XPS Measurements

S4.1 – Experimental details

Samples of **2** were analysed using the Kratos AXIS ULTRA with a mono-chromated Al K*α* X-ray source (1486.6eV) operated at 10 mA emission current and 12 kV anode potential (120 W). A charge neutralizer filament was used to prevent surface charging. Hybrid–slot mode was used measuring a sample area of approximately 0.5 mm^2. The analysis chamber pressure was better than 5 x 10^{-9} mbar.

The sample material was mounted onto a Kratos powder stub using double sided tape (sellotape) in a glove box under nitrogen and transferred to the XPS airlock under nitrogen using a Kratos air sensitive transfer device, to avoid air exposure. Note that only a small amount of sample was available so the coverage of the substrate tape was not complete, the resulting spectra contain photoelectron peaks arising from the sample and the substrate and later de-convolution was required to separate out the two.

Three areas were analysed on the sample. A wide scan at low resolution (1200 to −5 eV binding energy range, pass energy 80 eV, step 1 eV, sweep time 20 minutes) These were used to estimate the total atomic % of the detected elements. High resolution spectra at pass energy 20 eV with step of 0.1 eV, sweep times of 5, 10 or 20 minutes each were also acquired for photoelectron peaks depending on signal intensity, from the detected elements and these were used to model the chemical composition. The high-resolution spectra were charge corrected to the C 1s peak set to 285 eV.

CasaXPS (version 2.3.18dev1.0x) software was used for quantification and spectral modelling.

Ga 2p and Ga 3d peaks were acquired as well as I 3d, Co 2p, C 1s, O 1s and Si 2p. Auger parameters for the Ga compound were estimated from the wide scan.

No degradation of the sample was observed over repeated analysis with X-ray exposure of ~ 12 hours.

S4.2 – Detector mode

The ULTRA was used in FAT (fixed analyser transmission) mode, with pass energy of 80eV for wide scans and pass energy 20 eV for high resolution scans. A Hybrid magnetic/electrostatic lens mode is used for maximum electron signal. The magnetic immersion lens system allows the area of analysis for to be defined by apertures, a 'slot' aperture of 300 x 700 µm for wide/survey scans and high-resolution scans. The take-off angle for the photoelectron analyser is 90° and acceptance angle of 9° for hybrid lens mode utilised.

S4.3 – Calibrations

The energy range of the XPS was calibrated using Cu, Ag and Au samples. The resolution for the photoelectron detector was based on Ag 3d$_{5/2}$ peak FWHM of less than 0.55 eV at PE 20 in hybrid slot mode. The transmission function of the instrument was calibrated using a clean gold sample for all lens modes and pass energies. Last date of calibrations: Energy range, resolution check and Transmission function, Dec 2017, Kratos settings.

S4.4 – Analysis of XPS data

Due to low coverage some areas of the sample were not used for data analysis, those with better coverage produced useable Ga, Co and I peaks. Note that even on these areas the Ga and Co signals were low at less than 4 at% detectable Co+Ga+I.

Table S1: Quantification of atom percentages for **2** estimated from wide scan measurement.

	C 1s	Co 2p	Ga 2p	I 3d	O 1s	Si 2p
%	73.68	0.75	0.34	1.35	14.49	9.39

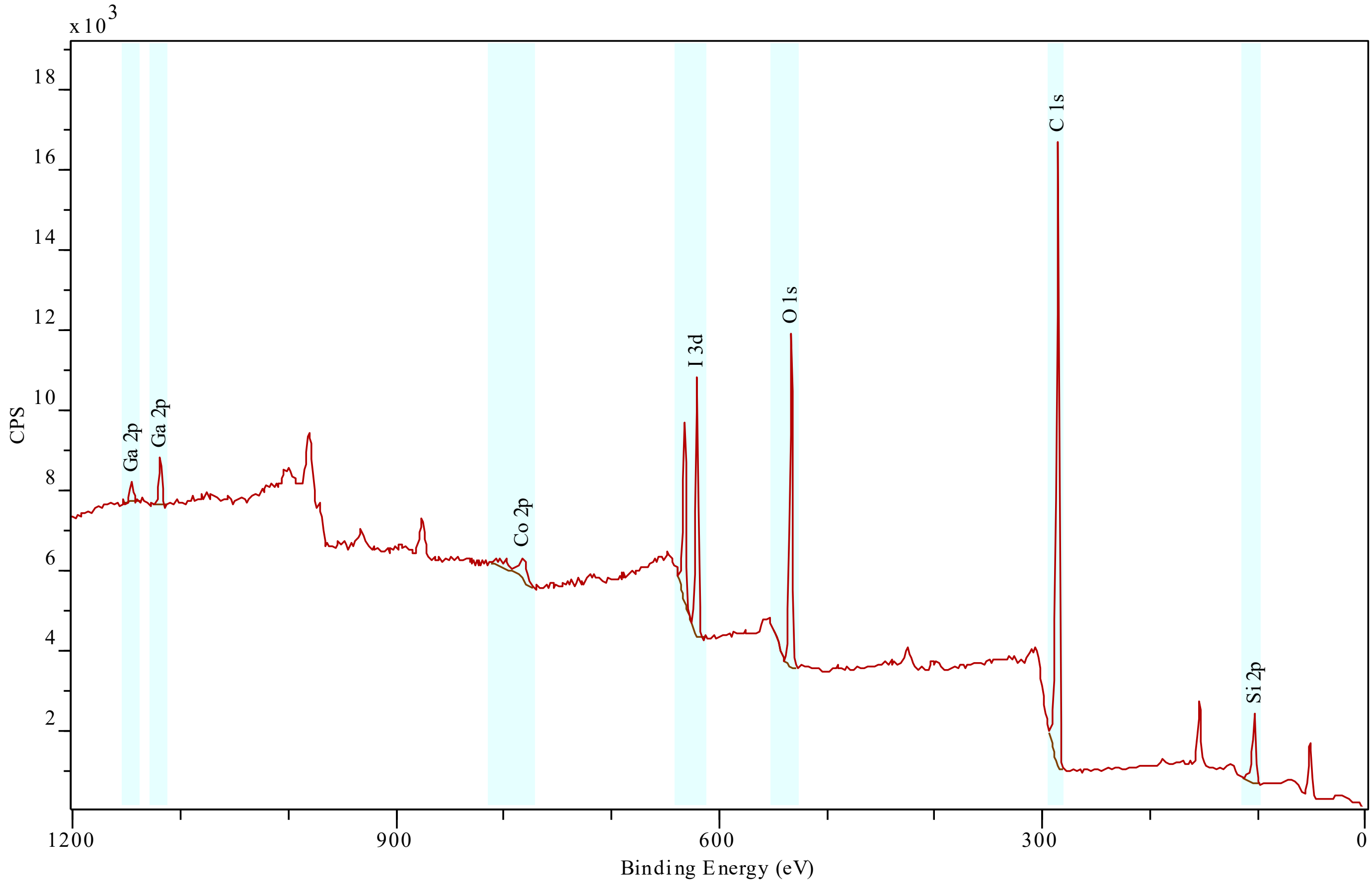


Figure S5: Example wide scan XPS spectrum for **2**.

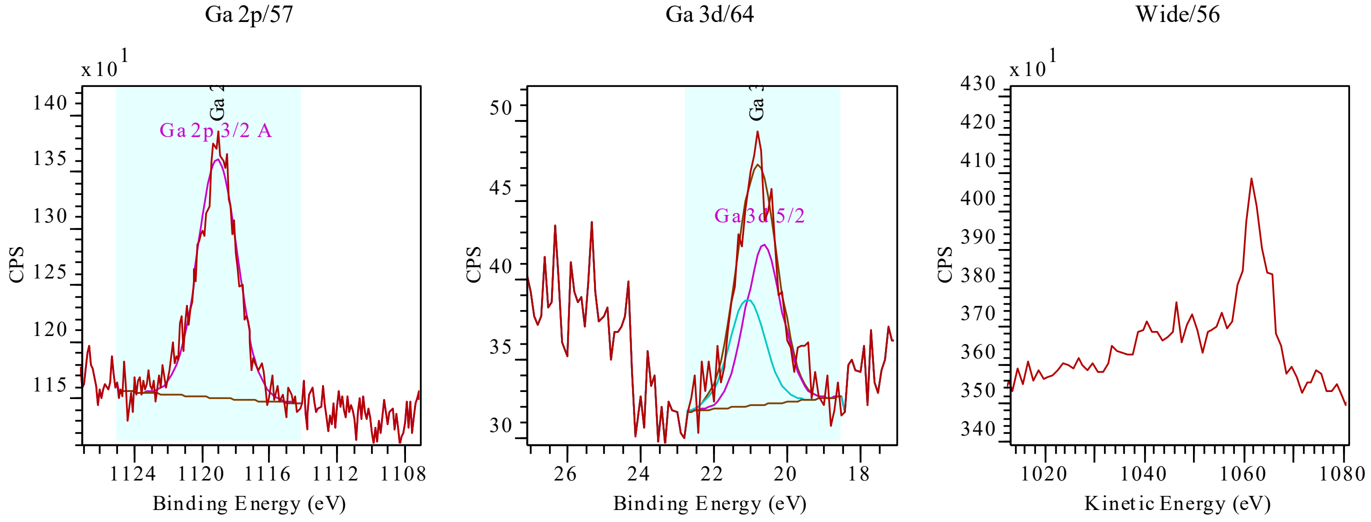
Table S2: Peak binding energies, Full Width at Half Maximum (FWHM) and assignments for **2** after charge correction.

	Binding Energy (eV)	FWHM (eV)	Assignment
Ga 2p$_{3/2}$	1119.1	2.7	
Co 2p$_{3/2}$	~779.4	-	
I 3d$_{5/2}$	620.4	1.9	Metal Iodide or I_2
	622.3	1.9	
O 1s	532.5	1.4	C–O, not metal oxides
	533.9	1.4	
	535.2	1.4	
C 1s	285.0	1.3	Reference value – Aliphatic Carbon
	286.2	1.3	C–O
	287.3	1.3	
	288.9	1.3	O–C=O
Si 2p	102.5	-	
Ga 3d	20.7	1.2	

Table S3: Auger parameters for Compound **2**

	Kinetic Energy (eV)
Ga LMMa	1061.7
Auger Parameter	
Ga 2p-Ga LMMa	2180.7
Ga 3d-Ga LMMa	1082.4

Although the oxidation state of the Ga is similar to that of Ga_2O_3, we can confirm that there is no metal oxide from the O 1s peak position. O 1s binding energy in Ga_2O_3 would be *ca.* 531 eV, whereas all the oxygen peaks measured here are at higher BE than this. This is consistent with C–O bonding in the substrate tape only.


Ga 2p/57

Ga 3d/64

Wide/56

Figure S6: Example spectra for Ga 2p$_{3/2}$ (left), Ga 3d high resolution spectra (middle), and Ga Auger from wide scan (right).

S5 – Crystallographic Methods

S5.1 – Experimental Procedure

Under a flow of N_2, crystals suitable for X-ray diffraction were quickly removed from the crystallisation vessel and covered with "fomblin" (YR-1800 perfluoropolyether oil). A suitable crystal was then mounted on a polymer-tipped MicroMount™ and cooled rapidly to 90K or 120K in a stream of cold N_2 using an Oxford Cryosystems open flow cryostat.[5] Single crystal X-ray diffraction data were collected either using an Agilent SuperNova diffractometer, Atlas CCD area detector (mirror-monochromated Cu-*Kα* radiation source; λ = 1.54184 Å or graphite-monochromated Mo-Kα radiation source; λ = 0.7103 Å; ω scans), an Agilent SuperNovaII diffractometer, Atlas S2 CCD area detector, an Agilent SuperNovaII diffractometer Titan S2 CCD area detector (mirror monochromated Cu-*Kα* radiation source; λ = 1.54184 Å; ω scans) or a Rigaku MM007 rotating anode X-ray source. Absorption corrections were applied using an analytical numerical method (CrysAlis Pro).[6] All non-H atoms were located using direct methods[7] and difference Fourier syntheses. Hydrogen atoms were placed and refined using a geometric riding model. All fully occupied non-H atoms were refined with anisotropic displacement parameters, unless otherwise specified. Crystal structures were solved and refined using the Olex2 software package.[8] Programs used include CrysAlisPro[9] (control of Supernova, data integration and absorption correction), SHELXL[10] (structure refinement), SHELXS[11] (structure solution), SHELXT[12] (structure solution), OLEX2[8a] (molecular graphics). CIF files were checked using checkCIF.[13] CCDC 2004404-2004408 contain the supplementary data for these complexes. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

S5.2 – Crystallographic Data

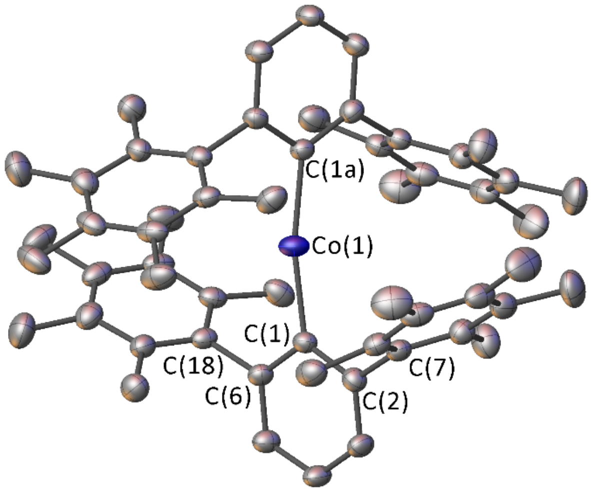


Figure S7: Crystal structure of **1** with displacement ellipsoids set at 50% probability. Hydrogen atoms omitted for clarity. Symmetry operation a: 1–x, +y, ½ –z. Selected bond lengths (Å) and angles (°): Co(1)–C(1) 1.993(2), C(1)–Co(1)–C(1a) 168.5(1).

Crystal data for $[2,6\text{-}Pmp_2C_6H_3]_2Co$ (**1**): CCDC 2004404

$C_{56}H_{66}Co$ (M = 798.01 g/mol): monoclinic, space group *C*2/c (no. 15), a = 17.579(7), b = 14.548(6), c = 17.555(9) Å, β = 92.350(8)°, V = 4486(3) Å^3 , Z = 4, T = 90(2) K, μ(Mo-Kα) = 0.71073 mm^{-1} , Dcalc = 1.182 g/cm^3, 19122 reflections measured (4.262° ≤ 2Θ ≤ 54.944°), 5057 unique (Rint = 0.0710, Rsigma = 0.0657) which were used in all calculations. The final R1 was 0.0521 (I > 2σ(I)) and wR2 was 0.1489 (all data).

Crystal data for $(2,6\text{-}Pmp_2C_6H_3)CoGa_3I_5$ (**2**): CCDC 2004407

$C_{28}H_{33}CoGa_3I_5$ (M = 1272.13 g/mol): orthorhombic, space group *P*bca (no. 61), a = 16.6877(4), b = 17.7466(4), c = 24.3929(6) Å, V = 7223.9(3) Å^3 , Z = 8, T = 120(2) K, μ(Cu-Kα) = 1.54184 mm^{-1} , Dcalc = 2.339 g/cm^3, 95072 reflections measured (8.126° ≤ 2Θ ≤ 133.16°), 6238 unique (Rint = 0.2880, Rsigma = 0.1396) which were used in all calculations. The final R1 was 0.2497 (I > 2σ(I)) and wR2 was 0.5981 (all data).

Crystal data for **2**·$GaI_3(THF)$: CCDC 2004405

$C_{32}H_{41}CoGa_4I_8O$ (M = 1794.66 g/mol): monoclinic, space group *P*2$_1$/c (no. 14), a = 20.1625(9), b = 13.8708(6), c = 17.0402(8) Å, β = 101.025(5)°, V = 4677.7(4) Å^3 , Z = 4, T = 120(2) K, μ(Cu-Kα) = 1.54184 mm^{-1} , Dcalc = 2.548 g/cm^3, 27808 reflections measured (7.784° ≤ 2Θ ≤ 150.022°), 9227 unique (Rint = 0.1043, Rsigma = 0.0930) which were used in all calculations. The final R1 was 0.0922 (I > 2σ(I)) and wR2 was 0.2667 (all data).

Crystal data for $(2,6\text{-}Pmp_2C_6H_3)_2GaI$ (**3**): CCDC 2004408

$C_{56}H_{66}GaI$ (M = 935.70 g/mol): monoclinic, space group *P*2$_1$/n (no. 14), a = 15.1817(3), b = 17.9327(4), c = 16.9613(3) Å, β = 91.9796(18)°, V = 4614.94(17) Å^3 , Z = 4, T = 120(2) K, μ(Cu-Kα) = 1.54184 mm^{-1} , Dcalc = 1.347 g/cm^3, 25851 reflections measured (7.176° ≤ 2Θ ≤ 148.392°), 9139 unique (Rint = 0.0479, Rsigma = 0.0385) which were used in all calculations. The final R1 was 0.0484 (I > 2σ(I)) and wR2 was 0.1315 (all data).

Crystal data for $[(2,6\text{-}Pmp_2C_6H_3)_2Ga]^+[GaI_4]^-$ (**4**): CCDC 2004406

$C_{62}D_6Ga_2H_{66}I_4$ (M = 1470.27 g/mol): monoclinic, space group *P*2$_1$/n (no. 14), a = 12.2172(2), b = 30.7592(5), c = 16.4155(3) Å, β = 109.962(2)°, V = 5798.18(19) Å^3 , Z = 4, T = 120(2) K, μ(Cu-Kα) = 1.54184 mm^{-1} , Dcalc = 1.684 g/cm^3, 42377 reflections measured (5.746° ≤ 2Θ ≤ 149.924°), 11626 unique (Rint = 0.0357, Rsigma = 0.0318) which were used in all calculations. The final R1 was 0.0352 (I > 2σ(I)) and wR2 was 0.0972 (all data).

S6 – DFT Calculations

S6.1 – Optimisation in different spin states

Restricted and unrestricted geometry optimisations were performed for a model of **2** (using coordinates derived from the X-ray crystal structure of **2**·GaI_3(THF)) with the number of unpaired spins set to 0, 2, and 4 to give optimised structures **2^0**, **2^2**, and **2^4** respectively. The models were geometry optimised without restraints using the Amsterdam Density Functional (ADF) suite version 2014.01.[14] The DFT geometry optimizations employed all-electron Slater type orbital (STO) triple-ζ-plus polarization basis sets (from the ZORA/TZP database of the ADF suite)[15] for all atoms. Scalar relativistic approaches were used within the ZORA Hamiltonian for the inclusion of relativistic effects[16] and the local density approximation (LDA) with the correlation potential due to Vosko *et al*. was used in all the calculations.[17] Gradient corrections were performed with Grimme's 3rd generation dispersion correction using the BP86-D3 density functional.[18,19] The structures of **2**, **2^0**, **2^2**, and **2^4** are shown in Figure S, with a comparison of key interatomic distances to the experimentally determined values in

Table S4.

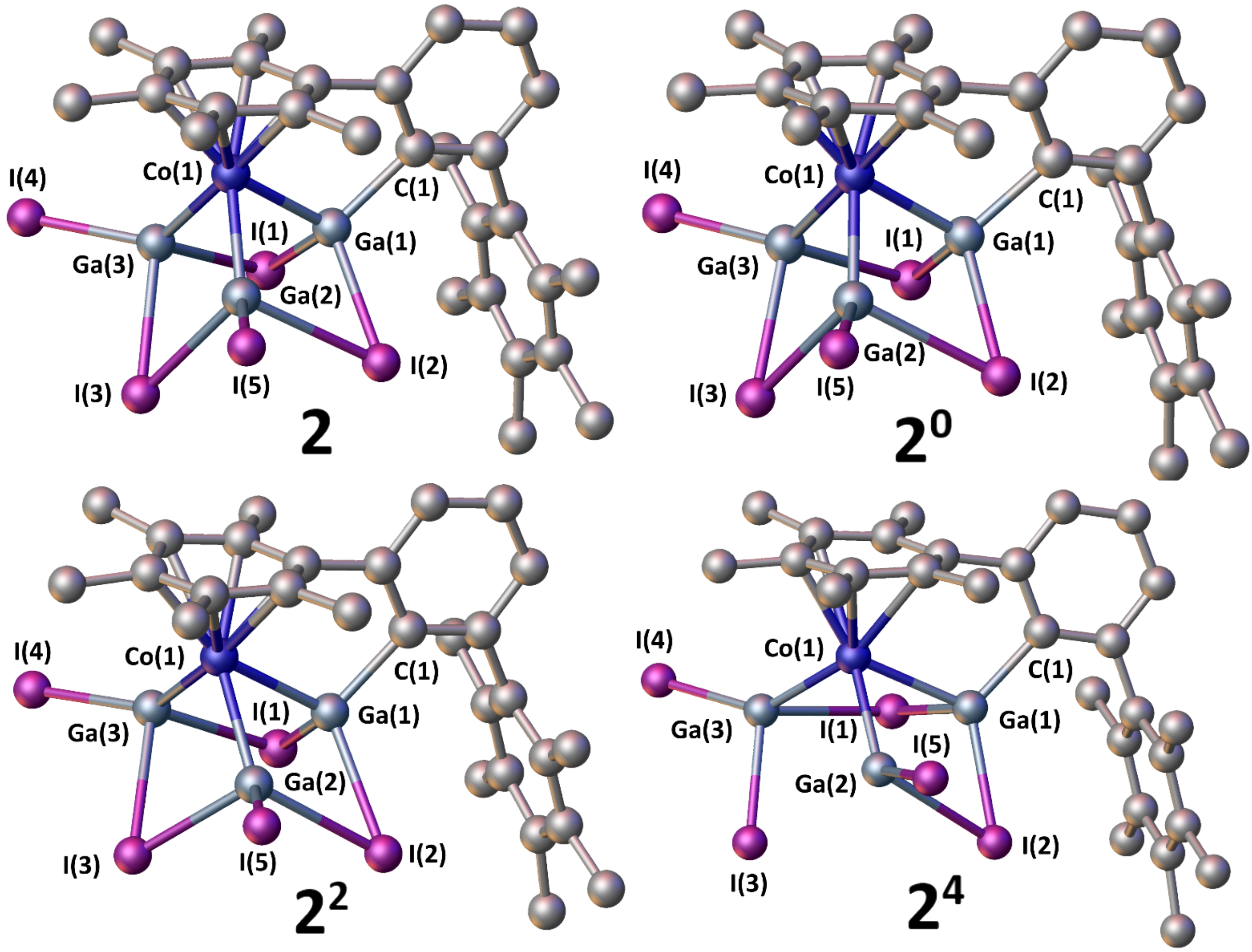


Figure S8: Structures of **2** (experimentally determined from crystal structure of **2**·GaI$_3$(THF)) and geometry optimised models of **2** with 0 (**2^0**), 2 (**2^2**), and 4 (**2^4**) unpaired electrons.

Table S4: Selected interatomic distances from the crystal structure of **2**·GaI_3(THF) and geometry optimised models of **2** with either 0 (**2^0**), 2 (**2^2**) or 4 (**2^4**) unpaired electrons.

	2·GaI_3(THF)	**2^0**	**2^2**	**2^4**
C(1)–Ga(1)	1.96(2)	1.9832	1.9906	1.9927
Ga(1)–Co(1)	2.374(3)	2.3816	2.5063	2.5140
Ga(2)–Co(1)	2.296(3)	2.3087	2.4274	2.5251
Ga(3)–Co(1)	2.277(4)	2.3018	2.4012	2.4325
Ga(1)–I(1)	2.661(2)	2.7033	2.6720	2.7724
Ga(1)–I(2)	2.698(2)	2.6973	2.7644	2.6624
Ga(2)–I(2)	2.862(3)	2.8986	2.8252	2.9509
Ga(3)–I(1)	2.917(3)	2.9212	2.9372	2.9950
Ga(2)–I(3)	2.696(3)	2.7924	2.7295	3.2677
Ga(3)–I(3)	2.772(2)	2.7946	2.9604	2.6887
Ga(3)–I(4)	2.540(2)	2.5783	2.6254	2.5971
Ga(2)–I(5)	2.532(2)	2.5795	2.5881	2.6848
Ga(1)···Ga(2)	2.966(3)	2.9491	2.6986	2.8356
Ga(1)···Ga(3)	3.017(3)	3.0619	3.1861	3.9855
Ga(2)···Ga(3)	2.948(3)	2.9292	3.4303	3.5723

S6.2 – QTAIM Analysis

A geometry optimisation was performed for a model of **2** using coordinates derived from the X-ray crystal structure of **2**·GaI_3(THF). This model was geometry optimised without restraints using the ORCA 4.2.1. software package.[20] The DFT geometry optimisation was performed using the BP86 density functional[18] with RI-J acceleration[21]and employed all-electron ZORA corrected[22] TZVP basis sets[23] along with SARC/J auxiliary basis sets decontracted def2/J up to Kr[24] and SARC auxiliary basis sets beyond Kr.[25] Gradient corrections were performed with Grimme's 3rd generation dispersion correction.[19] The optimisation was performed with TightOpt and DFT integration settings of Grid6, FinalGrid7. Molden and extended wavefunction (.wfx) files were generated using the orca_2mkl and orca_2aim utility programs provided by ORCA 4.2.1 and analysed using MultiWFN 3.6.[26] DDEC6 charges were computed from the .wfx file using the CHARGEMOL program,[27] available at [https://sourceforge.net/projects/ddec/].

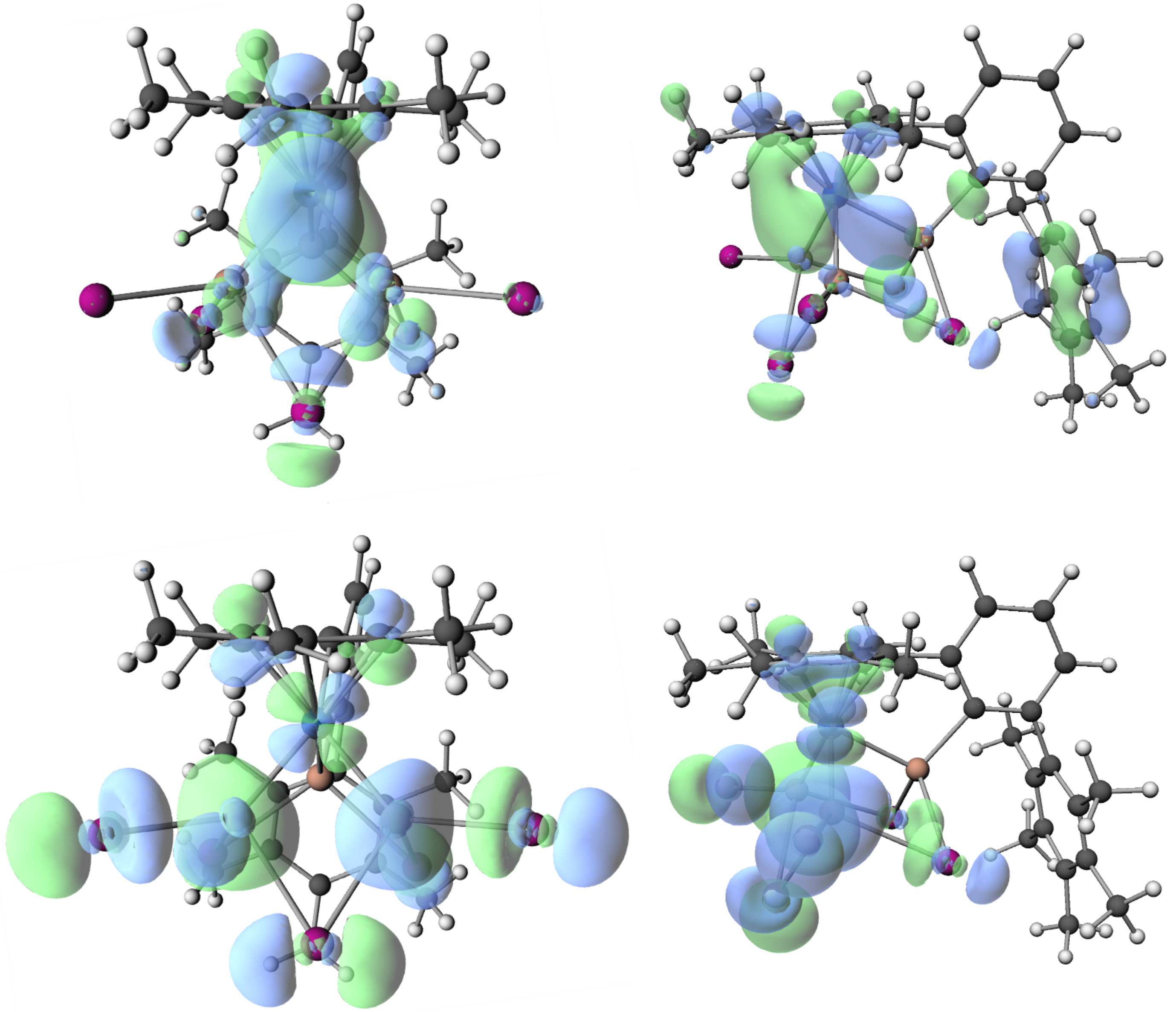


Figure S9: Visualisation of the HOMO (top, left and right) and LUMO (bottom, left and right) of **2**. Images generated by the MultiWFN 3.6 software package,[26] all isosurfaces set to 0.030 e·a_0^{-3}.

Table S5: Table of computed QTAIM parameters for atom interactions in the $[CoGa_3I_5C]$ cluster of **2**. All values in standard atomic units. CP Signature = Signature of critical point (CP) located between the two atoms in question. ρ_{CP} = Electron density at CP. $\nabla\rho_{CP}$ = Laplacian of the electron density at CP. G_{CP}, V_{CP}, H_{CP} = Kinetic Energy, Potential Energy, and Energy Density at CP, respectively. BD = Bond Degree (H_{BCP}/ρ_{BCP}).[28] $|V_{CP}|/G_{CP}$ = Parameter used to distinguish between closed shell, shared shell, and transit shared shell interactions.[28] Ellipticity = Measure of how circularly symmetric a bond is at a bond critical point, 0 = perfectly circularly symmetric. Only valid for bond critical points, signature (3,-1). Delocalisation Index = Measure of the degree of electron sharing between two atomic basins.[29]

Interaction	**CP Signature**	ρ_{CP}	$\nabla\rho_{CP}$	G_{CP}	V_{CP}	H_{CP}	**BD**	$\lvert V_{CP}\rvert/G_{CP}$	**Ellipticity**	**Delocalisation Index**
Ga(1)–Co(1)	3,−1	0.0671	0.0415	0.0335	−0.0566	−0.0231	-0.34	1.69	0.016	0.652
Ga(2)–Co(1)	3, −1	0.0721	0.0623	0.0414	−0.0672	−0.0258	-0.36	1.62	0.040	0.800
Ga(3)–Co(1)	3, −1	0.0729	0.0635	0.0421	−0.0684	−0.0263	-0.36	1.62	0.023	0.808
Ga(1)···Ga(2)	3,+1	0.0254	0.0392	0.0118	−0.0137	−0.0020	-0.08	1.17	-	0.125
Ga(2)···Ga(3)	3,+1	0.0251	0.0424	0.0124	−0.0141	−0.0018	-0.07	1.14	-	0.128
Ga(1)···Ga(3)	3,+1	0.0231	0.0397	0.0111	−0.0122	−0.0011	-0.05	1.10	-	0.097
Ga(1)–C(1)	3, −1	0.1097	0.1907	0.0862	−0.1247	−0.0385	-0.35	1.45	0.048	0.717
Ga(1)–I(1)	3, −1	0.0515	0.0404	0.0246	−0.0391	−0.0145	-0.28	1.59	0.020	0.592
Ga(1)–I(2)	3, −1	0.0514	0.0421	0.0250	−0.0394	−0.0145	-0.28	1.58	0.033	0.581
Ga(3)–I(1)	3, −1	0.0366	0.0336	0.0163	−0.0242	−0.0079	-0.22	1.48	0.101	0.443
Ga(2)–I(2)	3, −1	0.0389	0.0343	0.0175	−0.0264	−0.0089	-0.23	1.51	0.118	0.462
Ga(3)–I(3)	3, −1	0.0446	0.0366	0.0205	−0.0319	−0.0114	-0.26	1.55	0.064	0.542
Ga(2)-I(3)	3, −1	0.0450	0.0365	0.0207	−0.0322	−0.0116	-0.26	1.56	0.057	0.542
Ga(2)–I(5)	3, −1	0.0641	0.0413	0.0307	−0.0511	−0.0204	-0.32	1.66	0.010	0.805
Ga(3)–I(4)	3, −1	0.0644	0.0413	0.0309	−0.0515	−0.0206	-0.32	1.67	0.012	0.813

Table S6: Computed DDEC6 charges[27] for atoms in the [CoGa$_3$I$_5$C] core of compound **2**.

Atom	**Atomic charge**
I(1)	−0.176
I(2)	−0.164
I(3)	−0.170
I(4)	−0.268
I(5)	−0.265
Ga(1)	+0.395
Ga(2)	+0.321
Ga(3)	+0.328
Co(1)	−0.434
C(1)	−0.263

S6.3 – Geometry Optimised Coordinates

*S6.3.1 – Optimised Coordinates for **2**^{0}(ADF 2014.01)*

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I	14.24719022	10.63310789	6.45707802
I	11.04201199	7.99945173	5.57004295
I	10.51768786	12.08151217	4.72432555
I	12.74902017	14.63104487	7.25613270
I	7.21987196	9.76159778	6.27137912
Ga	12.28006448	9.20573271	7.64063601
Ga	9.70298827	10.30110361	6.71527095
Ga	11.88590631	12.20351551	7.15803860
Co	10.84078300	10.80643974	8.65949729
C	12.67820034	7.91165260	9.08973304
C	13.45440794	6.74321565	9.03253177
C	13.53329685	5.92673663	10.17058425
H	14.13370584	5.01599164	10.13156850
C	12.85096588	6.27170787	11.34218637
H	12.92046447	5.62689049	12.21986434
C	12.08456358	7.44027636	11.40077639
H	11.56082442	7.71412982	12.31847826
C	12.00135639	8.26413669	10.27010487
C	14.15603902	6.44031276	7.74862065
C	15.35620744	7.11637445	7.44844264
C	15.89724516	7.01492402	6.15102988
C	15.22740714	6.25835211	5.16626423
C	14.09400522	5.49243686	5.51127933
C	13.54374542	5.59192567	6.80538923
C	16.05932031	7.94243993	8.50348289
H	16.29311921	8.95303644	8.14209879
H	17.01145465	7.47237131	8.79761494
H	15.45114184	8.04515352	9.40810629
C	17.17622970	7.75161531	5.81906193
H	16.96677580	8.78534829	5.49548795
H	17.73887706	7.26122784	5.01635666
H	17.84039882	7.81820296	6.68909620
C	15.71655951	6.28504149	3.73305850
H	16.45868289	5.49431233	3.53255421

H	16.18699381	7.24479082	3.48976459
H	14.89081189	6.14640713	3.02567962
C	13.42666780	4.59452083	4.49296166
H	13.01193676	3.69433555	4.96310405
H	14.12230023	4.26312993	3.71401084
H	12.58941731	5.11212528	3.99421513
C	12.29082869	4.82200536	7.15903718
H	12.51132713	3.75053543	7.29419507
H	11.52970254	4.90277337	6.37198717
H	11.84234882	5.18660902	8.08907629
C	11.24128526	9.55590787	10.29171291
C	9.82660035	9.57836567	10.05614068
C	9.13834091	10.83875153	10.00886258
C	9.87466714	12.06047363	10.10057458
C	11.28269513	12.02666209	10.37678271
C	11.96933496	10.77655753	10.47940435
C	9.08907923	8.28237326	9.82377998
H	8.35858032	8.37878740	9.01127213
H	8.55314186	7.97084540	10.73355787
H	9.79011053	7.48545870	9.55669555
C	7.63530805	10.89049511	9.88148917
H	7.31670301	11.33609797	8.93063105
H	7.21969429	11.49895906	10.69736534
H	7.18400094	9.89725971	9.93505577
C	9.17432968	13.38693404	9.93093612
H	9.78464538	14.07462974	9.33362916
H	8.98482944	13.86189671	10.90631540
H	8.21610138	13.27367727	9.41726335
C	12.05348824	13.29118225	10.65051504
H	13.04675978	13.27674843	10.19025638
H	12.18957822	13.38973237	11.73970651
H	11.54410536	14.18676046	10.29036091
C	13.45679709	10.76016836	10.74110325
H	13.82792211	9.73822042	10.85455896
H	13.69449138	11.32163901	11.65530786
H	14.00533498	11.22516670	9.90949782

S6.3.2 – Optimised Coordinates for $\mathbf{2}^2$*(ADF 2014.01)*

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I	14.20524778	10.58919907	6.43356536
I	11.21252355	7.96643913	5.28534073
I	10.25231111	12.23747118	5.01525638
I	13.19812790	14.82330173	7.25986555
I	7.29842908	9.32873913	6.28540170
Ga	12.16530875	9.26044043	7.53466314
Ga	9.77267007	10.03746766	6.55799991
Ga	12.10169213	12.43854936	7.31809605
Co	10.68669607	10.98157545	8.59896189
C	12.55189438	8.03755826	9.05698927
C	13.35115151	6.87946954	9.02227022
C	13.52057719	6.13141996	10.19736602
H	14.13788811	5.23192318	10.16452795
C	12.91539534	6.52881194	11.39213468

H	13.05813338	5.93822253	12.29858566
C	12.13259794	7.68535475	11.43221019
H	11.66328802	8.00550192	12.36425825
C	11.94931483	8.43849349	10.26451978
C	14.00706021	6.48320103	7.73969881
C	15.23386288	7.07815930	7.38380305
C	15.76227041	6.84904448	6.09738667
C	15.06036438	6.03512003	5.18314989
C	13.90348409	5.34146836	5.59773625
C	13.36015057	5.57772566	6.87685347
C	15.99065878	7.93450469	8.37461751
H	16.35276015	8.86574432	7.92115033
H	16.87070862	7.39394177	8.76011319
H	15.36939776	8.20308927	9.23563388
C	17.07005037	7.50539833	5.71398474
H	16.91494725	8.55819597	5.42301712
H	17.56257501	6.99765163	4.87795929
H	17.77619697	7.50748445	6.55431027
C	15.53790995	5.91573976	3.75068515
H	16.25237085	5.08623090	3.61831037
H	16.03545784	6.83386491	3.41757362
H	14.70166984	5.74015940	3.06409193
C	13.20303106	4.37961255	4.66400345
H	12.73480356	3.55469482	5.21458686
H	13.89064454	3.93601833	3.93509489
H	12.40047170	4.88569574	4.10010473
C	12.07749904	4.89479695	7.29566346
H	12.24339107	3.82278242	7.48954541
H	11.30773771	4.97223522	6.51612485
H	11.66648241	5.33518107	8.21016308
C	11.13271738	9.69116829	10.30031615
C	9.71772524	9.62850608	10.10382355
C	8.98604528	10.84862213	9.99560696
C	9.66405040	12.10479585	10.16489884
C	11.03239848	12.14847999	10.55453159
C	11.79571485	10.94434423	10.51844162
C	9.03651438	8.29724153	9.91714387
H	8.40132619	8.29726937	9.02154027
H	8.39743479	8.06791510	10.78330042
H	9.77030068	7.49247464	9.81634830
C	7.49313927	10.85010363	9.77494372
H	7.22759125	11.29435569	8.80700117
H	6.99827013	11.43674087	10.56257403
H	7.07530234	9.84120842	9.78302126
C	8.90623796	13.39465183	9.96168333
H	9.57087587	14.19115881	9.61030432
H	8.43682834	13.72862061	10.90083756
H	8.11131286	13.27445197	9.21872953
C	11.68860250	13.45512195	10.91808994
H	12.09133036	13.97703216	10.03439979
H	12.52400353	13.29462105	11.60832939
H	10.97551381	14.13054824	11.40459978
C	13.29007482	10.99547171	10.71854700
H	13.76909217	10.08210939	10.35433631
H	13.53468439	11.09906697	11.78717818

H	13.72901382	11.84729446	10.18466424

S6.3.3 – Optimised Coordinates for ***2****^{4}(ADF 2014.01)*

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I	13.97425653	10.90372886	7.17620157
I	11.54043571	8.13207064	5.07286147
I	10.71897982	12.64188537	4.60284916
I	12.93492833	15.20637282	7.34647408
I	7.49700287	8.55726193	6.45570069
Ga	12.02996054	8.96390749	7.55416813
Ga	9.71377221	10.06789818	6.34700351
Ga	11.75329114	12.91025328	7.07008411
Co	10.87678831	11.04597481	8.36369498
C	12.57464179	7.86109088	9.12199307
C	13.28416594	6.65114006	9.03807980
C	13.61397328	5.96660530	10.21745693
H	14.16454823	5.02662429	10.15021485
C	13.24287026	6.48019304	11.46333396
H	13.50475953	5.93998711	12.37460546
C	12.53704126	7.68381663	11.54968583
H	12.24505713	8.08606604	12.52168512
C	12.19813420	8.37679210	10.37913172
C	13.65602494	6.13227073	7.68610542
C	14.83656876	6.59270193	7.06744136
C	15.11206234	6.21042632	5.73828471
C	14.19717659	5.39723189	5.03728739
C	13.05350092	4.88813459	5.68821734
C	12.76704853	5.27090107	7.01350893
C	15.78941125	7.50287244	7.81076293
H	16.03334733	8.39733552	7.22065239
H	16.73860802	6.99045259	8.03445897
H	15.36619395	7.84143972	8.76214399
C	16.37337448	6.70432477	5.06271162
H	16.18627447	7.63138871	4.49562292
H	16.77625144	5.96475427	4.36015419
H	17.16430487	6.92536978	5.78793675
C	14.40489961	5.10145910	3.56718073
H	14.84813786	4.10482668	3.40588333
H	15.06264208	5.83543684	3.09041764
H	13.45170346	5.12365402	3.02330968
C	12.08073379	4.00721937	4.93972288
H	11.54188592	3.32975825	5.61197800
H	12.57904835	3.39153030	4.18177991
H	11.32026771	4.61871723	4.42368186
C	11.46475769	4.84820990	7.65445224
H	11.38764646	3.75395208	7.74112746
H	10.60958975	5.18778896	7.04954761
H	11.34970049	5.26782403	8.65890189
C	11.43356433	9.66590471	10.43621410
C	10.02761343	9.65298512	10.21415690
C	9.33048516	10.88485085	10.03330437
C	10.04351252	12.12275243	10.15805439
C	11.41021207	12.11967792	10.57576309

C	12.12212182	10.89233568	10.64384803
C	9.28181505	8.35334330	10.10904159
H	8.87216687	8.21675655	9.09535276
H	8.42530365	8.34563597	10.79818407
H	9.92731687	7.50080169	10.33643488
C	7.83926063	10.84677567	9.81165993
H	7.56538396	10.12464629	9.03179625
H	7.42991745	11.81913740	9.52846624
H	7.33871572	10.53407128	10.74169827
C	9.34113995	13.44081336	9.92233109
H	10.05236820	14.22204373	9.63453121
H	8.80562555	13.77432985	10.82496226
H	8.61055208	13.35699508	9.11081618
C	12.10817719	13.40969325	10.91495261
H	12.56474376	13.87359458	10.02496880
H	12.90855645	13.24259436	11.64369948
H	11.41233616	14.14032480	11.34190123
C	13.60237587	10.89096646	10.92132421
H	14.05627114	9.94296894	10.61802777
H	13.79185602	11.02720412	11.99804526
H	14.10734895	11.69981232	10.38093467

*S6.3.3 – Optimised Coordinates for **2** (ORCA 4.2.1)*

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I	14.30222058799502	10.62575838625508	6.48846806341056
I	11.16121381824480	8.03108138991442	5.57795532424540
I	10.64037229475393	12.05889608829881	4.75864354220936
I	12.86362279654085	14.57716956950375	7.26984793946049
I	7.35254155986511	9.72650322031442	6.19352267780205
Ga	12.35610137601397	9.20352775625520	7.68085558107582
Ga	9.80755347215469	10.27411364014759	6.70759104206397
Ga	11.97180491318170	12.17383252885488	7.19074796312795
Co	10.90112764794661	10.78535746881392	8.66015812964421
C	12.72261319353882	7.91031703027435	9.13542198505174
C	13.47960804678632	6.73101809317795	9.07566370455491
C	13.54220163649828	5.90960325483666	10.21079723595896
H	14.12749102506021	4.98875913102010	10.17342410611687
C	12.85999244518566	6.26341234607322	11.38006001991134
H	12.91714048028687	5.61646042136033	12.25718001738678
C	12.10471990131444	7.43950483651860	11.43692515188831
H	11.57573655737417	7.71368953336478	12.35180306212179
C	12.03531055874143	8.26656898165818	10.30788451208667
C	14.15875988071646	6.43023124063015	7.78122177191489
C	15.34756508615222	7.11806840836836	7.45961776697560
C	15.84169119684057	7.05386848826923	6.14224286600215
C	15.14905335627760	6.30511087468456	5.16833575297963
C	14.03373335916155	5.52458744352533	5.53095385350669
C	13.51939704684500	5.59949384439269	6.84074099636020
C	16.07864419658958	7.91022213302548	8.52009717373898
H	16.18089191259095	8.97038855864301	8.24451746401919
H	17.09377305810716	7.51347391685418	8.67879245904395
H	15.55490445101506	7.86704360803162	9.48122100803516
C	17.08977878963586	7.81266575926321	5.75679360532424

H	16.84242859508746	8.72295452753344	5.18485217844026
H	17.75595227822588	7.20564920628603	5.12752447193526
H	17.66202797834671	8.13186193685071	6.63435699464534
C	15.61388587474109	6.33461741797613	3.73075229060229
H	16.33081703845286	5.52456280179494	3.51129338342956
H	16.11181076329145	7.28171062172979	3.49046290946825
H	14.77299352518698	6.22311569219887	3.03503469593020
C	13.34865322763747	4.64941767561512	4.50829783998651
H	12.85842245602867	3.78862236161142	4.97899338115132
H	14.05487470599264	4.26044915103036	3.76423387740919
H	12.56756130340124	5.20615619496357	3.96127700758847
C	12.27615135648528	4.82605763178556	7.21302126922148
H	12.48351881400336	3.74508109305190	7.27931499256832
H	11.47867281355254	4.96115387442341	6.46921436016987
H	11.88051071537802	5.14579332973590	8.18321642301251
C	11.26810081227043	9.55119467541756	10.30831997409595
C	9.86157084487879	9.55761799990323	10.03031979516357
C	9.16403346882533	10.81077249693469	9.95236925013512
C	9.88514012082257	12.03976608616028	10.05907025805346
C	11.28503175713652	12.02293368113670	10.37128618925860
C	11.98048542827805	10.77990272132194	10.50064777737911
C	9.14077892625262	8.25555405185923	9.79336652220991
H	8.43389272038198	8.33232743872028	8.95697484157469
H	8.57605739153321	7.95362041553034	10.69008594188564
H	9.85423590686839	7.45701160407889	9.56356917358112
C	7.66689833723158	10.84358451007588	9.78337210632585
H	7.36236372740151	11.27705239669794	8.82112446157480
H	7.21987079359415	11.45036401071545	10.58474133565945
H	7.23041561473566	9.84250288683738	9.83191142202047
C	9.16932511758473	13.35231008004225	9.86819134477341
H	9.78585013133699	14.06096149272794	9.30159582676136
H	8.92833175827218	13.81768829067462	10.83807488672957
H	8.23359323975712	13.21989748773334	9.31660613253917
C	12.03050278466852	13.29719212134739	10.65644750290692
H	13.05376702950378	13.27501498894800	10.26633740814936
H	12.09227459616558	13.43356304839500	11.74941106600112
H	11.54236928087113	14.17864859908383	10.23403959406520
C	13.45609837323917	10.77740921791906	10.80866430856183
H	13.84579613760079	9.75706622775224	10.86882683540071
H	13.64851360216655	11.27960621084837	11.76877608136573
H	14.02763516739458	11.31080825021993	10.03551944225022

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