Electronic Supplementary Information

Synthesis and decarbonylation chemistry of gallium phosphaketenes

Daniel W. N. Wilson,[a] William K. Myers,[b] and Jose M. Goicoechea[a,*]

a. Department of Chemistry, University of Oxford, Chemistry Research Laboratory, 12 Mansfield Road, Oxford, OX1 3TA, U.K.

b. Department of Chemistry, University of Oxford, Centre for Advanced ESR, Inorganic Chemistry Laboratory, South Parks Road, Oxford, OX1 3QR, UK.

E-mail: jose.goicoechea@chem.ox.ac.uk

Contents

1. Experimental Section

1.1. General synthetic methods

All reactions and product manipulations were carried out under an inert atmosphere of argon or dinitrogen using standard Schlenk-line or glovebox techniques (MBraun UNIlab glovebox maintained at <0.1 ppm H_2O and <0.1 ppm O_2). **1a** and [Na(dioxane)$_x$](PCO) and the N-heterocyclic carbenes 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (^{Me2}IPr) and 1,3-dimesitylimidazol-2-ylidene (IMes) were synthesized according to previously reported synthetic procedures.[1–4] Hexane (hex; Sigma Aldrich, HPLC grade), and toluene (Sigma Aldrich, HPLC grade) were purified using an MBraun SPS-800 solvent system. Diethyl ether and pyridine were dried over sodium metal/benzophenone and distilled prior to use. C_6D_6 (Aldrich, 99.5%) was degassed prior to use. All dry solvents were stored under argon in gas-tight ampoules. All solvents were stored over 3 Å molecular sieves.

Additional characterization techniques: NMR spectra were acquired on a Bruker AVIII 500 MHz NMR spectrometer (^{1}H 500 MHz, ^{13}C 126 MHz) and Bruker AVIII 400 MHz NMR spectrometer (^{1}H 400 MHz, ^{31}P 162 MHz). ^{1}H and ^{13}C NMR spectra were referenced to the most downfield solvent resonance (^{1}H NMR C_6D_6: $\delta = 7.16$ ppm; ^{13}C NMR C_6D_6: $\delta = 188.06$ ppm). ^{31}P NMR spectra were externally referenced to an 85% solution of H_3PO_4 in H_2O. Elemental analyses were carried out by Elemental Microanalyses Ltd. (Devon, U.K.). Samples (approx. 5 mg) were submitted in sealed Pyrex ampoules.

1.2. Synthesis of (Dipp-Bian) Gallium iodides 1a–c.

The gallium iodides were made in one pot syntheses adapted from Fedushkin and co-workers original synthesis of **1a**. Note: These compounds are extremely oxygen sensitive and require careful handling during filtration and crystallisation steps.

General procedure: Dipp-Bian (0.5g, 1.0 mmol) was dissolved in toluene in an ampoule with an excess of gallium metal. The ampoule was sealed under vacuum, and heated to 130 °C overnight. The solution turns from orange to deep blue. The solution was cooled to room temperature and iodine (0.13 g, 0.5 mmol) was added with rapid stirring. The solution was stirred for two hours, turning brick red in colour. Volatiles were removed under reduced pressure, and the resulting red powder dissolved in pyridine (20 ml). Heating this suspension to reflux causes the colour to turn bright blue. The remaining synthesis depends on the derivative (**a**–**c**):

1a: Volatiles were removed and the resulting blue powder crystallized by cooling a concentrated toluene solution (yields 40–65 %). NMR characterisation can be found in the original publication.

1b: Volatiles were removed and the blue powder redissolved in toluene, followed by the addition of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (^{Me2}IPr) (0.18 g, 1.0 mmol). The solution changed colour from blue to green. Concentration of the solution and cooling resulted in formation of analytically pure green powders of **1b** (typical yields 40–50%).

Alternatively route to **1b** from **1a**: To a solution of (Dipp-Bian)GaI(Pyr) (200 mg, 0.26 mmol) in toluene (10 mL) was added 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (46 mg, 0.26

mmol) and an immediate colour change from blue to green was observed. The reaction mixture was stirred overnight and the solvent removed. The green solid was extracted in toluene and filtered. The filtrate was concentrated and placed in the freezer to yield (dipp-Bian)GaI(NHC) as an emerald green crystalline powder (120 mg, 52.6 %). **CHN** Anal. Calcd. for $C_{47}H_{61}Ga_{I}N_4$: C, 64.25; H, 7.00; N, 6.38. Found: C, 65.21; H, 7.21; N, 6.49. **^{1}H NMR** (500 MHz, C_6D_6): δ (ppm) 7.36 (dd, $^3J_{\mathrm{H–H}}$ = 7.6, 1.6 Hz, 2H, Ar*H*), 7.27 (t, $^3J_{\mathrm{H–H}}$ = 7.6 Hz, 2H, Ar*H*), 7.22 (dd, $^3J_{\mathrm{H–H}}$ = 7.6, 1.6 Hz, 2H, Ar*H*), 7.14–7.10 (m, 2H, Ar*H*), 6.88 (dd, $^3J_{\mathrm{H–H}}$ = 8.2 Hz, 7.0, 2H, Ar*H*), 6.20 (d, $^3J_{\mathrm{H–H}}$ =6.9 Hz, 2H, Ar*H*), 4.89 (sept, $^3J_{\mathrm{H–H}}$ = 6.8 Hz, 2H, {C*H*(CH_3)$_2$}), 4.26 (sept, $^3J_{\mathrm{H–H}}$ = 6.9 Hz, 2H, {C*H*(CH_3)$_2$}), 3.82 (sept, $^3J_{\mathrm{H–H}}$ = 6.9 Hz, 2H, {C*H*(CH_3)$_2$}), 1.55 (d, $^3J_{\mathrm{H–H}}$ = 6.9 Hz, 6H, {CH(C*H*$_3$)$_2$}), 1.42 (d, $^3J_{\mathrm{H–H}}$ = 6.7 Hz, 6H, {CH(C*H*$_3$)$_2$}), 1.23 (s, 6H, NHC {CH(C*H*$_3$)$_2$}), 1.08 (dd, $^3J_{\mathrm{H–H}}$ = 15.9, 6.9 Hz, 14H, {CH(C*H*$_3$)$_2$}), 0.92 (d, $^3J_{\mathrm{H–H}}$ = 6.7 Hz, 12H, {CH(C*H*$_3$)$_2$}). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ (ppm) 148.92 (s, Ar*C*), 148.23 (Ar*C*), 145.78 (Ar*C*), 136.24 (Ar*C*), 134.25 (Ar*C*), 127.47 (Ar*C*), 127.08 (Ar*C*), 125.76 (Ar*C*), 124.67 (Ar*C*), 124.29 (Ar*C*), 123.80 (Ar*C*), 118.51 (NHC N*C*N), 54.84 (NHC), 29.75 (Dipp methine*C*), 27.95 (Dipp methine*C*), 26.32 (Dipp methyl*C*), 26.04 (Dipp methyl*C*), 24.74 (Dipp methyl*C*), 24.05 (Dipp methyl*C*), 21.79 (NHC backbone methyl), 9.85 (NHC Dipp methyl*C*).

1c: Volatiles were removed and the blue powder dissolved in toluene, followed by the addition of IMes (0.30 g, 1.0 mmol) resulting in a colour change from blue to green. Concentration of the toluene solution and cooling resulted in precipitation of **1c** (typical yields ranging from 30–40%). **CHN** Anal. Calcd. for $C_{63}H_{76}Ga_{I}N_4$: C, 69.68; H, 7.05; N, 5.16. Found: C, 69.10; H, 6.61; N, 5.65. **^{1}H NMR** (500 MHz, C_6D_6): δ (ppm) 7.37 (d, $^3J_{\mathrm{H–H}}$ = 9.3 Hz, 2H, Ar*H*), 7.27 (t, $^3J_{\mathrm{H–H}}$ = 7.6 Hz, 2H, Ar*H*), 7.19 (d, $^3J_{\mathrm{H–H}}$ = 9.5 Hz, 2H, Ar*H*), 7.02 (dd, $^3J_{\mathrm{H–H}}$ = 14.3 Hz, 7.8 Hz, 5H), 6.93 (d, $^3J_{\mathrm{H–H}}$ = 14.5, 2H, Ar*H*), 6.83 (t, $^3J_{\mathrm{H–H}}$ = 7.6 Hz, 2H, $^3J_{\mathrm{H–H}}$), 6.65 (d, $^3J_{\mathrm{H–H}}$ = 17.4 Hz, 4H, Ar*H*), 6.44 (s, 2H), 6.28 (d, $^3J_{\mathrm{H–H}}$ = 6.9 Hz, 2H), 6.24 (s, 1H, abnormal NHC C*H*), 4.64

(sept, $^3J_{\mathrm{H–H}}$ = 6.8 Hz, 2H, $\{\mathrm{C}H(\mathrm{CH}_3)_2\}$), 3.96 (sept, $^3J_{\mathrm{H–H}}$ = 6.8 Hz, 2H, $\{\mathrm{C}H(\mathrm{CH}_3)_2\}$), 2.14–2.09 (m, 9H, Mes$\mathrm{C}H_3$), 1.94 (s, 3H, Mes$\mathrm{C}H_3$), 1.76 (s, 6H, Mes$\mathrm{C}H_3$), 1.58 (s, 6H, Mes$\mathrm{C}H_3$), 1.54 (s, 6H, Mes$\mathrm{C}H_3$), 1.40 (d, $^3J_{\mathrm{H–H}}$ = 6.7, 6H, $\{\mathrm{CH}(\mathrm{C}H_3)_2\}$), 1.34 (d, $^3J_{\mathrm{H–H}}$ = 6.7, 6H, $\{\mathrm{CH}(\mathrm{C}H_3)_2\}$), 1.19 (d, $^3J_{\mathrm{H–H}}$ = 6.7, 6H, $\{\mathrm{CH}(\mathrm{C}H_3)_2\}$), 1.13 (d, $^3J_{\mathrm{H–H}}$ = 7.0, 6H, $\{\mathrm{CH}(\mathrm{C}H_3)_2\}$). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ (ppm) 148.40 (s, Ar*C*), 146.68 (Ar*C*), 145.88 (Ar*C*), 140.36 (Ar*C*), 139.16 (Ar*C*), 137.65 (Ar*C*), 137.53 (Ar*C*), 137.40 (Ar*C*), 136.82 (Ar*C*), 135.43 (Ar*C*), 134.76 (Ar*C*), 133.50 (Ar*C*), 132.03 (Ar*C*), 130.58 (Ar*C*), 129.57 (Ar*C*), 129.42 (Ar*C*), 129.22 (Ar*C*), 128.96 (Ar*C*), 128.70 (Ar*C*), 126.81 (Ar*C*), 125.33 (Ar*C*), 124.39 (Ar*C*), 124.22 (Ar*C*), 123.23 (Ar*C*), 122.85 (Ar*C*), 120.31 (NHC *C*Ga), 117.43 (NHC backbone), 28.30 ($\{\mathrm{C}H(\mathrm{CH}_3)_2\}$), 28.00 (($\{\mathrm{C}H(\mathrm{CH}_3)_2\}$)), 26.08 ($\mathrm{C}H_3$), 25.24 ($\mathrm{C}H_3$), 24.79 ($\mathrm{C}H_3$), 21.06 ($\mathrm{C}H_3$), 20.73 ($\mathrm{C}H_3$), 20.66 ($\mathrm{C}H_3$), 20.56 ($\mathrm{C}H_3$), 17.79 ($\mathrm{C}H_3$), 17.26 ($\mathrm{C}H_3$), 16.66 ($\mathrm{C}H_3$).

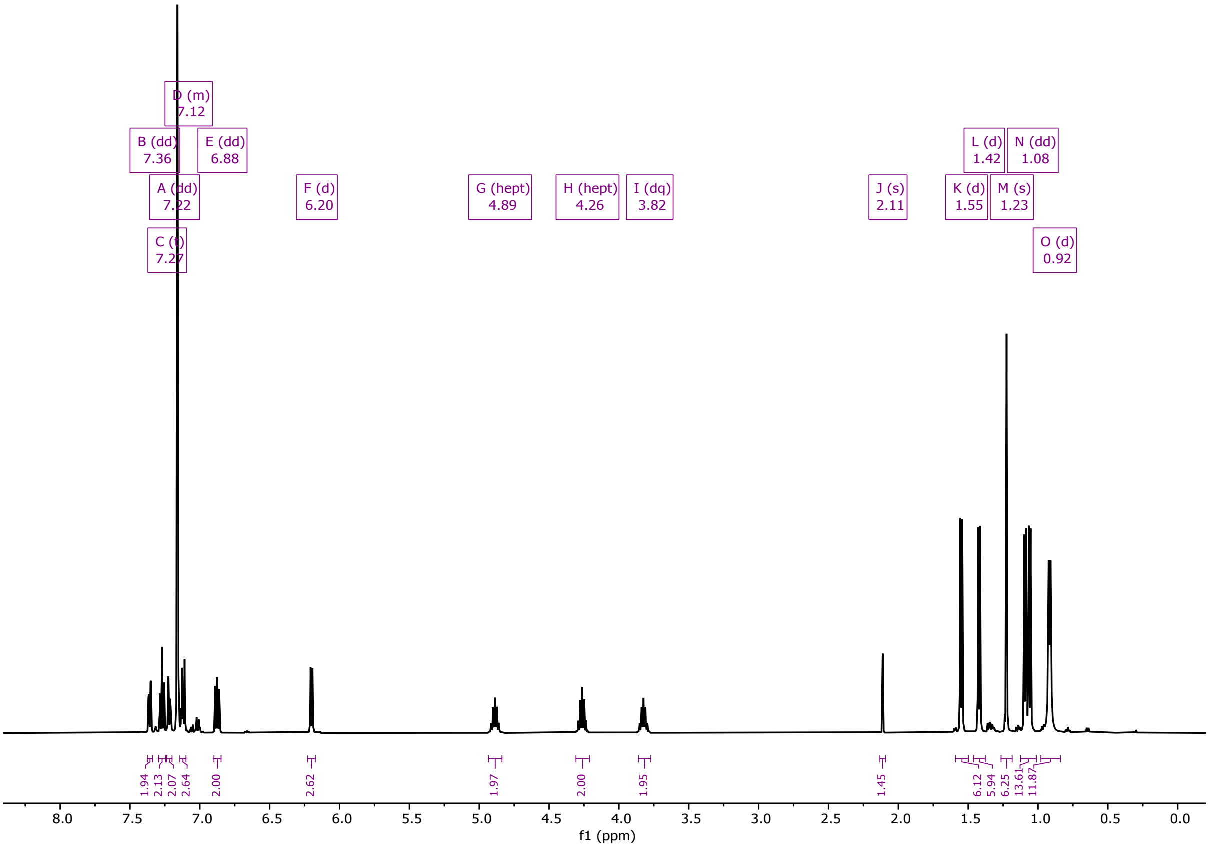


Figure S1. ^{1}H NMR spectrum of **1b** in C_6D_6.

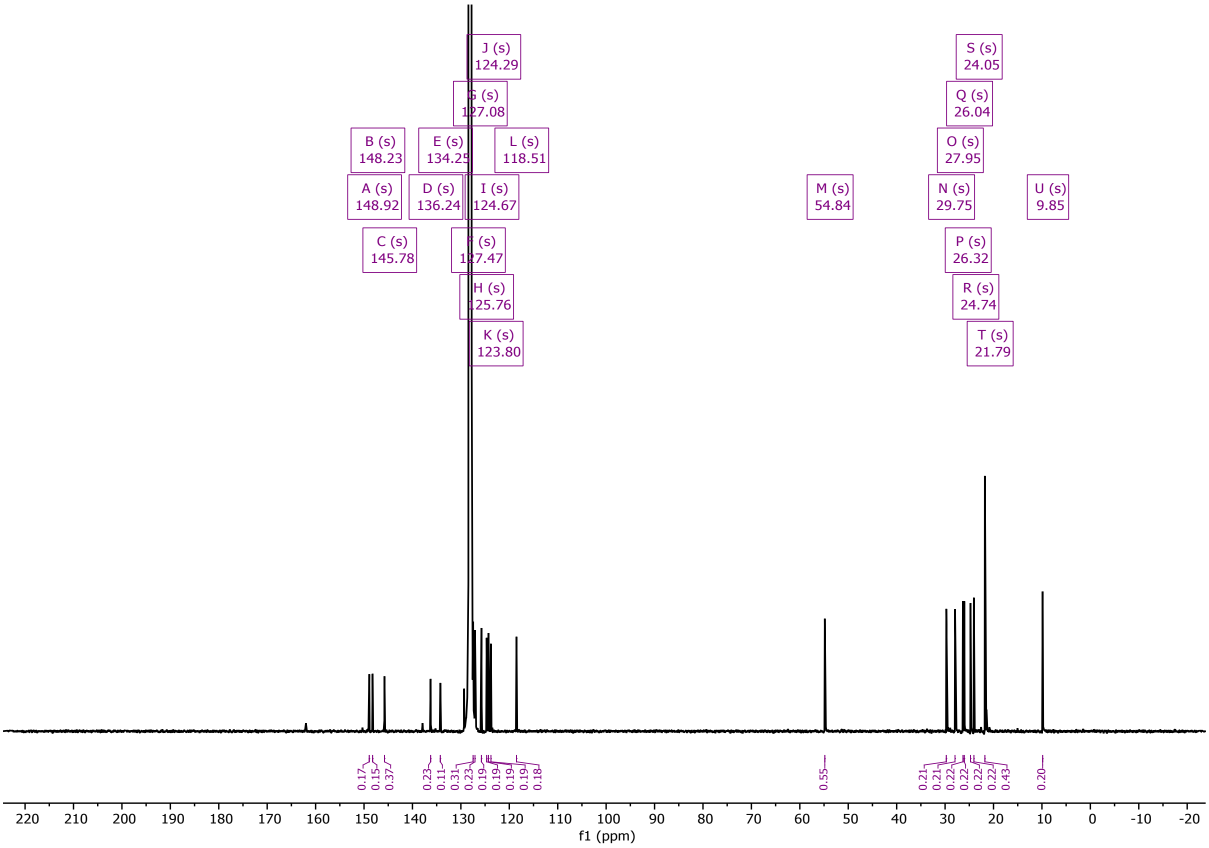


Figure S2. ^{13}C NMR spectrum of **1b** in C_6D_6.

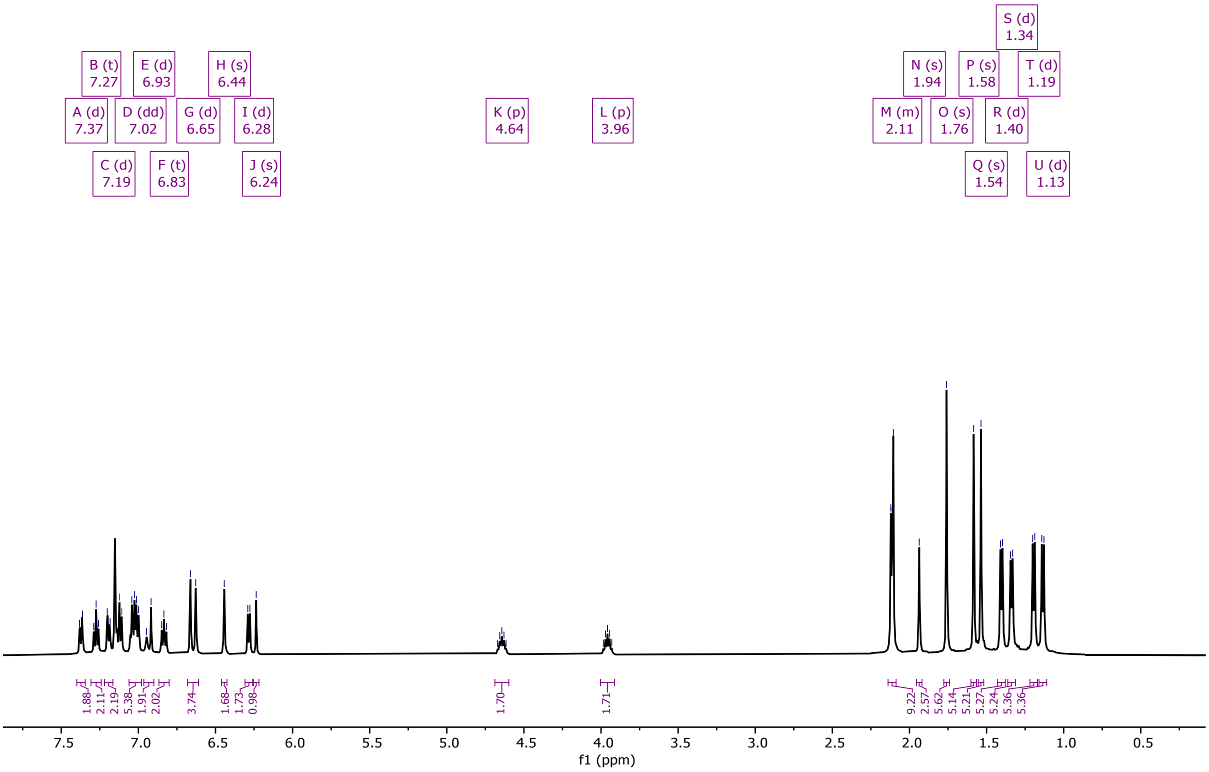


Figure S3. ^{1}H NMR spectrum of **1c** in C_6D_6.

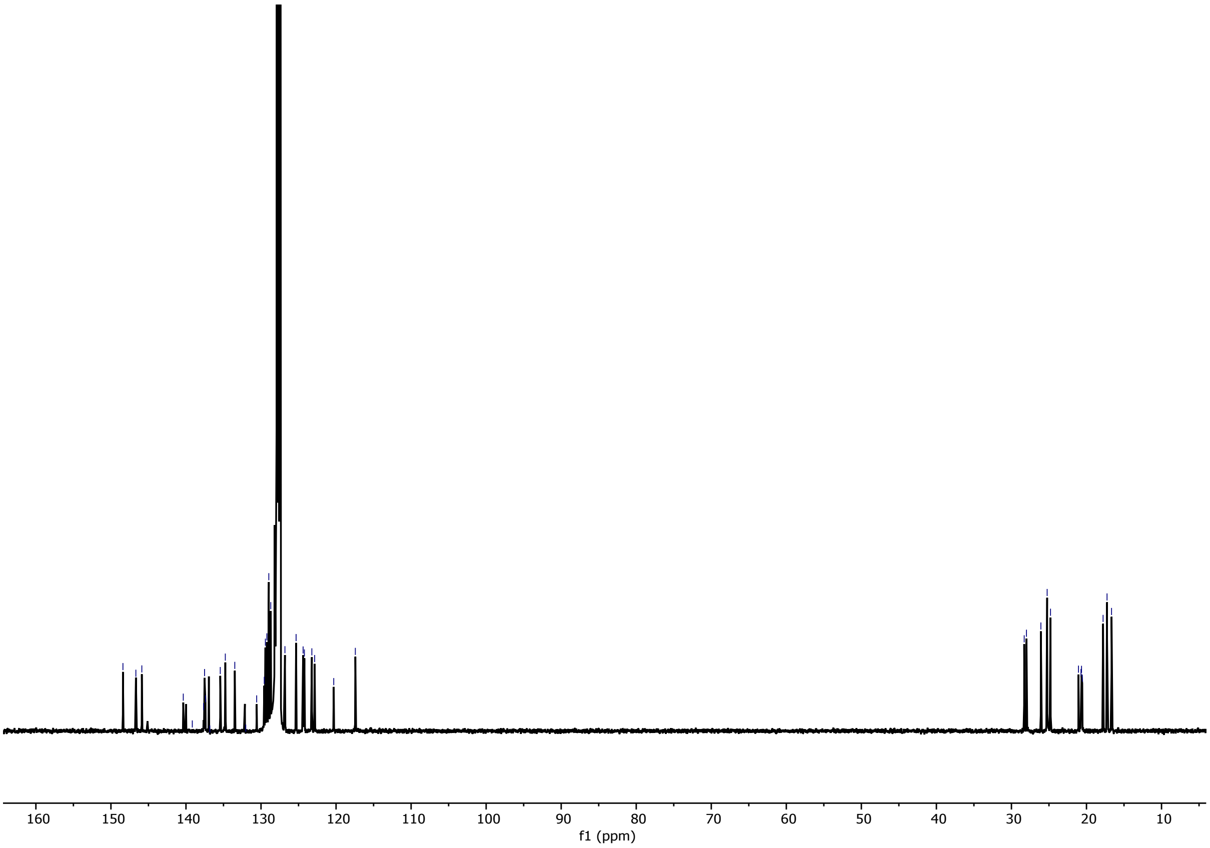


Figure S4. ^{13}C NMR spectrum of **1c** in C_6D_6.

1.4. Synthesis of (Dipp-Bian)Ga(Pyr)(PCO) (2a).

To a solution of (Dipp-Bian)GaI(Pyr) (100 mg, 0.13 mmol) in toluene (2 mL) was added [Na(dioxane)$_{0.6}$](PCO) (21 mg, 0.16 mmol) and the reaction mixture was stirred for 10 minutes. The solution was filtered and the solvent removed to yield (Dipp-Bian)Ga(PCO)(Pyr) (81 mg, 88.7 %) as a dark blue powder. Single crystals suitable for X-ray diffraction were grown by cooling a concentrated toluene solution to –30 °C.

CHN Anal. Calcd. For $C_{42}H_{45}GaN_3OP$: C, 71.20; H, 6.40; N, 5.93. Found: C, 72.56; H, 6.43; N, 5.25. **^{1}H NMR** (500 MHz, C_6D_6) $\delta = 8.63$ (d, $^3J_{H-H} = 5.0$ Hz, 2H, pyr *ortho* C*H*), 7.29−7.31 (m, 4H, Ar*H*), 7.19−7.22 (m, 2H, Ar*H*), 7.09 (d, $J = 8.2$ Hz, 2H, Ar*H*), 6.89 (dd, $^3J_{H-H} = 8.25$, 6.94 Hz, 2H, Ar*H*), 6.68 (t, $^3J_{H-H} = 7.7$ Hz, 1H, pyr *para* C*H*), 6.41 (d, $^3J_{H-H} = 6.8$ Hz, 2H, Ar*H*), 6.27 (m, 2H, pyr *meta* C*H*), 3.96 (sept, $^3J_{H-H} = 6.7$ Hz, 2H, $\{CH(CH_3)_2\}$), 3.29 (sept, $^3J_{H-H} = 6.8$ Hz, 2H, $\{CH(CH_3)_2\}$), 1.54 (d, $^3J_{H-H} = 6.9$ Hz, 6H, $\{CH(CH_3)_2\}$), 1.25 (d, $^3J_{H-H} = 6.9$ Hz, 6H, $\{CH(CH_3)_2\}$), 1.15 (d, $^3J_{H-H} = 6.8$ Hz, 6H, $\{CH(CH_3)_2\}$), 0.42 (d, $^3J_{H-H} = 6.8$ Hz, 6H, $\{CH(CH_3)_2\}$). **^{13}C NMR** (126 MHz, C_6D_6) $\delta = 180.76$ (d, $^1J_{C-P} = 101.0$ Hz, P*C*O), 148.27 (Ar*C*), 147.47 (pyr*C*), 146.42 (Ar*C*), 143.38 (Ar*C*), 141.23 (pyr*C*), 135.92 (Ar*C*), 127.39 (Ar*C*), 126.15 (Ar*C*), 125.30 (pyr*C*), 124.93, 124.18 (Ar*C*), 123.04 (Ar*C*), 117.98 (Ar*C*), 28.83 ($\{CH(CH_3)_2\}$), 28.68 ($\{CH(CH_3)_2\}$), 25.76 (($\{CH(CH_3)_2\}$)), 25.04 (($\{CH(CH_3)_2\}$)), 24.32 (($\{CH(CH_3)_2\}$)), 24.17 ($\{CH(CH_3)_2\}$)). **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ (ppm) –394.6 (s).

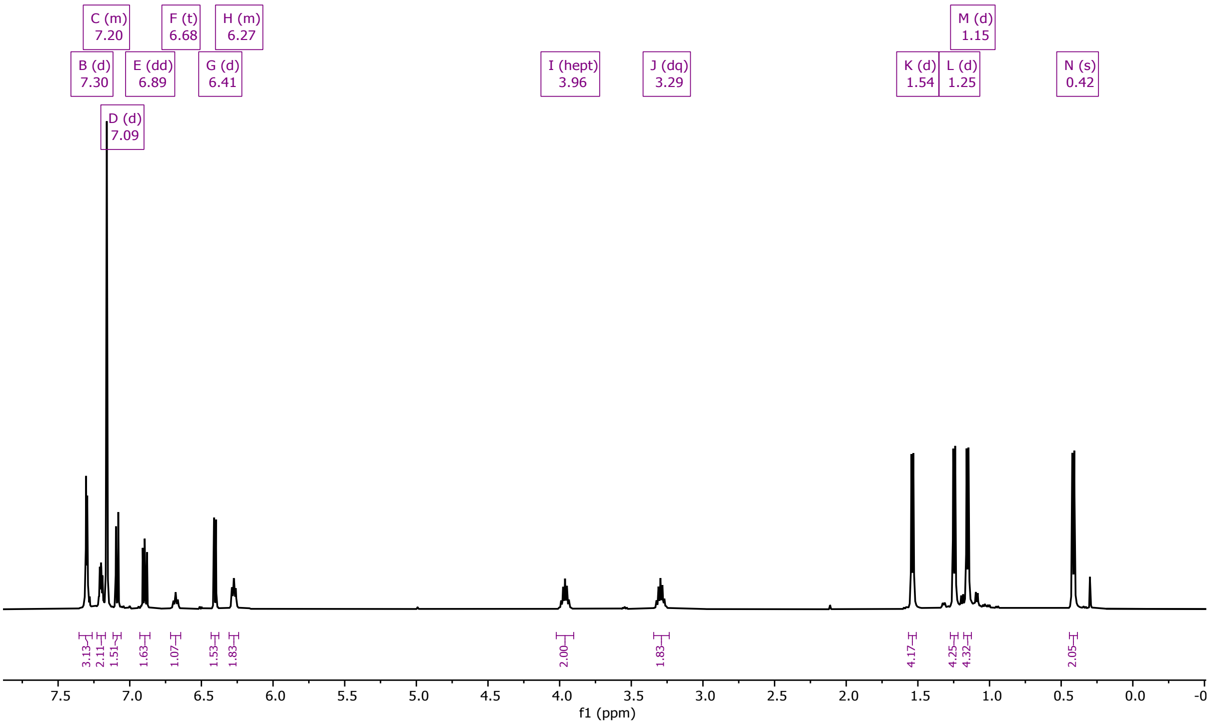


Figure S5. ^{1}H NMR spectrum of **2a** in C_6D_6.

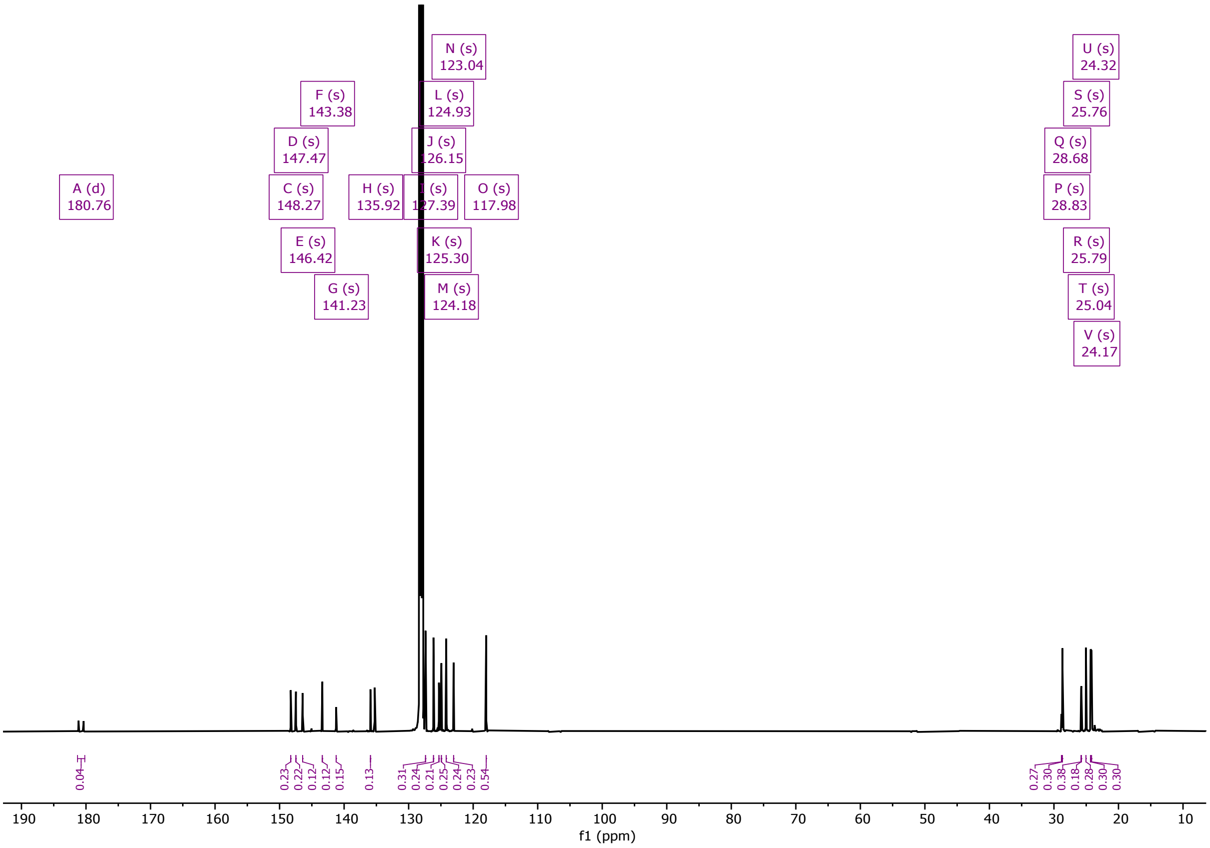


Figure S6. ^{13}C NMR spectrum of **2a** in C_6D_6.

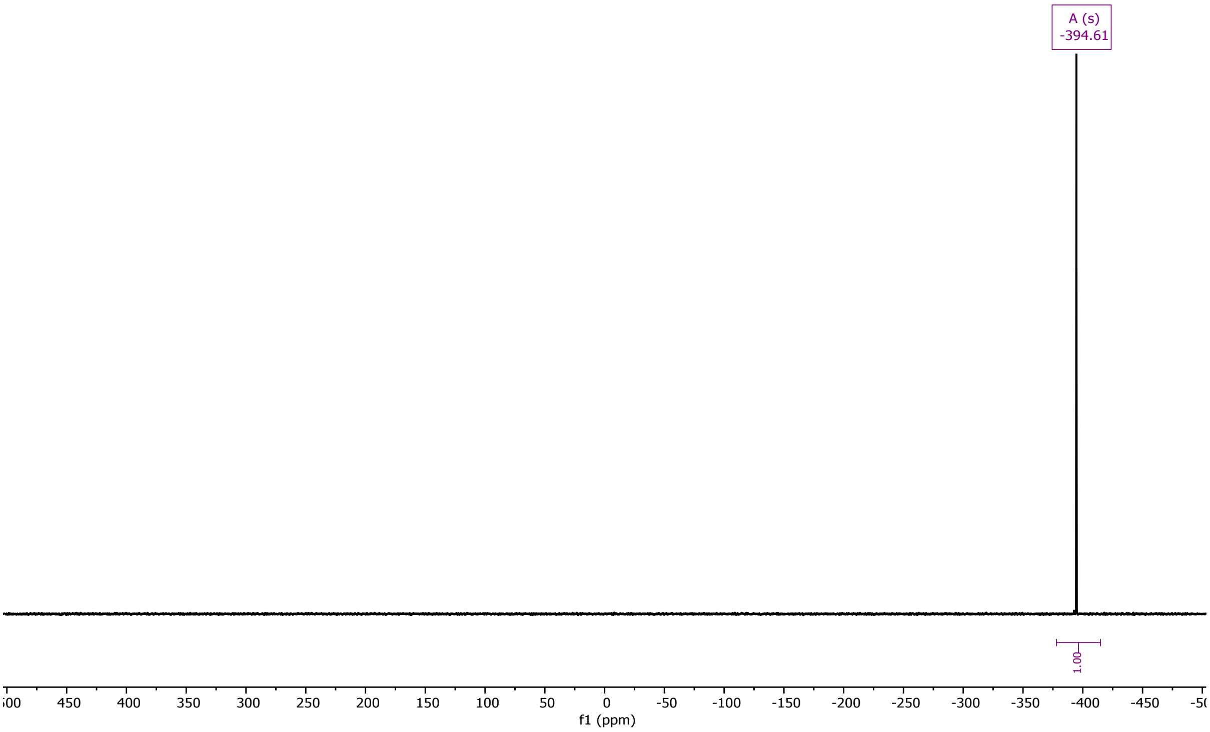


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of **2a** in C_6D_6.

1.5. Synthesis of (Dipp-Bian)Ga(PCO)(^{Me2}IPr) (2b).

This complex can be synthesised from (Dipp-Bian)GaI(NHC), however due to the sensitivity of these compounds, which undergo decomposition during crystallisation even in Schlenk tubes, the compound is synthesised directly from the ligand with minimal filtration and recrystallisation steps.

Dipp-Bian (500 mg, 1.0 mmol) was refluxed (110 °C) in an ampoule fitted with a J. Young tap over an excess of gallium metal (> 10 eq.) for 12 hours. The resulting dark blue solution was filtered and iodine (130 mg, 1.0 mmol) was added. The solution was stirred for 6 hours, forming a brick red suspension, and the solvent removed. Pyridine (20 mL) was added and the reaction heated to reflux, at which point the solution turns from red to blue. The solvent was removed and the blue solid redissolved in toluene. 1,3-Diisopropyl-4,5-dimethylimidazol-2-ylidene (180 mg, 1.0 mmol) was added and the solution turned from blue to green. After 2 hours [Na(dioxane)$_{0.6}$](PCO) (1.2 eq, 1.2 mmol) was added and the solution filtered to a second ampoule before being concentrated and stored at 5 °C overnight to yield (Dipp-Bian)Ga(PCO)(^{Me2}IPr) as a green powder (280 mg, 35%). The solution was then concentrated and cooled to yield a second crop.

CHN Anal. Calcd. for $C_{48}H_{61}GaN_4OP$: C, 71.11; H, 7.58; N, 6.91. Found: C, 69.43; H, 7.90; N, 6.86. **^{1}H NMR** (400 MHz, C_6D_6) δ = 7.34 (dd, $^3J_{H-H}$ = 7.4, 1.8, 2H, Ar*H*), 7.30–7.19 (m, 6H, Ar*H*), 7.11 (s, 2H, Ar*H*), 6.91–6.82 (m, 2H, Ar*H*), 6.20 (d, $^3J_{H-H}$ = 6.9, 2H, Ar*H*), 4.67–4.55 (m, 2H, NHC{C*H*(CH$_3$)$_2$}), 4.34 (sept, $^3J_{H-H}$ = 6.7, 2H, {C*H*(CH$_3$)$_2$}), 3.88 (sept, $^3J_{H-H}$ = 7.0, 2H, {C*H*(CH$_3$)$_2$}), 1.53 (d, $^3J_{H-H}$ = 6.9, 6H, {CH(C*H*$_3$)$_2$}), 1.43 (d, $^3J_{H-H}$ = 6.7, 6H, {CH(C*H*$_3$)$_2$}), 1.28 (s, 6H, C*H*$_3$), 1.09 (dd, $^3J_{H-H}$ = 13.9, 6.9, 12H, {CH(C*H*$_3$)$_2$}), 0.93 (d, $^3J_{H-H}$ = 6.8, 12H, {CH(C*H*$_3$)$_2$}). **^{13}C NMR** (126 MHz, C_6D_6) δ = 186.39 (d, $^1J_{C-P}$ = 85.4 Hz, P*C*O), 160.15 (Ar*C*), 147.77 (Ar*C*), 145.82 (Ar*C*), 136.10 (Ar*C*), 134.88 (Ar*C*), 134.54 (Ar*C*), 125.09

(Ar*C*), 124.40 (Ar*C*), 123.69 (Ar*C*), 123.56 (Ar*C*), 123.37 (Ar*C*), 117.98 (Ar*C*), 54.43 (NHC {*C*H(CH$_3$)$_2$}), 29.95 ({*C*H(CH$_3$)$_2$}), 29.02 ({*C*H(CH$_3$)$_2$}), 27.52 ({CH(*C*H$_3$)$_2$}), 25.59 ({CH(*C*H$_3$)$_2$}), 24.38 ({CH(*C*H$_3$)$_2$}), 23.28 ({CH(*C*H$_3$)$_2$}), 21.69, 9.62 ({CH(*C*H$_3$)$_2$}). **^{31}P{^{1}H} NMR** (162 MHz, C$_6$D6) δ = –354.9.

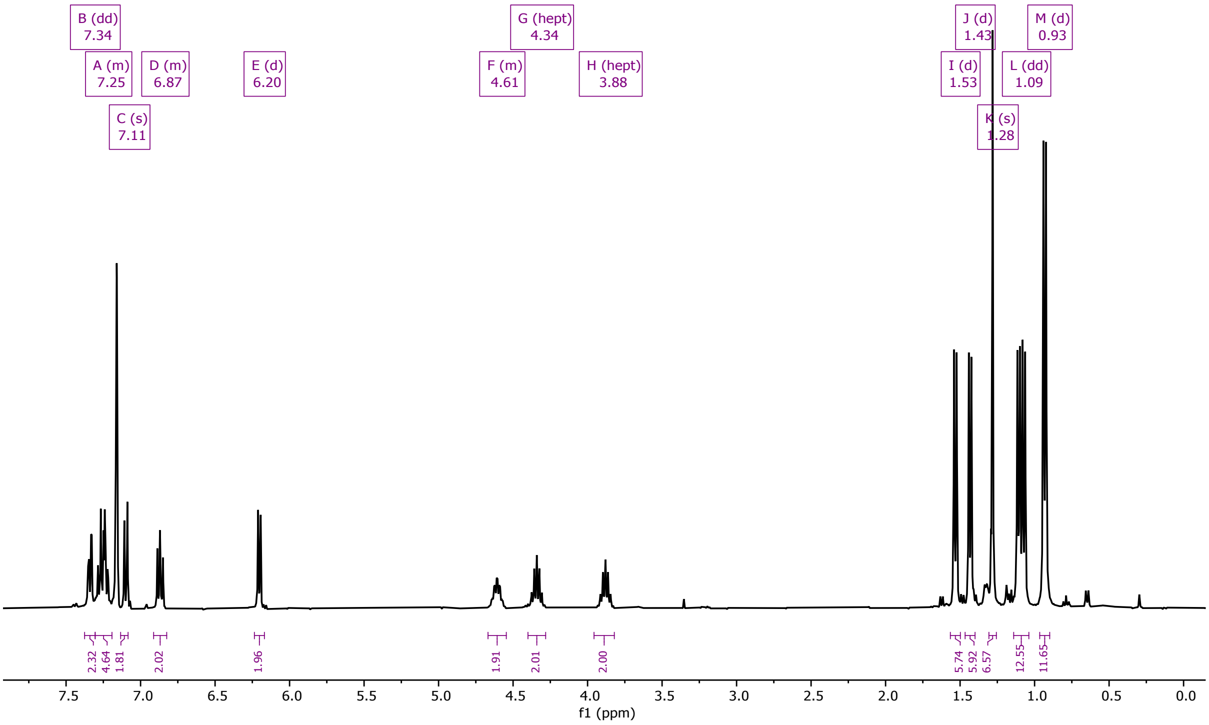


Figure S8. ^{1}H NMR spectrum of **2b** in C$_6$D$_6$.

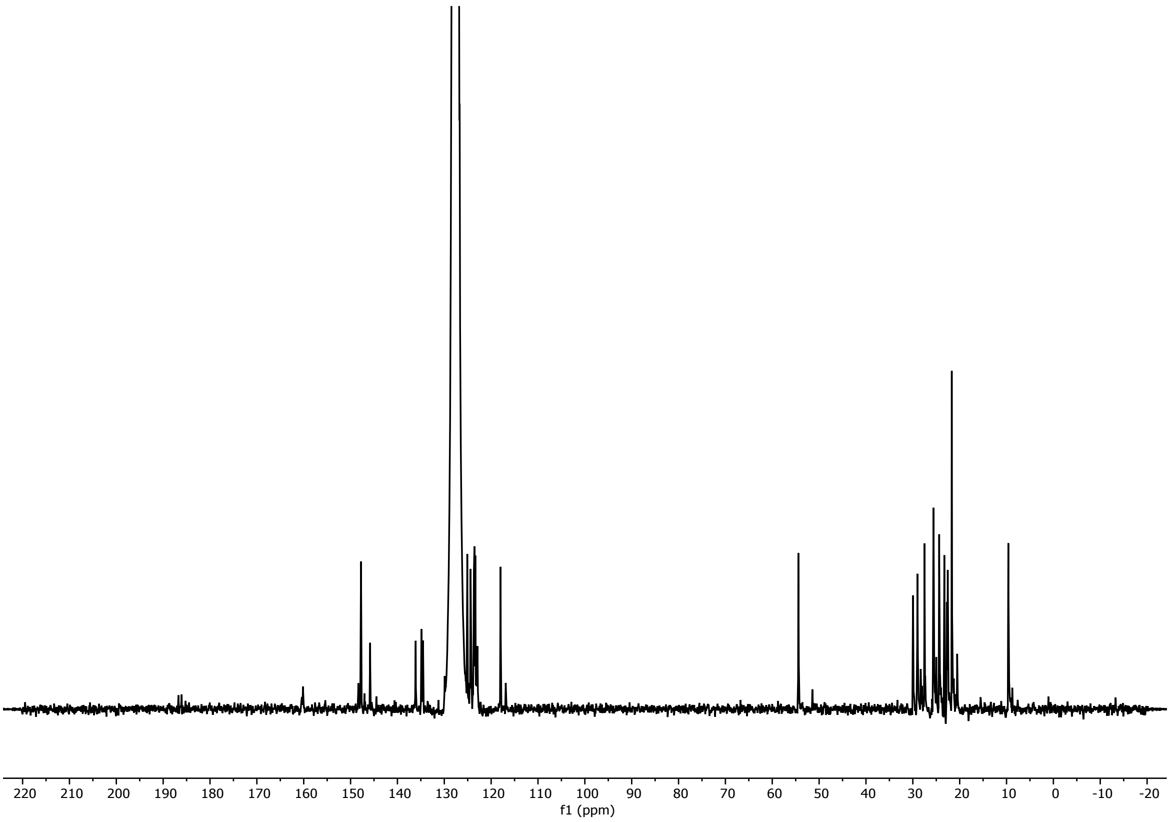


Figure S9. ^{13}C NMR spectrum of **2b** in C_6D_6.

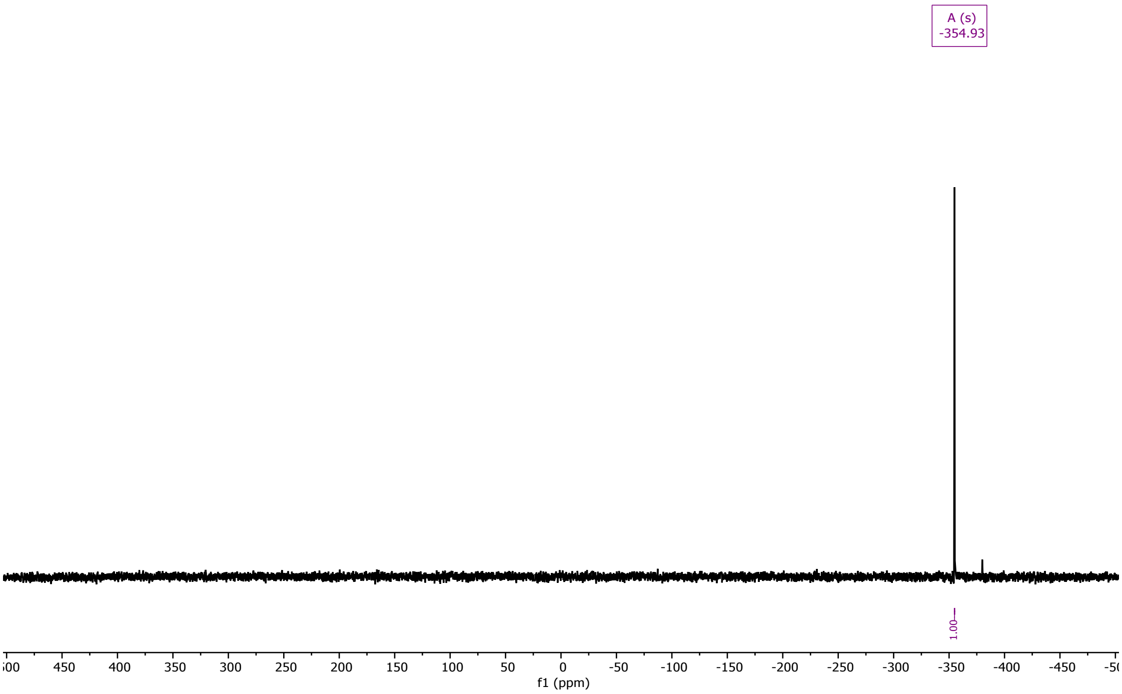


Figure S10. ^{31}P NMR spectrum of **2b** in C_6D_6.

1.6. Synthesis of (Dipp-Bian)Ga(PCO)(IMes) (2c).

Dipp-Bian (500 mg, 1.0 mmol) was refluxed (110 °C) in an ampoule fitted with a J. Young tap over an excess of gallium metal (> 10 eq.) for 12 hours. The resulting dark blue solution was filtered and iodine (130 mg, 1.0 mmol) was added. The solution was stirred for 6 hours, forming a brick red suspension, and the solvent removed. Pyridine (20 mL) was added and the reaction heated to reflux, at which point the solution turns from red to blue. The solvent was removed and the blue solid dissolved in toluene. IMes (0.30 g, 1.0 mmol) was added and the solution turned from blue to green. After 2 hours [Na(dioxane)$_{0.6}$](PCO) (1.2 eq, 1.2 mmol) was added and the solution filtered to a second ampoule before being concentrated and stored at –35°C overnight to yield (dipp-Bian)Ga(PCO)(IMes) as a green powder (410 mg, 40%). Crystals suitable for X-ray diffraction were obtained by cooling a concentrated diethyl ether solution of **2c** to –35°C.

CHN Anal. Calcd. for $C_{64}H_{76}GaN_4OP$: C, 75.51; H, 7.53; N, 5.50. Found: C, 74.75; H, 7.61; N, 6.03. **^{1}H NMR** (400 MHz, C_6D_6) δ = 7.40–7.26 (m, 6H, Ar*H*), 7.15–6.98 (m, 8H, Ar*H*), 6.89 (t, $^3J_{H\text{–}H}$ = 7.5 Hz, 2H, Ar*H*), 6.59 (s, 2H, Ar*H*), 6.51 (s, 2H, Ar*H*), 6.29 (d, $^3J_{H\text{–}H}$ = 6.8 Hz, 2H, Ar*H*), 5.48 (s, 1H, IMes C*H*), 4.40 (sept, $^3J_{H\text{–}H}$ = 8.4 Hz, 7.5, 2H, {C*H*(CH_3)$_2$}), 3.98–3.87 (sept, $^3J_{H\text{–}H}$ = 8.4 Hz, 2H, {C*H*(CH_3)$_2$}), 2.11 (s, 3H, IMes C*H*$_3$), 2.05 (s, 3H, IMes C*H*$_3$), 1.99 (s, 3H, IMes C*H*$_3$), 1.67 (d, $^3J_{H\text{–}H}$ = 10.8 Hz, 11H), 1.49 (d, $^3J_{H\text{–}H}$ = 6.8 Hz, 6H), 1.31 (dd, $^3J_{H\text{–}H}$ = 16.3 Hz, 6.7, 12H), 1.19 (d, $^3J_{H\text{–}H}$ = 7.0 Hz, 6H). **^{13}C NMR** (126 MHz, C_6D_6) δ = 203.37 (NHC *C*), 183.67 ($^1J_{C\text{–}P}$ = 87.3 Hz, P*C*O), 148.39 (Ar*C*), 146.69 ($^2J_{C\text{-}P}$ = 24.3 Hz), 146.09 (Ar*C*), 140.47 (Ar*C*), 140.34 (Ar*C*), 138.03 (Ar*C*), 137.53 (Ar*C*), 137.05 (Ar*C*), 136.61 (Ar*C*), 135.51 (Ar*C*), 134.35 (Ar*C*), 133.58 (Ar*C*), 132.38 (Ar*C*), 130.70 (Ar*C*), 129.49 (Ar*C*), 129.24 (Ar*C*), 128.97 (Ar*C*), 128.20 (Ar*C*), 126.81 (Ar*C*), 125.33 (Ar*C*), 124.51 (Ar*C*), 124.34 (Ar*C*), 122.86 (Ar*C*), 122.73 (Ar*C*), 117.48 (Ar*C*), 29.73 ({CH(*C*H$_3$)$_2$}), 28.46 ({*C*H(CH_3)$_2$}), 28.33 ({*C*H(CH_3)$_2$}), 25.67 ({*C*H(CH_3)$_2$}), 25.63 (*C*H$_3$), 25.53(*C*H$_3$), 25.33(*C*H$_3$), 24.18 (*C*H$_3$), 21.55 (CH_3), 20.64 (CH_3), 20.50 (CH_3), 17.50 (CH_3), 17.10 (CH_3). **$^{31}P\{^1H\}$ NMR** (162 MHz, C_6D_6) δ = –374.2 ppm.

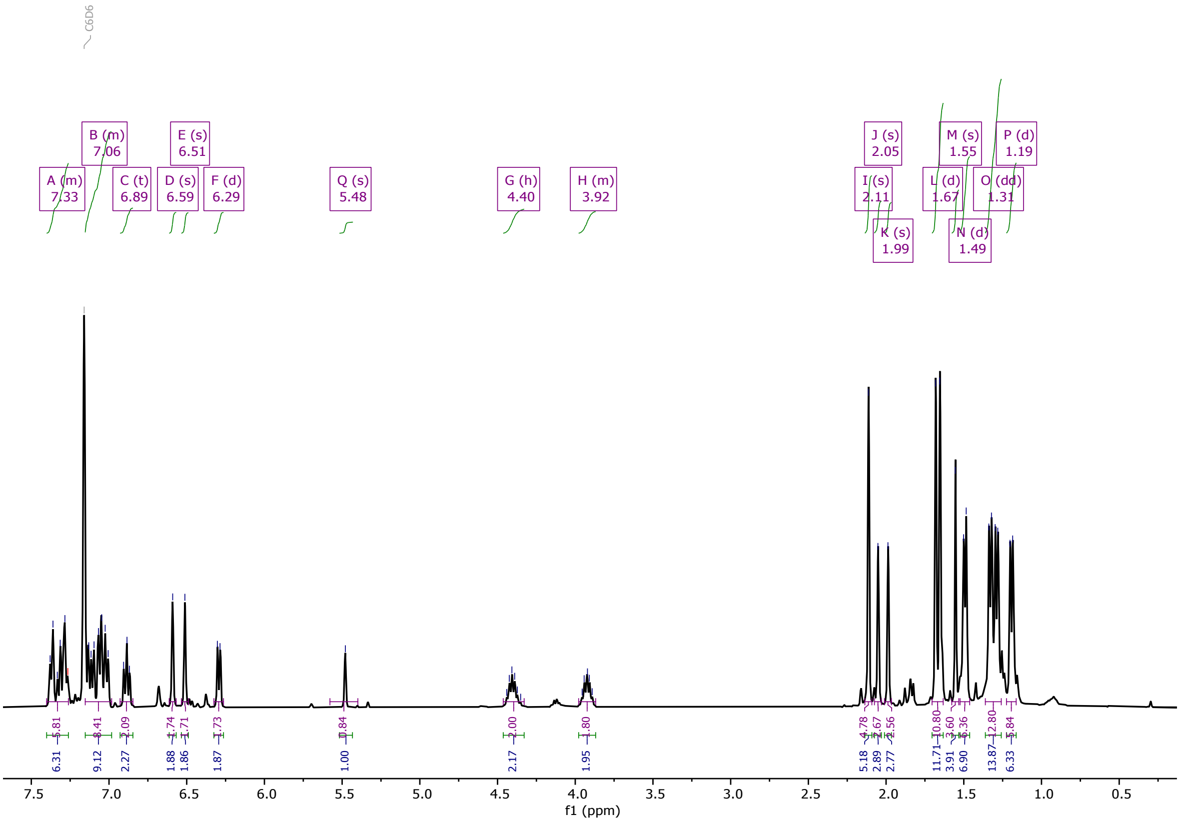


Figure S11. ^{1}H NMR spectrum of **2c** in C_6D_6.

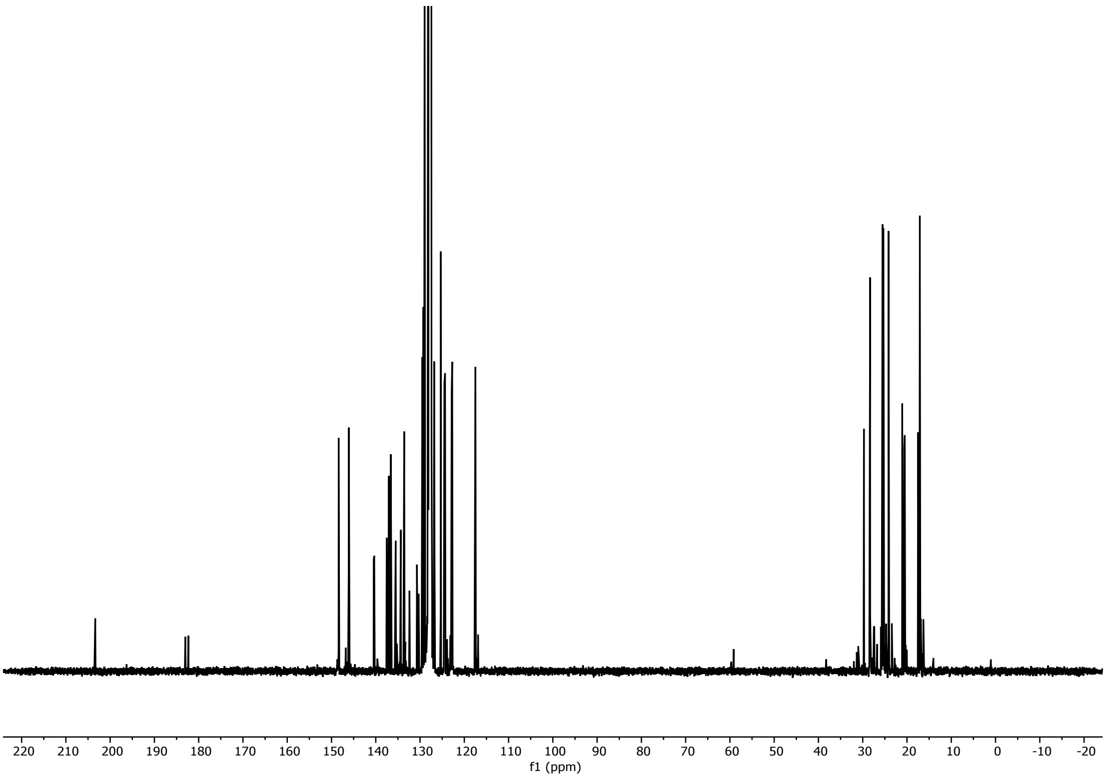


Figure S12. ^{13}C NMR spectrum of **2c** in C_6D_6.

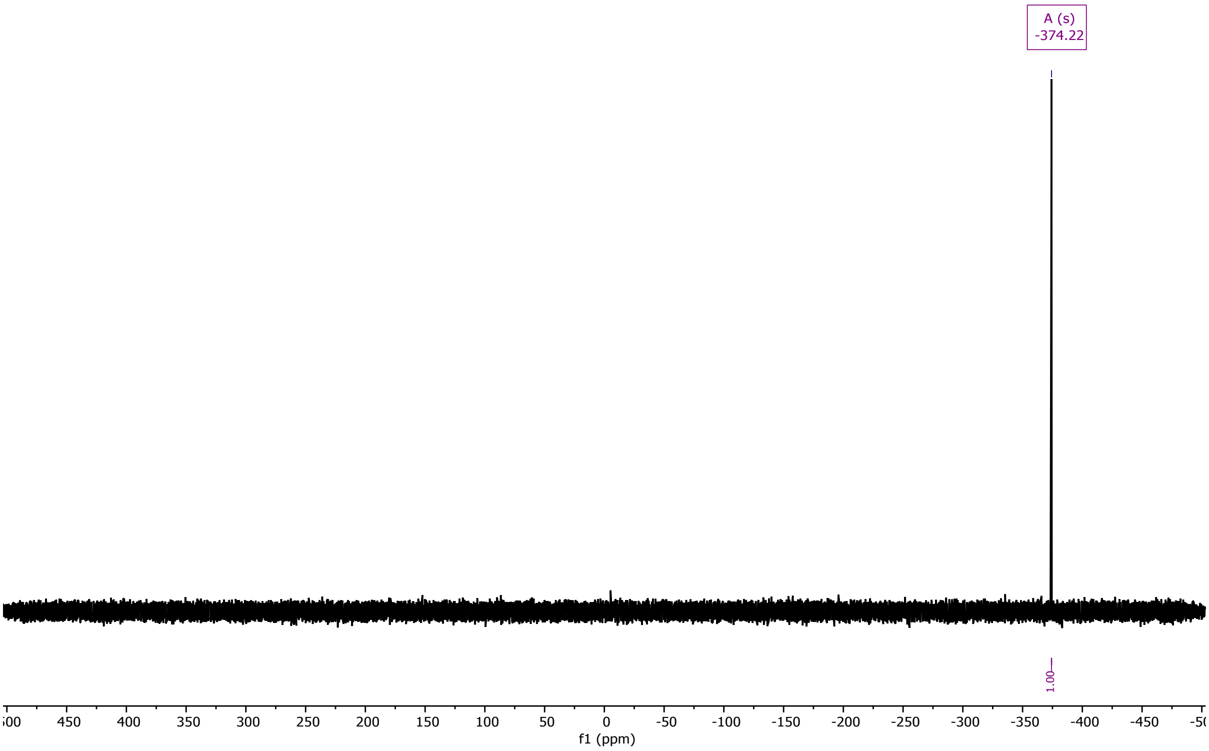


Figure S13. ^{31}P{^{1}H} NMR spectrum of **2c** in C_6D_6.

1.7 Synthesis of (Dipp-Bian)GaPPGa(Dipp-Bian) (3).

A solution containing **1a** (100 mg, 0.13 mmol) in toluene (0.5 mL) was irradiated for 4 × 9 hours, resulting in significantly reduced intensity in both the ^{31}P and ^{1}H NMR spectra. Crystallisation of the solution by vapour diffusion of hexane/diethyl ether allowed for crystallographic characterisation of diphosphene **3**. The crystals were dissolved and ^{31}P NMR spectroscopy allowed for identification of a peak at 774.9 ppm, which immediately and irreversibly disappeared upon warming. **CHN** Anal. Calcd. for $C_{82}H_{92}Ga_2N_6O_4P_2$: C, 69.02; H, 6.50; N, 5.89. Found: C, 69.98; H, 6.78; N, 5.53. **^{1}H NMR** (400 MHz, C_6D_6) δ = 8.28 (br s), 7.08 (d, *J* = 6.8 Hz, possibly Dipp Ar*H*), 6.89 (t, *J* = 6.8 Hz, possibly Dipp Ar*H*), 6.49 (br s), 6.36 (d, *J* = 6.8 Hz, possibly Dipp Ar*H*), 3.27 (THF), 1.23 (hexane), 1.11 (THF), 0.88 (hexane). **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ (ppm) 774.9 ppm.

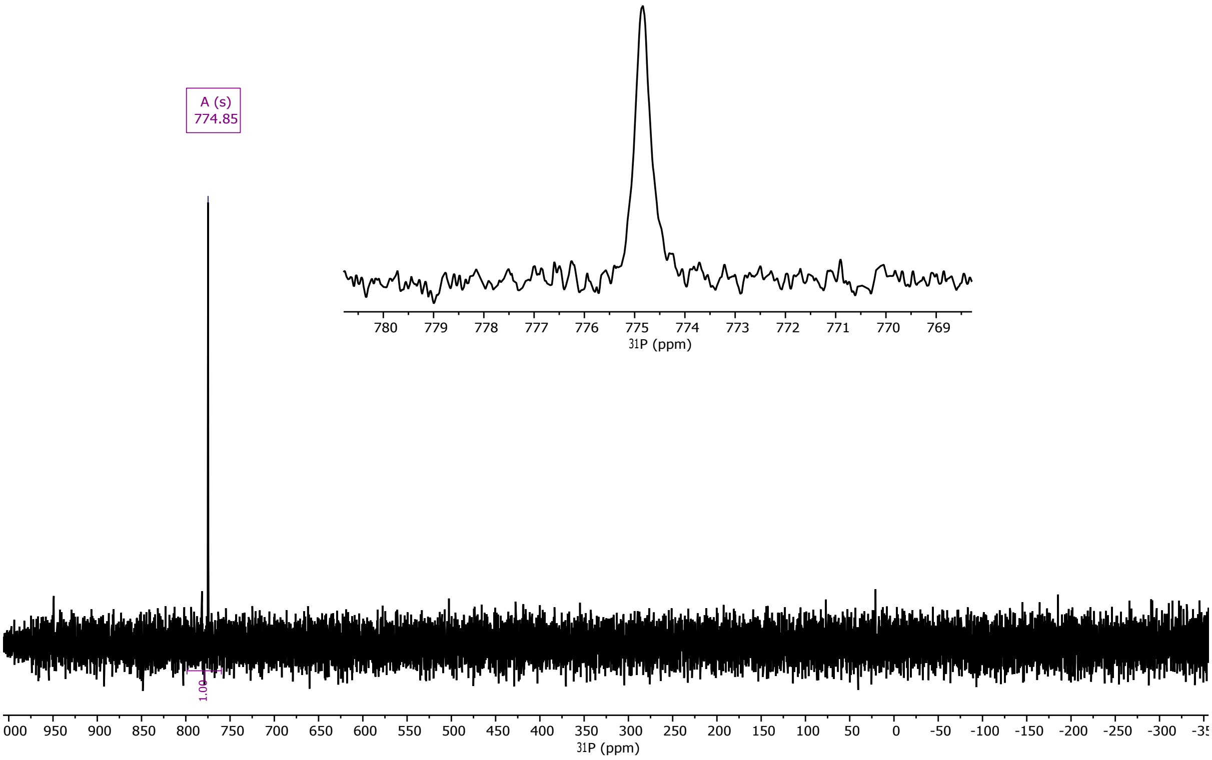


Figure S14. ^{31}P{^{1}H} NMR spectrum of crystals of **3** in C_6D_6.

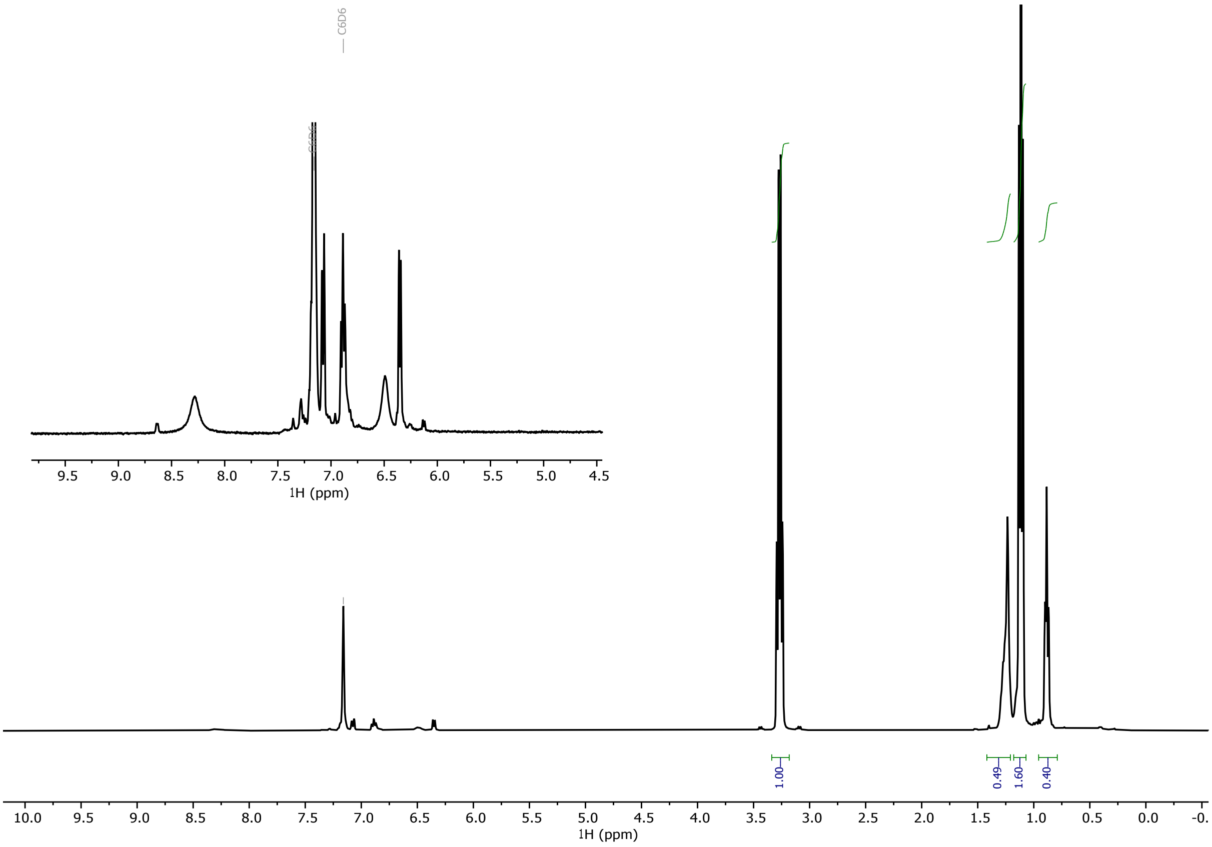


Figure S15. ^{1}H NMR spectrum of crystals of **3** showing residual diethyl ether and hexane. Inset: enhancement of small peaks around aromatic region.

1.8. Synthesis of (Dipp-Bian)Ga(Pyr)($PPMe_3$) (4a).

To a solution of **1a** (100 mg, 0.13 mmol) in toluene (2 mL) was added an excess of trimethylphosphine (20 mg, 0.26 mmol). The volatiles were removed under reduced pressure and the resulting blue solid was taken up into toluene, filtered and concentrated. Cooling the solution to –35°C or a week resulted in bright blue, heterochromic crystals of **4a** (71 mg, 66.7 %).

CHN Anal. Calcd. for $C_{44}H_{55}GaN_3O_2P_2$ + toluene: C, 69.47; H, 7.20; N, 4.77; Found: C, 70.81; H, 7.93; N, 4.21. **^{1}H NMR** (500 MHz, C_6D_6) δ = 9.08 (d, $^3J_{H-H}$ = 5.5 Hz, 2H, *ortho*- Pyr*H*), 7.27 (s, 6H, ArC*H*), 7.08 (d, $^3J_{H-H}$ = 8.2 Hz, 2H, ArC*H*), 6.91 (t, $^3J_{H-H}$ = 7.6 Hz, 2H, ArC*H*), 6.84 (t, $^3J_{H-H}$ = 7.7 Hz, 1H, *para*-Pyr*H*), 6.45 (t, $^3J_{H-H}$ = 6.7 Hz, 2H, ArC*H*), 6.36 (d, $^3J_{H-H}$ = 6.9 Hz, 2H, PyrC*H*), 3.71 (sept, $^3J_{H-H}$ = 6.9 Hz, 4H, {C*H*(CH_3)$_2$}), 3.27 (q, $^3J_{H-H}$ = 6.9 Hz, 2H), 1.21 (t, $^3J_{H-H}$ = 6.3 Hz, 12H, {C*H*(CH_3)$_2$}), 0.79 (dd, $^3J_{H-H}$ = 12.1 Hz, 2.1, 12H, {C*H*(CH_3)$_2$}),). **^{13}C NMR** (126 MHz, C_6D_6) δ = 149.29 (Ar*C*), 147.47(Ar*C*), 145.69 (Ar*C*), 139.33 (Ar*C*), 135.95 (Ar*C*), 135.18 (Ar*C*), 126.94 (Ar*C*), 125.01 (Ar*C*), 123.80 (Ar*C*), 123.47 (Ar*C*), 123.33 (Ar*C*), 117.39 (Ar*C*), 65.54 ({*C*H(CH_3)$_2$}), 27.88 ({CH(*C*H$_3$)$_2$}), 24.63 ({CH(*C*H$_3$)$_2$}), 22.75 (dd, $^1J_{P\text{-}C}$ = 43.8 Hz, $^2J_{P\text{-}C}$ = 7.9 Hz, P(*C*H$_3$)$_3$). **^{31}P NMR** (202 MHz, C_6D_6) δ = 14.7 (d, $^1J_{P-P}$ =527.4 Hz, *P*Me$_3$), –263.0 (d, $^1J_{P-P}$ = 527.4 Hz, Ga*P*PMe$_3$).

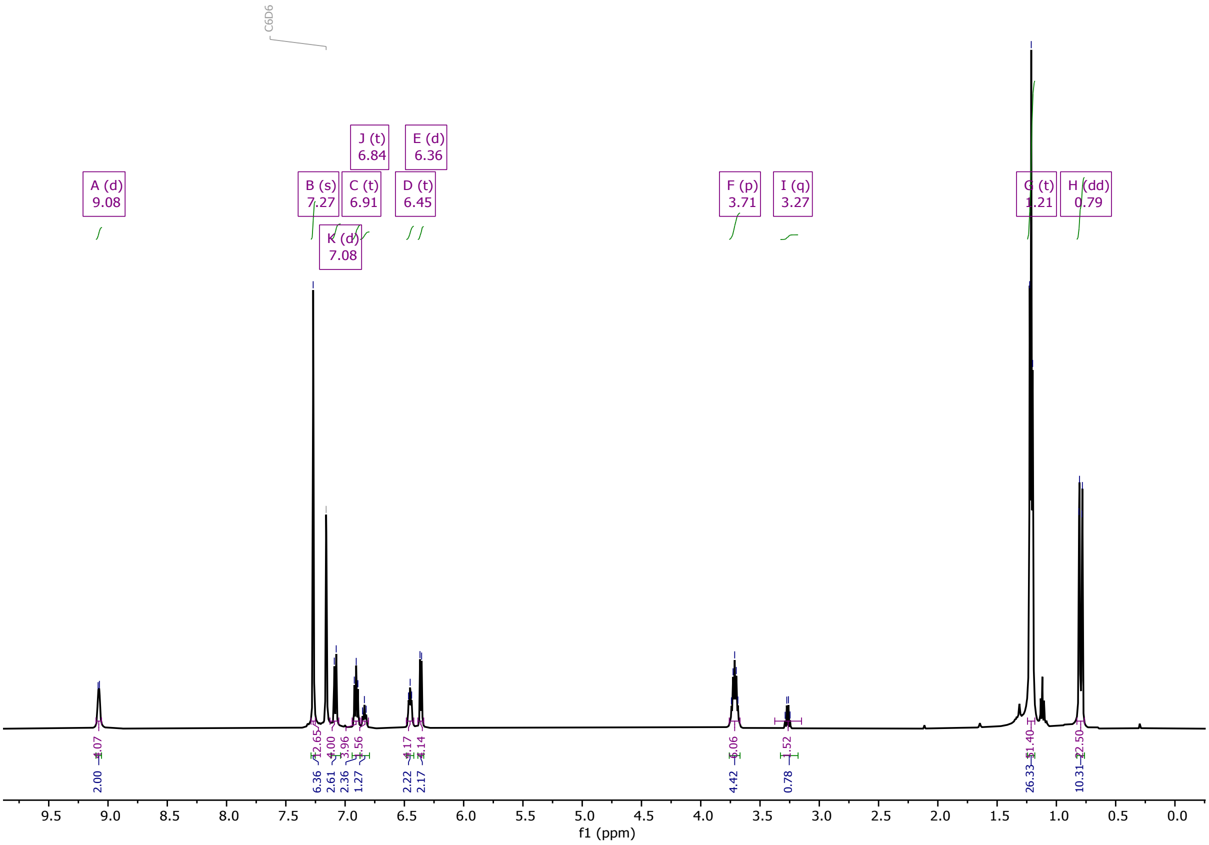


Figure S16. ^{1}H NMR spectrum of **4a** in C_6D_6.

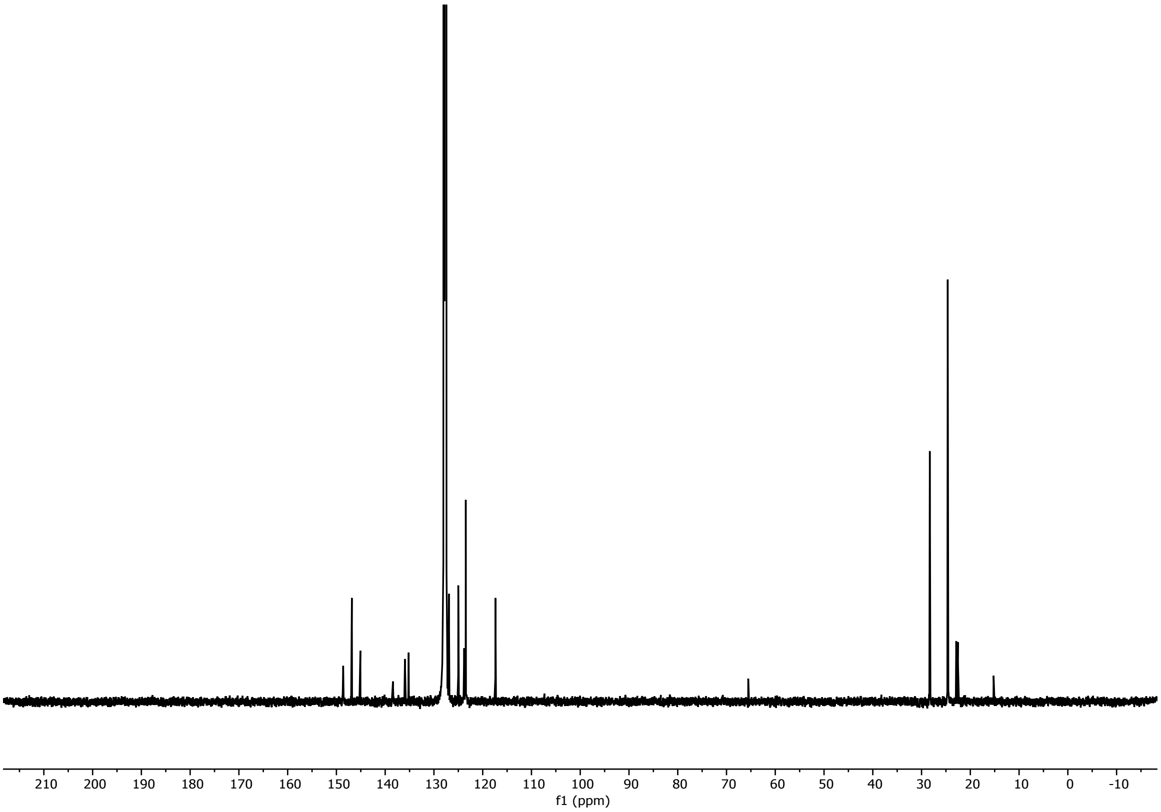


Figure S17. ^{13}C NMR spectrum of **4a** in C_6D_6.

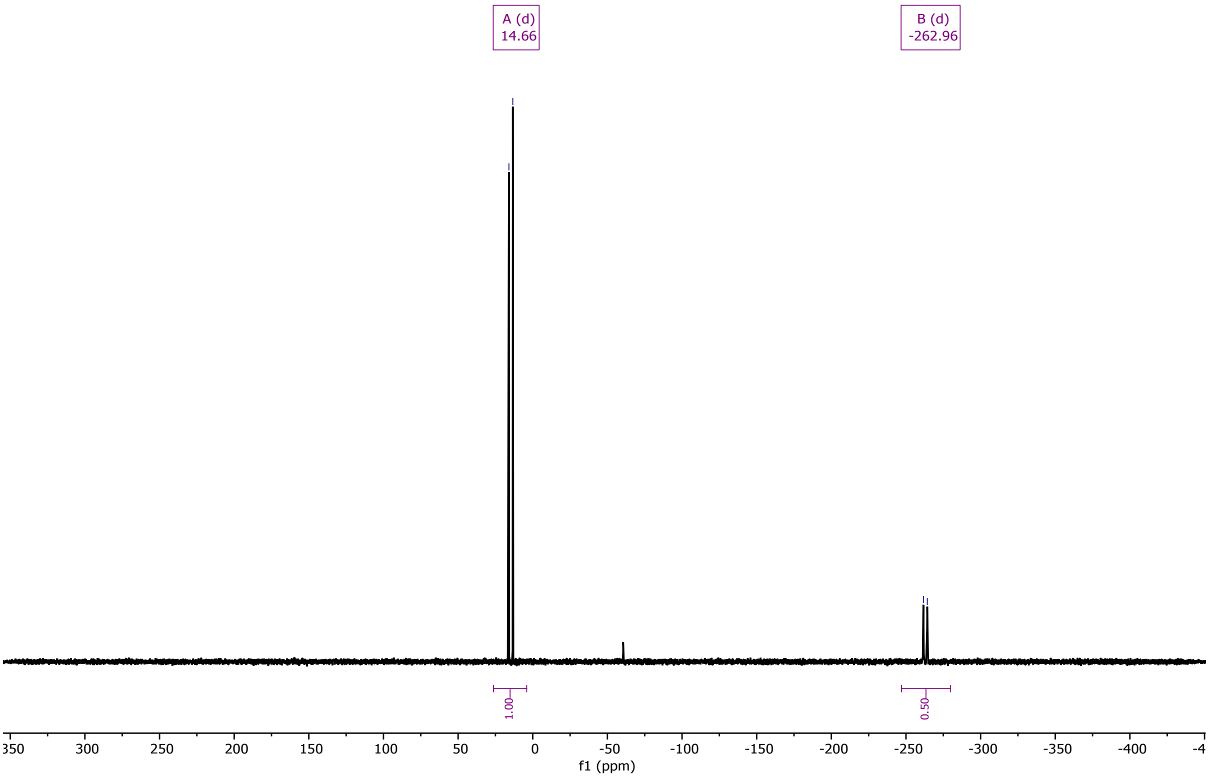


Figure S18. $^{31}P\{^1H\}$ NMR spectrum of **4a** in C_6D_6.

1.9. Synthesis of (Dipp-Bian)GaP Ga(Nacnac) (5).

Ga(NacNac) (NacNac = HC[C(Me)N-(C_6H_3)-2,6-^{i}Pr$_2$]$_2$; 24 mg, 0.05 mmol) was added to a solution of **2a** (36.5 mg, 0.05 mmol) in toluene (0.5 mL). The solution was heated to 90°C and allowed to cool slowly. Upon cooling blue crystals began to precipitate. The reaction mixture was left overnight. The solvent was decanted and placed in the freezer. After a few days a second crop of crystals formed (combined yield 35 mg, 60%).

CHN Anal. Calcd. for $C_{70}H_{87}Ga_2N_5O_2P$: C, 70.01; H, 7.30; N, 5.83. Found: C, 69.12; H, 7.01; N, 6.12. **^{1}H NMR** (500 MHz, C_6D_6) δ = 8.81 (br s, 2H, Pyr*H*), 7.36 (s, 6H, Ar*H*), 7.02 (t, $^3J_{H–H}$ = 7.2 Hz, 6H, Ar*H*), 6.88–6.82 (m, 4H, Ar*H*), 6.35 (s br, 2H, Pyr*H*), 6.23 (d, $^3J_{H–H}$ = 7.0 Hz, 2H, Ar*H*), 4.79 (s, 1H, {*H*C(C(NR)(CH$_3$))$_2$), 3.90 (sept, $^3J_{H–H}$ = 6.9 Hz, 4H, Bian {C*H*(CH$_3$)$_2$}), 3.61–3.06 (m, 4H, β-diketiminate {C*H*(CH$_3$)$_2$}), 2.11 (s, 1H, impurity), 1.45 (s, 6H, {HC(C(NR)(C*H*$_3$))$_2$)}), 1.31 (m, 12H,{CH(C*H*$_3$)$_2$}), 1.19 (d, $^3J_{H–H}$ = 6.9 Hz, 12H, β-diketiminate {CH(C*H*$_3$)$_2$}), 1.07 (d, $^3J_{H–H}$ = 6.9 Hz, 12H), 0.99 (m br, 12H, {CH(C*H*$_3$)$_2$}). **^{13}C NMR** (126 MHz, C_6D_6) δ = 169.43 (Ar*C*), 160.23 (br, Pyr*C*), 158.75, 148.35 (br, Pyr*C*), 146.46 (Ar*C*), 145.36 (Ar*C*), 143.02 (br, Pyr*C*), 140.97 (Ar*C*), 139.93 (Ar*C*), 137.52 (Ar*C*), 135.54 (Ar*C*), 134.88 (Ar*C*), 133.73 (Ar*C*), 128.96 (Ar*C*), 128.20 (Ar*C*), 126.85 (Ar*C*), 125.33 (Ar*C*), 124.78 (Ar*C*), 123.68 (Ar*C*), 123.09 (Ar*C*), 123.02 (Ar*C*), 116.97 (({HC(*C*(NR)(CH$_3$))$_2$), 96.73 ({H*C*(C(NR)(CH$_3$))$_2$), 59.69 ({HC(C(NR)(*C*H$_3$))$_2$), 38.24 ({(*C*H(CH$_3$)$_2$}), 31.34 ({(*C*H(CH$_3$)$_2$}), 29.85 ({(*C*H(CH$_3$)$_2$}), 29.02 ({(*C*H(CH$_3$)$_2$}), 28.34 (CH$_3$), 24.94 (CH$_3$), 24.31 (CH$_3$), 24.19 (CH$_3$), 23.48(CH$_3$), 23.34 (CH$_3$), 22.76 (CH$_3$), 22.54 (CH$_3$), 21.07 (CH$_3$). **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6) δ = –319.0.

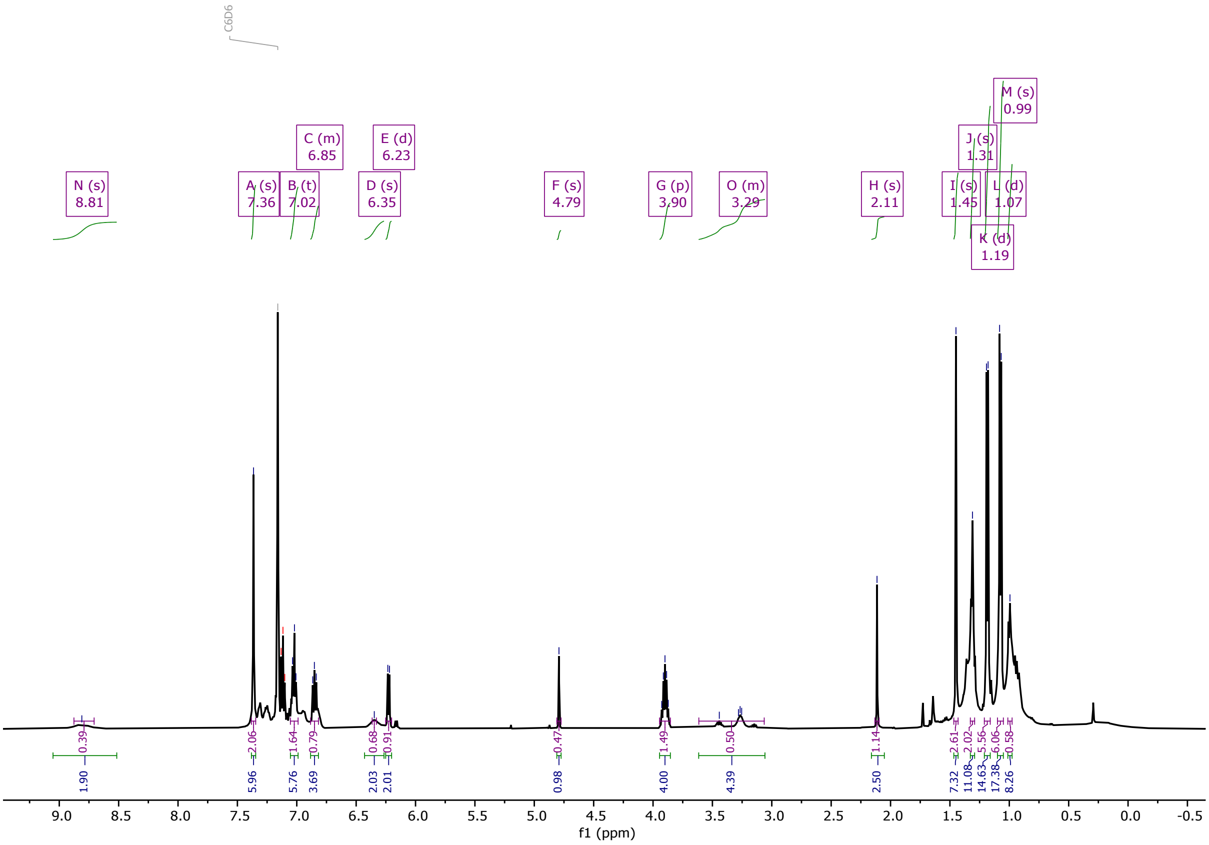


Figure S19. ^{1}H NMR spectrum of **5** in C_6D_6.

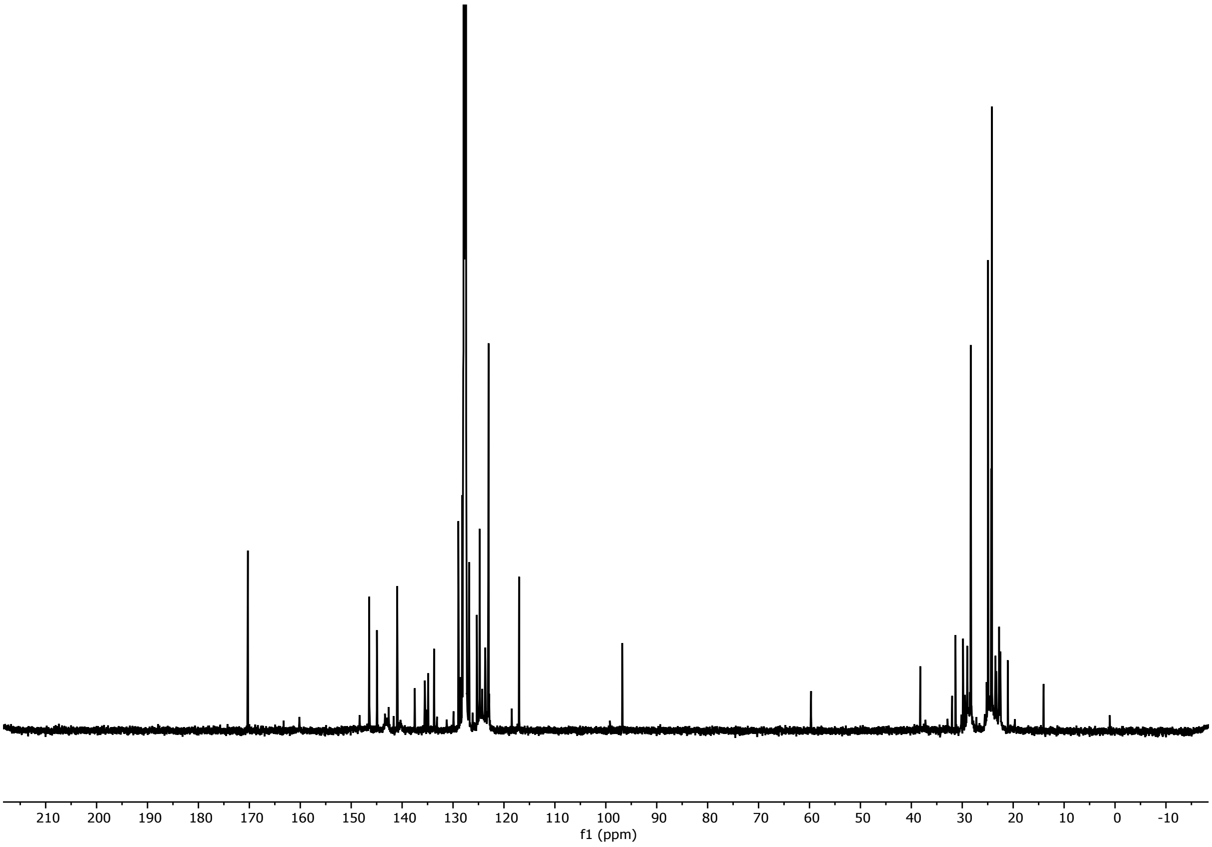


Figure S20. ^{13}C NMR spectrum of **5** in C_6D_6.

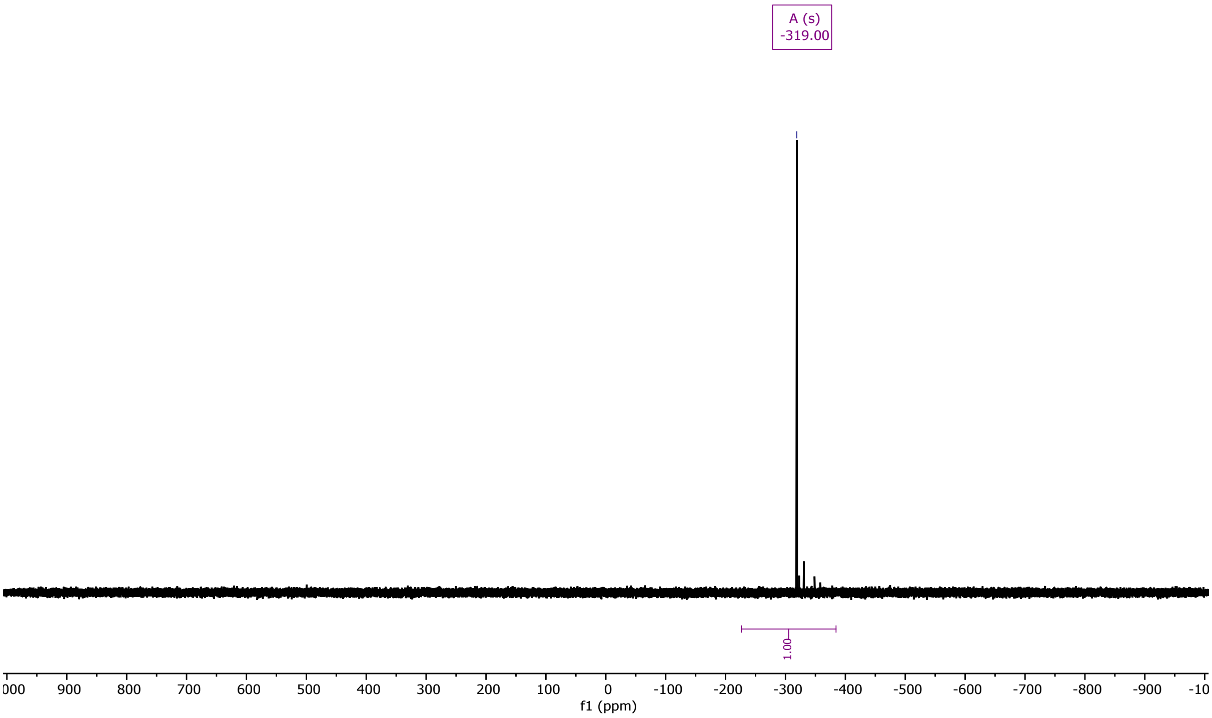


Figure S21. $^{31}P\{^1H\}$ NMR spectrum of **5** in C_6D_6.

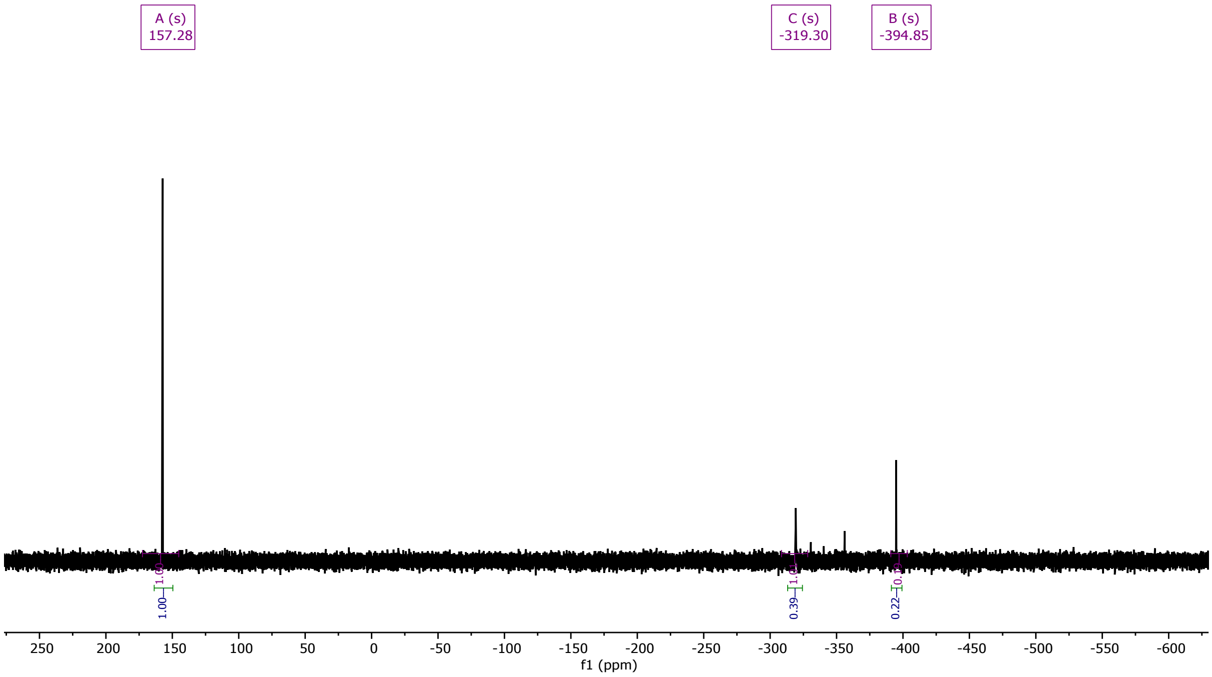


Figure S22. Intermediate observed during the conversion of **2a** to **5**.

2. Single crystal X-ray diffraction studies

Single-crystal X-ray diffraction data were collected using an Oxford Diffraction Supernova dual-source diffractometer equipped with a 135 mm Atlas CCD area detector. Crystals were selected under Paratone-N oil, mounted on micromount loops and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device. Data were collected at 150 K using mirror monochromated Cu K_α (λ = 1.54184 Å) or Mo K_α radiation (λ = 0.71073 Å) and processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro).[5] Equivalent reflections were merged and diffraction patterns processed with the CrysAlisPro suite. Structures were subsequently solved using direct methods and refined on F^2 using the SHELXL package.[6]

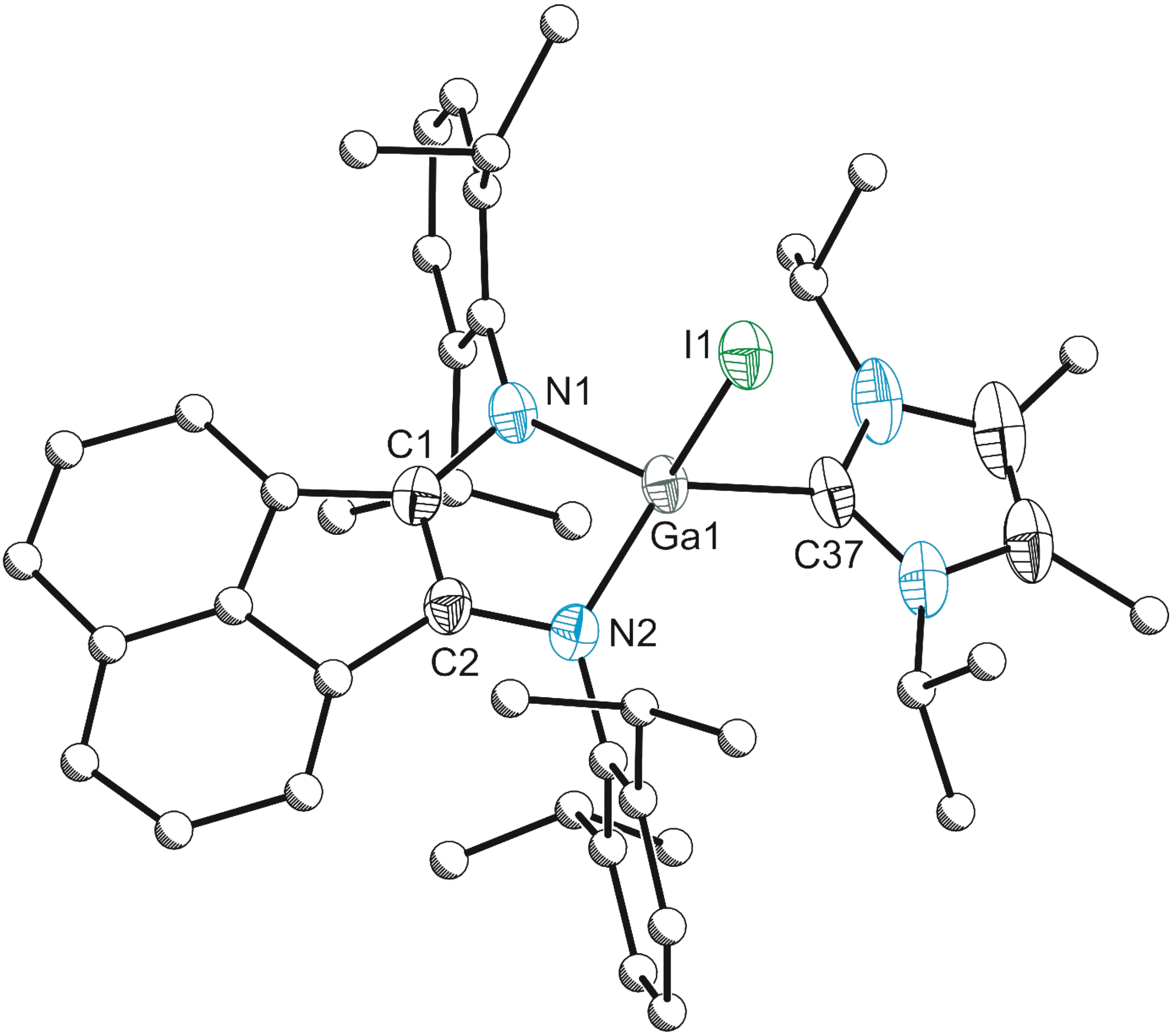


Figure S23. Molecular structure of **1b**. Ellipsoids set at 50% probability; hydrogen atoms omitted for clarity. Atoms of the Dipp groups are pictured as spheres of arbitrary radius. Selected interatomic distances [Å] and angles [°]: Ga1–N2 1.914(5), Ga1–N1 1.924(4), Ga1–C37 2.034(5), Ga1–I1 2.6407(7), N1–C1 1.394(7), N2–C2 1.388(7), N2-Ga1-N1 90.4(2), N2-Ga1-C37 122.6(2), N1-Ga1-C37 123.8(2), N2-Ga1-I1 111.68(14), N1-Ga1-I1 111.64(14).

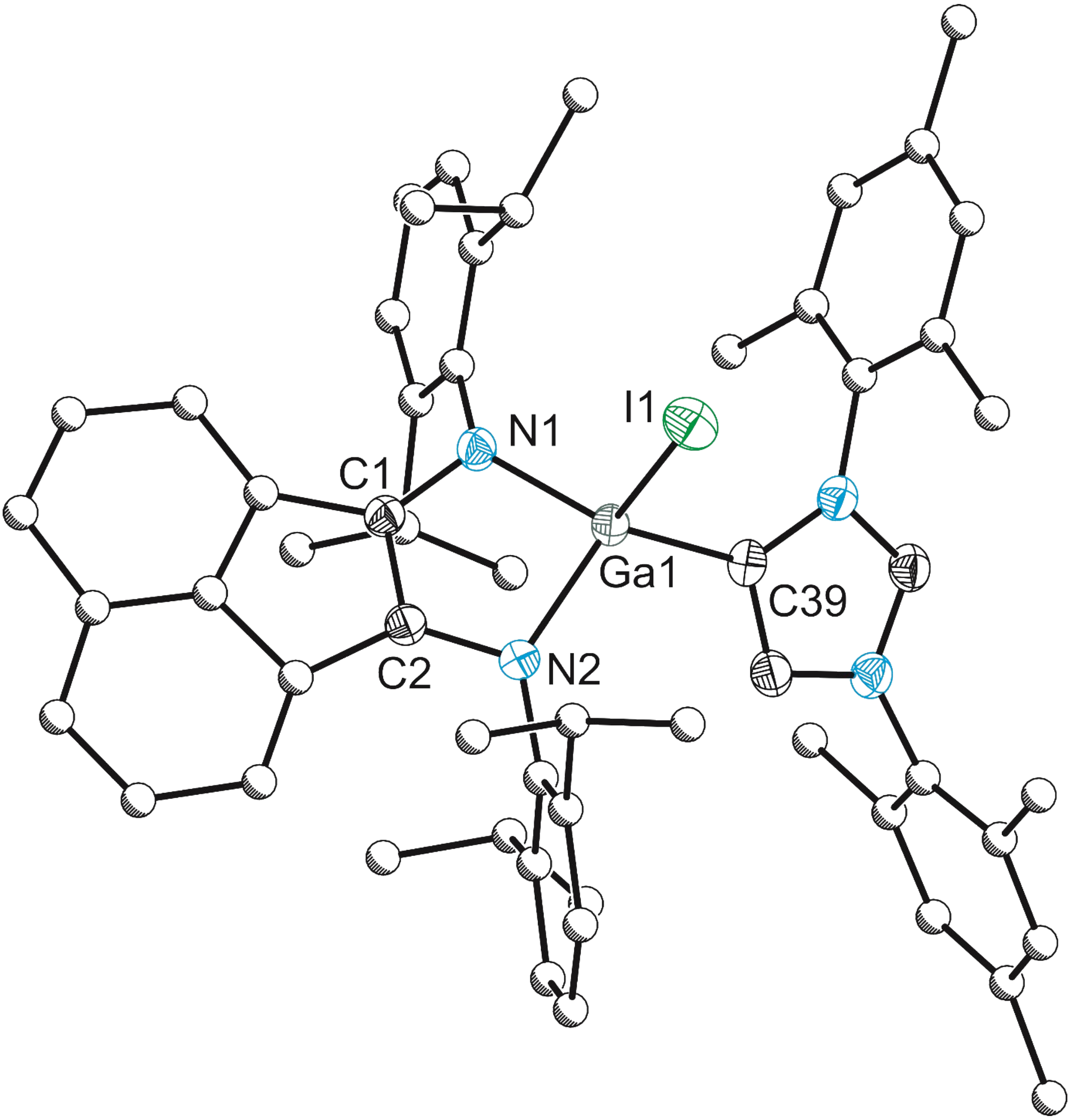


Figure S24. Molecular structure of **1c**. Ellipsoids set at 50% probability; hydrogen atoms omitted for clarity. Atoms of the Dipp groups are pictured as spheres of arbitrary radius. Selected interatomic distances [Å] and angles [°]:Ga1–N1 1.907(2), Ga1–N2 1.925(2), Ga1–C39 1.985(3), Ga1–I1 2.6037(4), N1–C1 1.383(3), N2–C2 1.388(4), N1-Ga1-N2 89.86(10), N1-Ga1-C39 123.85(11), N2-Ga1-C39 111.39(11), N1-Ga1-I1 111.73(7), N2-Ga1-I1 113.95(7), C39-Ga1-I1 105.71(8).

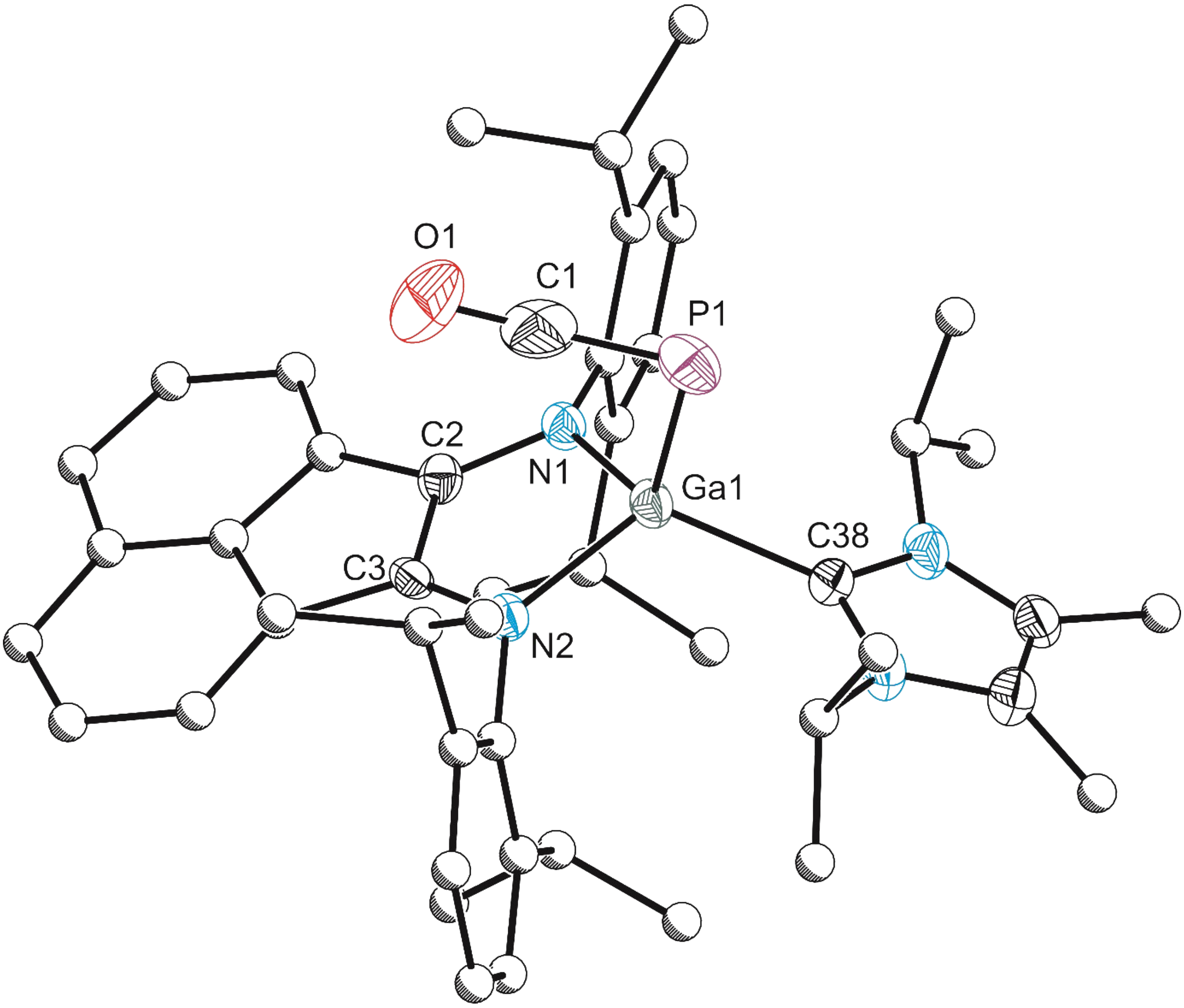


Figure S25. Molecular structure of **2b**. Ellipsoids set at 50% probability; hydrogen atoms omitted for clarity. Atoms of the Dipp groups are pictured as spheres of arbitrary radius. Selected interatomic distances [Å] and angles [°]: Ga1–N2 1.915(4), Ga1–N1 1.917(5), Ga1–C38 2.036(5), Ga1–P1 2.4303(17), P1–C1 1.598(9), C1–O1 1.192(10), N1–C2 1.389(7), N2–C3 1.389(7), N2-Ga1-N1 89.6(2), N2-Ga1-C38 118.6(2), N1-Ga1-C38 122.3(2), N2-Ga1-P1 112.54(14), N1-Ga1-P1 116.13(15), C38-Ga1-P1 98.79(17), C1-P1-Ga1 87.8(3), O1-C1-P1 177.4(7).

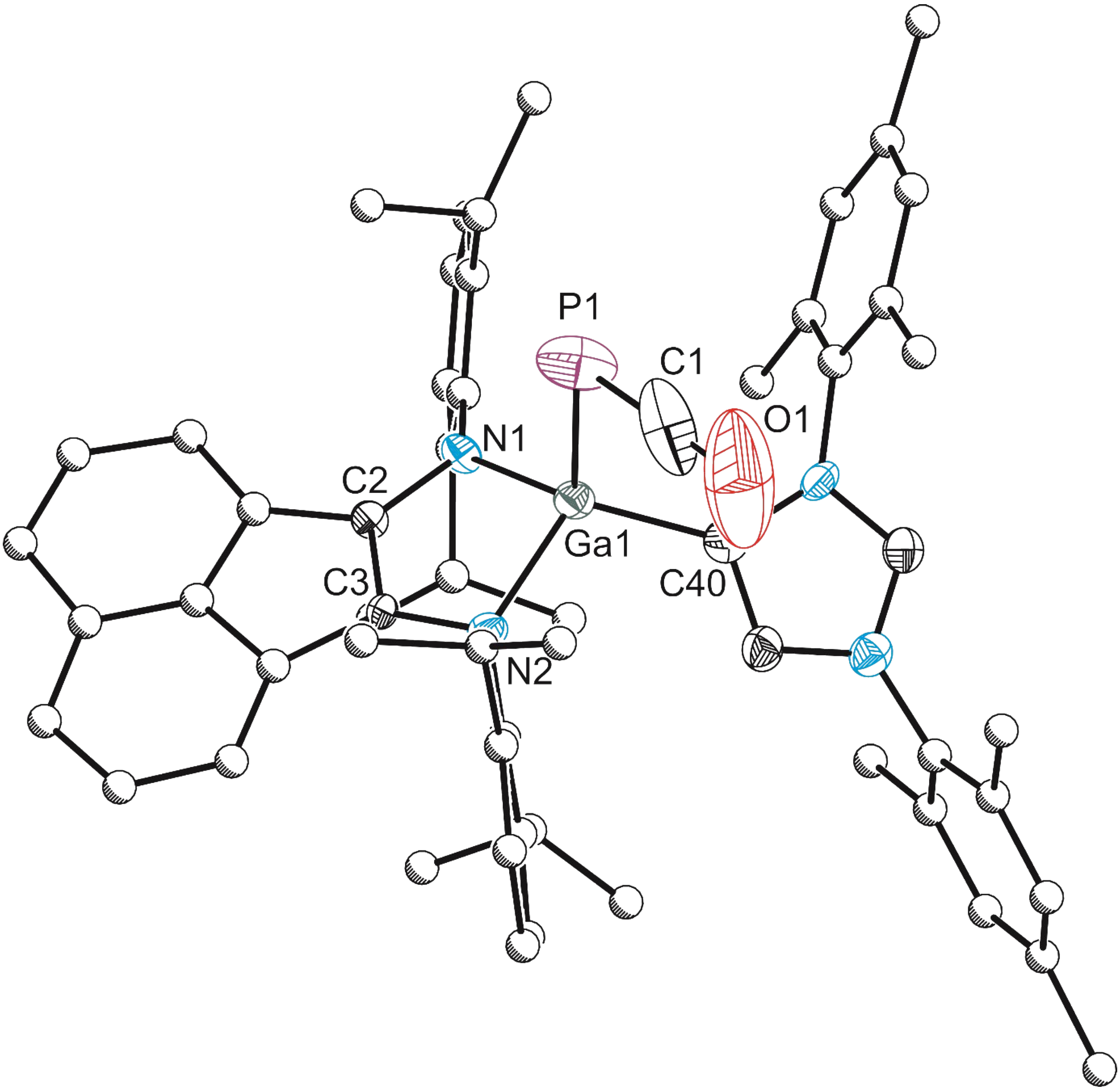


Figure S26. Molecular structure of **2c**. Ellipsoids set at 50% probability; hydrogen atoms omitted for clarity. Atoms of the Dipp groups are pictured as spheres of arbitrary radius. Selected interatomic distances [Å] and angles [°]: Ga1–N1 1.919(5), Ga1–N2 1.928(5), Ga1–C40 1.978(7), Ga1–P1 2.411(3), P1–C1 1.523(13), C1–O1 1.230(13), N1–C2 1.387(8), N2–C3 1.403(8), N1-Ga1-N2 89.7(2), N1-Ga1-C40 121.8(2), N2-Ga1-C40 111.2(2), N1-Ga1-P1 106.67(17), N2-Ga1-P1 113.71(18), C40-Ga1-P1 112.0(2), C1-P1-Ga1 91.0(5), O1-C1-P1 177.2(11).

Table S1. Selected X-ray data collection and refinement parameters for **1b**·0.33tol**, 1c**·2tol**, 2a**·tol.

	1b·0.33tol	**1c**·2tol	**2a**·tol
Formula	$C_{49.33}H_{59.67}GaIN_4$	$C_{71}H_{80}GaIN_4$	$C_{49}H_{53}GaN_3OP$
CCDC	2025224	2025225	2025226
Fw [g mol^{-1}]	905.29	1186.01	800.63
Crystal system	trigonal	orthorhombic	monoclinic
Space group	*R*3*c*	*P*2$_1$2$_1$2$_1$	*P*2$_1$/*n*
a (Å)	30.5012(5)	13.65400(10)	12.4092(2)
b (Å)	30.5012(5)	18.29020(10)	19.3221(3)
c (Å)	25.1712(7)	24.71570(10)	17.8085(3)
α (°)	90	90	90
β (°)	90	90	90.204(2)
γ (°)	120	90	90
V (Å^3)	20280.0(9)	6172.36(6)	4269.95(12)
Z	18	4	4
Radiation, λ (Å)	Cu Kα, 1.54184	Cu Kα, 1.54184	Cu Kα, 1.54184
Temp (K)	150(2)	150(2)	150(2)
ρ_{calc} (g cm^{-3})	1.334	1.276	1.245
μ (mm^{-1})	6.484	4.861	1.53
Reflections collected	43818	76989	47742
Independent reflections	9219	12864	8915
Parameters	509	710	505
R(int)	0.0571	0.0392	0.0259
R1/wR2,[a] $I \geq 2\sigma I$ (%)	3.28/7.52	2.59/6.62	3.32/9.26
R1/wR2,[a] all data (%)	3.97/8.16	2.79/6.83	3.62/9.52
GOF	1.035	1.082	1.234

[a] $R1 = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$; $wR2 = \{[\Sigma w[(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2]/3$ where A and B are 0.0352 and 24.0515 for **1b**·0.33tol, 0.0413 and 0.9451 for **1c**·2tol, and 0.0466 and 0.9783 for **2a**·tol.

Table S2. Selected X-ray data collection and refinement parameters for **2b**·0.5tol**,** **2c**·2tol and **3**·2Et$_2$O

	2b·0.5tol	**2c**·2tol	**3**·2Et$_2$O
Formula	$C_{51.5}H_{64}GaN_4OP$	$C_{72}H_{80}GaN_4OP$	$C_{90}H_{110}Ga_2N_6O_2P_2$
CCDC	2025227	2025228	2025229
Fw [g mol^{-1}]	855.75	1118.09	1509.21
Crystal system	orthorhombic	orthorhombic	Monoclinic
Space group	$Fdd2$	$P2_12_12_1$	$P2_1/c$
a (Å)	39.4865(13)	13.6214(10)	12.2300(3)
b (Å)	36.1344(15)	18.3845(12)	22.2691(4)
c (Å)	12.8743(6)	24.7906(11)	15.9009(4)
α (°)	90	90	90
β (°)	90	90	111.732(3)
γ (°)	90	90	90
V (Å^3)	18369.3(13)	6208.1(7)	4022.83(18)
Z	16	4	2
Radiation, λ (Å)	Cu Kα, 1.54184	MoKα, 0.71073	MoKα, 0.71073
Temp (K)	150(2)	150(2)	150(2)
ρ_{calc} (g cm^{-3})	1.238	1.196	1.246
μ (mm^{-1})	1.458	0.515	0.761
Reflections collected	18275	25542	58229
Independent reflections	8777	10916	11317
Parameters	544	728	470
R(int)	0.0448	0.0727	0.0456
R1/wR2,[a] $I \geq 2\sigma I$ (%)	4.91/12.08	6.51/11.17	4.13/8.73
R1/wR2,[a] all data (%)	6.71/13.94	11.13/12.79	6.76/9.90
GOF	1.013	1.009	1.026

[a] $R1 = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$; $wR2 = \{[\Sigma w[(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F_o^2)^2\}^{1/2}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2]/3$ where A and B are 0.0730 and 11.2096 for **2b**·0.5tol, 0.0436 and 0.0000 for **2c**·2tol, and 0.0348 and 3.3566 for **3**·2Et$_2$O.

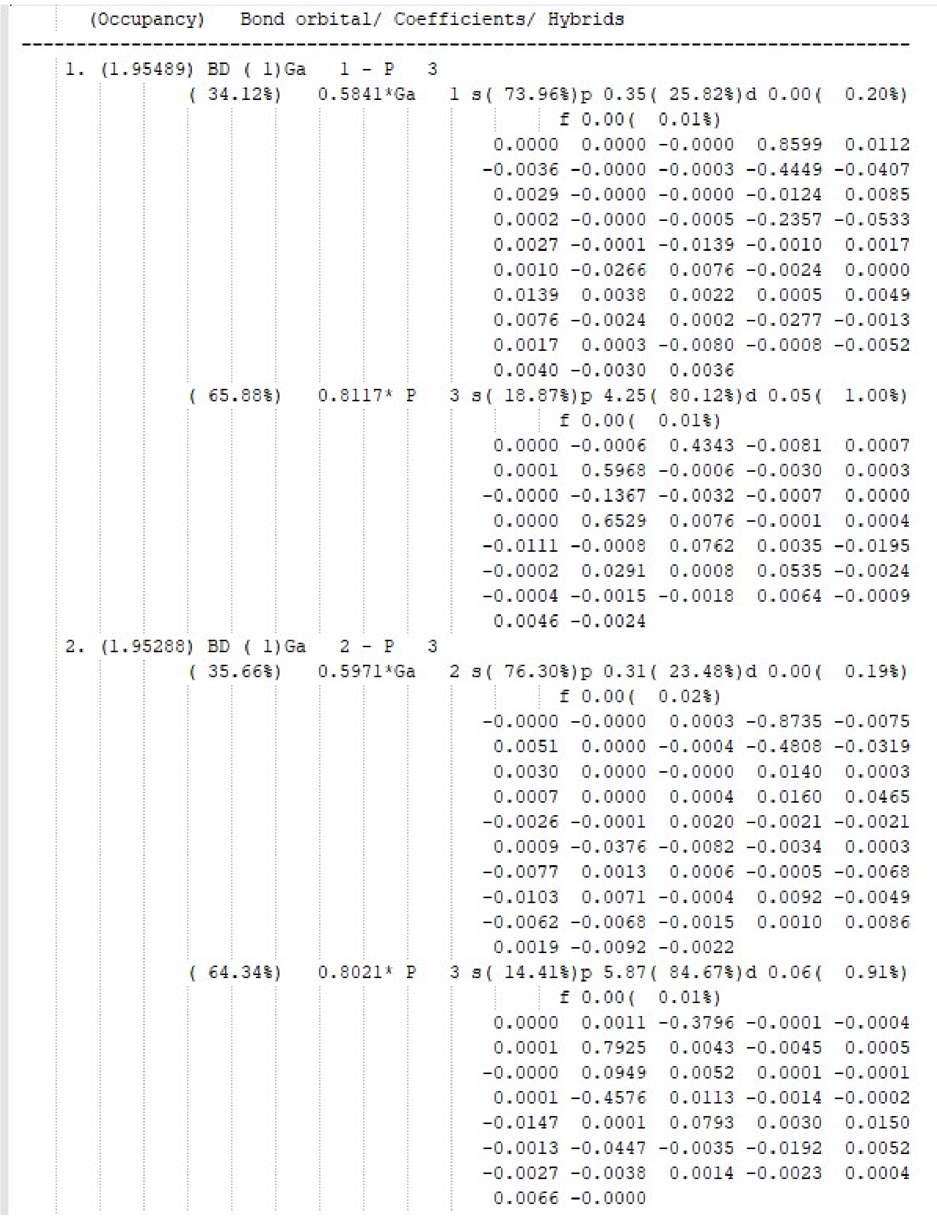
Table S3. Selected X-ray data collection and refinement parameters for **4a**, **4b**·$0.66Et_2O$ and **5**·2tol

	4a	**4b**·$0.66Et_2O$	**5**·2tol
Formula	$C_{44}H_{54}GaN_3P_2$	$C_{52.67}H_{75.67}GaN_4O_{0.67}P_2$	$C_{84}H_{102}Ga_2N_5P$
CCDC	2025230	2025231	2025232
Fw [g mol^{-1}]	756.56	907.16	1352.11
Crystal system	monoclinic	trigonal	orthorhombic
Space group	$P2_1/c$	*P*–3	*Pbca*
a (Å)	9.35570(10)	46.3247(5)	27.3275(2)
b (Å)	19.1486(2)	46.3247(5)	17.6404(2)
c (Å)	22.4817(2)	12.9618(2)	31.0011(3)
α (°)	90	90	90
β (°)	96.9660(10)	90	90
γ (°)	90	120	90
V (Å^3)	3997.83(7)	24089.1(6)	14944.6(2)
Z	4	18	8
Radiation, λ (Å)	Cu Kα, 1.54184	Cu Kα, 1.54184	Cu Kα, 1.54184
Temp (K)	150(2)	150(2)	150(2)
ρ_{calc} (g cm^{-3})	1.257	1.126	1.202
μ (mm^{-1})	1.947	1.541	1.432
Reflections collected	47290	264237	136257
Independent reflections	8269	33572	15813
Parameters	462	1639	827
R(int)	0.0397	0.0572	0.0656
R1/wR2,[a] $I \geq 2\sigma I$ (%)	3.26/7.92	8.54/22.66	4.12/10.01
R1/wR2,[a] all data (%)	4.30/8.28	9.39/23.22	6.13/11.08
GOF	1.081	1.248	1.036

[a] $R1 = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$; $wR2 = \{[\Sigma w[(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F_o{}^2)^2]\}^{1/2}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2]/3$ where A and B are 0.0291 and 3.1474 for **4a**, 0.0697 and 90.1248 for **4b**·$0.66Et_2O$, and 0.0484 and 11.7582 for **5**·2tol.

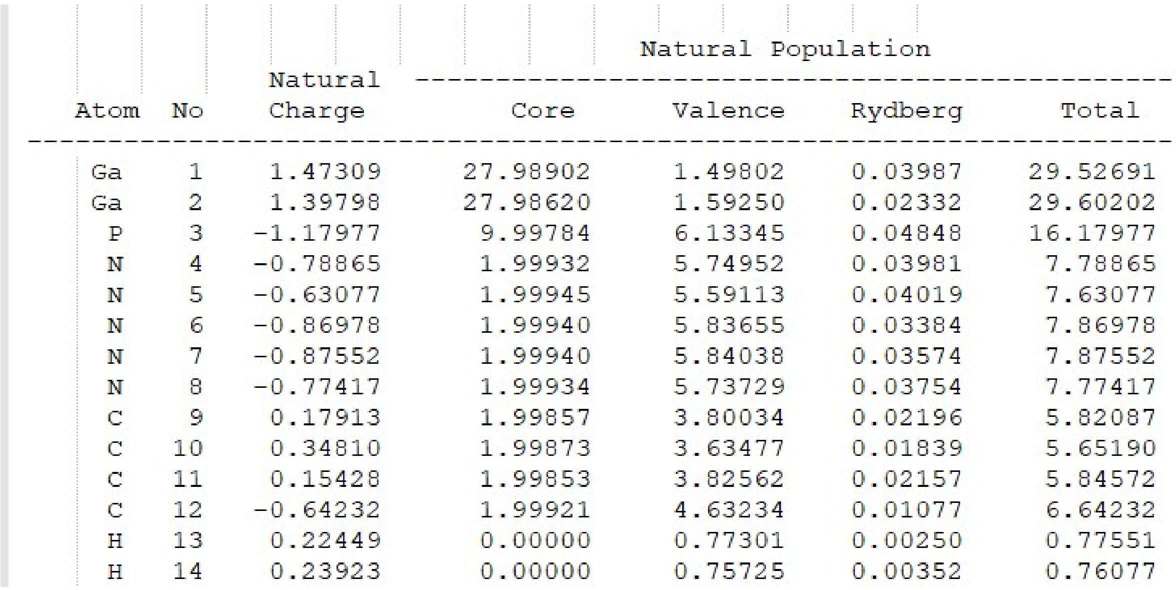
3. Computational details

Where available, optimisations were performed starting from the crystal structure geometry using the PBE0 functional and Def2SVP basis set.[7–9] The optimised structures were confirmed as a true minima via harmonic frequency calculations. A single point calculation was then performed using PBE0 with Def2TZVP for Ga, P, and N, and Def2SVP for C, H. All calculations were performed on the Gaussian16 software package,[10] natural bond order analysis was performed using NBO version 6.0 and NMR calculations were performed with the keyword NMR.[11] ^{31}P NMR calculations were performed using PBE0/6-31g(d,p),[12] as we have previously benchmarked this method to related low-valent phosphorus species with reasonable accuracy.[13] ^{31}P NMR calculations were referenced to phosphoric acid (δ_{calc} = 374 ppm).



```
     (Occupancy)   Bond orbital/ Coefficients/ Hybrids
 ---------------------------------------------------------------------------------
    1. (1.95489) BD ( 1)Ga   1 - P   3
                ( 34.12%)   0.5841*Ga   1 s( 73.96%)p 0.35( 25.82%)d 0.00(  0.20%)
                                                  f 0.00(  0.01%)
                                              0.0000  0.0000 -0.0000  0.8599  0.0112
                                             -0.0036 -0.0000 -0.0003 -0.4449 -0.0407
                                              0.0029 -0.0000 -0.0000 -0.0124  0.0085
                                              0.0002 -0.0000 -0.0005 -0.2357 -0.0533
                                              0.0027 -0.0001 -0.0139 -0.0010  0.0017
                                              0.0010 -0.0266  0.0076 -0.0024  0.0000
                                              0.0139  0.0038  0.0022  0.0005  0.0049
                                              0.0076 -0.0024  0.0002 -0.0277 -0.0013
                                              0.0017  0.0003 -0.0080 -0.0008 -0.0052
                                              0.0040 -0.0030  0.0036
                ( 65.88%)   0.8117* P   3 s( 18.87%)p 4.25( 80.12%)d 0.05(  1.00%)
                                                  f 0.00(  0.01%)
                                              0.0000 -0.0006  0.4343 -0.0081  0.0007
                                              0.0001  0.5968 -0.0006 -0.0030  0.0003
                                             -0.0000 -0.1367 -0.0032 -0.0007  0.0000
                                              0.0000  0.6529  0.0076 -0.0001  0.0004
                                             -0.0111 -0.0008  0.0762  0.0035 -0.0195
                                             -0.0002  0.0291  0.0008  0.0535 -0.0024
                                             -0.0004 -0.0015 -0.0018  0.0064 -0.0009
                                              0.0046 -0.0024
    2. (1.95288) BD ( 1)Ga   2 - P   3
                ( 35.66%)   0.5971*Ga   2 s( 76.30%)p 0.31( 23.48%)d 0.00(  0.19%)
                                                  f 0.00(  0.02%)
                                             -0.0000 -0.0000  0.0003 -0.8735 -0.0075
                                              0.0051  0.0000 -0.0004 -0.4808 -0.0319
                                              0.0030  0.0000 -0.0000  0.0140  0.0003
                                              0.0007  0.0000  0.0004  0.0160  0.0465
                                             -0.0026 -0.0001  0.0020 -0.0021 -0.0021
                                              0.0009 -0.0376 -0.0082 -0.0034  0.0003
                                             -0.0077  0.0013  0.0006 -0.0005 -0.0068
                                             -0.0103  0.0071 -0.0004  0.0092 -0.0049
                                             -0.0062 -0.0068 -0.0015  0.0010  0.0086
                                              0.0019 -0.0092 -0.0022
                ( 64.34%)   0.8021* P   3 s( 14.41%)p 5.87( 84.67%)d 0.06(  0.91%)
                                                  f 0.00(  0.01%)
                                              0.0000  0.0011 -0.3796 -0.0001 -0.0004
                                              0.0001  0.7925  0.0043 -0.0045  0.0005
                                             -0.0000  0.0949  0.0052  0.0001 -0.0001
                                              0.0001 -0.4576  0.0113 -0.0014 -0.0002
                                             -0.0147  0.0001  0.0793  0.0030  0.0150
                                             -0.0013 -0.0447 -0.0035 -0.0192  0.0052
                                             -0.0027 -0.0038  0.0014 -0.0023  0.0004
                                              0.0066 -0.0000
```

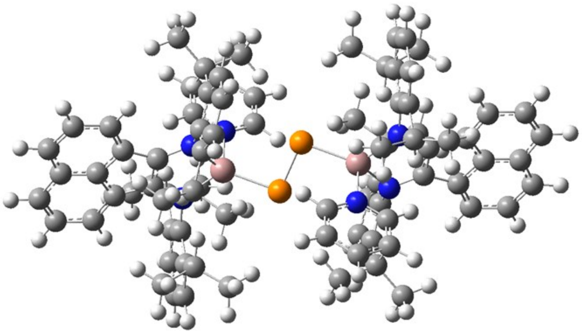
Figure S27. Section of the natural bond orbital analysis of **5**.



```
                                    Natural Population
              Natural  -----------------------------------------------
   Atom  No    Charge        Core      Valence    Rydberg      Total
 -----------------------------------------------------------------------
    Ga    1    1.47309     27.98902     1.49802    0.03987    29.52691
    Ga    2    1.39798     27.98620     1.59250    0.02332    29.60202
     P    3   -1.17977      9.99784     6.13345    0.04848    16.17977
     N    4   -0.78865      1.99932     5.74952    0.03981     7.78865
     N    5   -0.63077      1.99945     5.59113    0.04019     7.63077
     N    6   -0.86978      1.99940     5.83655    0.03384     7.86978
     N    7   -0.87552      1.99940     5.84038    0.03574     7.87552
     N    8   -0.77417      1.99934     5.73729    0.03754     7.77417
     C    9    0.17913      1.99857     3.80034    0.02196     5.82087
     C   10    0.34810      1.99873     3.63477    0.01839     5.65190
     C   11    0.15428      1.99853     3.82562    0.02157     5.84572
     C   12   -0.64232      1.99921     4.63234    0.01077     6.64232
     H   13    0.22449      0.00000     0.77301    0.00250     0.77551
     H   14    0.23923      0.00000     0.75725    0.00352     0.76077
```

Figure S28. Segment of the natural population analysis of **5**.

3.1 Coordinates of optimised structure 3



Ga	-0.67779500	-2.53126900	0.26989400
P	-0.15641300	-0.56682500	-0.85447900
N	0.48898200	-3.40374700	1.53620200
N	-1.14926900	-4.23821500	-0.47813400
N	-2.38234800	-2.13456400	1.47995300
C	-0.52092300	-5.18916100	0.29971200
C	0.86728400	-5.93662800	2.01054500
C	0.32504100	-4.76414900	1.32264700
C	1.68106300	-2.91196900	2.13018600
C	0.31237400	-7.06405700	1.34140400
C	-1.76335200	-4.59245200	-1.70807600
C	1.72184200	-6.17335500	3.07063000
H	2.19073800	-5.35494500	3.62147900
C	2.94470300	-3.15767100	1.53568300
C	-3.16019400	-4.81318300	-1.76767200
C	-0.54453000	-6.65545900	0.28116600
C	-0.97734100	-4.73348100	-2.87817900
C	0.52358500	-4.51181900	-2.87272700
H	0.79679200	-4.18561300	-1.85838900
C	0.57603800	-8.39001800	1.67764800
C	1.60301100	-2.15380700	3.32660400
C	-3.74231600	-5.16928100	-2.98826200
H	-4.82131200	-5.34097800	-3.03657100
C	-1.14408700	-7.64174100	-0.47914300

H	-1.79856100	-7.39985800	-1.31926300
C	-4.04080000	-4.67566700	-0.54114800
H	-3.37009600	-4.42536600	0.29198200
C	-1.60434200	-5.09401100	-4.07508200
H	-1.00143900	-5.20599700	-4.98043300
C	-2.69483900	-3.04181400	2.41484100
H	-2.01777000	-3.89594600	2.50464200
C	4.09542200	-2.67226700	2.16658300
H	5.07198900	-2.86487700	1.71367300
C	2.00225700	-7.52031500	3.43989500
H	2.67929500	-7.69546800	4.28022800
C	-0.06489000	-9.38554600	0.88180900
H	0.10176700	-10.44472500	1.09528500
C	3.09899400	-3.87358800	0.20378100
H	2.11464600	-4.26985000	-0.08196000
C	-2.97523200	-5.31363500	-4.13795300
H	-3.44564200	-5.59563600	-5.08329900
C	-0.88984100	-9.00600200	-0.15798300
H	-1.37031500	-9.77792200	-0.76493000
C	-3.15615000	-1.05762400	1.31396100
H	-2.84861600	-0.35481100	0.53466000
C	-5.04390500	-3.53178300	-0.70059900
H	-4.54076900	-2.58611600	-0.95398200
H	-5.61657200	-3.37877600	0.22868500
H	-5.76843300	-3.74202900	-1.50405700
C	0.26670700	-1.91820600	4.00502300
H	-0.47385400	-1.80600200	3.20037100
C	2.78065600	-1.67759800	3.90891300
H	2.72579700	-1.09345600	4.82936700
C	4.02403800	-1.93957100	3.34414500
H	4.93457400	-1.56547200	3.81888600
C	1.45994900	-8.60334300	2.77761600
H	1.70488600	-9.62159900	3.09100000
C	4.05398000	-5.06558100	0.27929500

H	5.08631500	-4.75124500	0.50382900
H	4.07576700	-5.60060700	-0.68331300
H	3.74006500	-5.77968000	1.05424200
C	-4.74718700	-5.98401500	-0.18317500
H	-5.44255600	-6.30141300	-0.97707200
H	-5.33580500	-5.86651800	0.74117500
H	-4.02482300	-6.79802600	-0.02241400
C	0.93390000	-3.39947300	-3.83876400
H	0.68874400	-3.65387700	-4.88246200
H	2.02029400	-3.22454000	-3.78946400
H	0.42970400	-2.45160700	-3.59607200
C	3.53098700	-2.89228200	-0.88883300
H	2.79608000	-2.08059800	-1.00775000
H	3.62414500	-3.40492800	-1.85952200
H	4.50954600	-2.44090100	-0.65332900
C	-3.81047100	-2.89870900	3.22996100
H	-4.03410100	-3.65957200	3.97940900
C	1.28428800	-5.80898500	-3.15548600
H	1.01258000	-6.59669100	-2.43700700
H	2.37186300	-5.64507000	-3.08530700
H	1.07146800	-6.18808900	-4.16848700
C	-4.28394300	-0.83530100	2.09582000
H	-4.88189200	0.06329000	1.93635600
C	-0.13088000	-3.13847900	4.84068400
H	-0.13940000	-4.05857800	4.23775900
H	-1.13110100	-3.00471000	5.28527400
H	0.58330300	-3.28994000	5.66643900
C	-4.61625300	-1.77266300	3.07025600
H	-5.49651600	-1.62755300	3.70139400
C	0.20847700	-0.64550600	4.84318600
H	0.83559300	-0.71184600	5.74674000
H	-0.82318100	-0.46473200	5.18367000
H	0.53180700	0.23239800	4.26440400
P	0.15641300	0.56682500	0.85447900

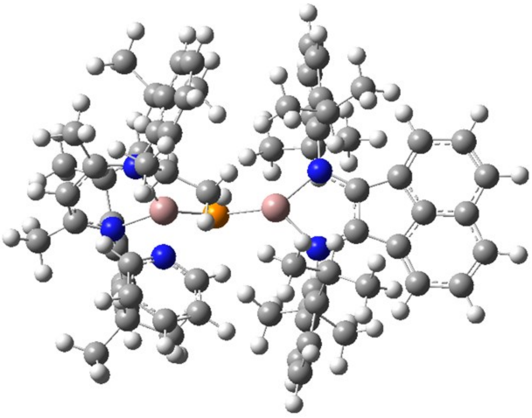
Ga	0.67779500	2.53126900	-0.26989400
N	-0.48898200	3.40374700	-1.53620200
N	1.14926900	4.23821500	0.47813400
N	2.38234800	2.13456400	-1.47995300
C	0.52092300	5.18916100	-0.29971200
C	-0.86728400	5.93662800	-2.01054500
C	-0.32504100	4.76414900	-1.32264700
C	-1.68106300	2.91196900	-2.13018600
C	-0.31237400	7.06405700	-1.34140400
C	1.76335200	4.59245200	1.70807600
C	-1.72184200	6.17335500	-3.07063000
H	-2.19073800	5.35494500	-3.62147900
C	-2.94470300	3.15767100	-1.53568300
C	3.16019400	4.81318300	1.76767200
C	0.54453000	6.65545900	-0.28116600
C	0.97734100	4.73348100	2.87817900
C	-0.52358500	4.51181900	2.87272700
H	-0.79679200	4.18561300	1.85838900
C	-0.57603800	8.39001800	-1.67764800
C	-1.60301100	2.15380700	-3.32660400
C	3.74231600	5.16928100	2.98826200
H	4.82131200	5.34097800	3.03657100
C	1.14408700	7.64174100	0.47914300
H	1.79856100	7.39985800	1.31926300
C	4.04080000	4.67566700	0.54114800
H	3.37009600	4.42536600	-0.29198200
C	1.60434200	5.09401100	4.07508200
H	1.00143900	5.20599700	4.98043300
C	2.69483900	3.04181400	-2.41484100
H	2.01777000	3.89594600	-2.50464200
C	-4.09542200	2.67226700	-2.16658300
H	-5.07198900	2.86487700	-1.71367300
C	-2.00225700	7.52031500	-3.43989500
H	-2.67929500	7.69546800	-4.28022800

C	0.06489000	9.38554600	-0.88180900
H	-0.10176700	10.44472500	-1.09528500
C	-3.09899400	3.87358800	-0.20378100
H	-2.11464600	4.26985000	0.08196000
C	2.97523200	5.31363500	4.13795300
H	3.44564200	5.59563600	5.08329900
C	0.88984100	9.00600200	0.15798300
H	1.37031500	9.77792200	0.76493000
C	3.15615000	1.05762400	-1.31396100
H	2.84861600	0.35481100	-0.53466000
C	5.04390500	3.53178300	0.70059900
H	4.54076900	2.58611600	0.95398200
H	5.61657200	3.37877600	-0.22868500
H	5.76843300	3.74202900	1.50405700
C	-0.26670700	1.91820600	-4.00502300
H	0.47385400	1.80600200	-3.20037100
C	-2.78065600	1.67759800	-3.90891300
H	-2.72579700	1.09345600	-4.82936700
C	-4.02403800	1.93957100	-3.34414500
H	-4.93457400	1.56547200	-3.81888600
C	-1.45994900	8.60334300	-2.77761600
H	-1.70488600	9.62159900	-3.09100000
C	-4.05398000	5.06558100	-0.27929500
H	-5.08631500	4.75124500	-0.50382900
H	-4.07576700	5.60060700	0.68331300
H	-3.74006500	5.77968000	-1.05424200
C	4.74718700	5.98401500	0.18317500
H	5.44255600	6.30141300	0.97707200
H	5.33580500	5.86651800	-0.74117500
H	4.02482300	6.79802600	0.02241400
C	-0.93390000	3.39947300	3.83876400
H	-0.68874400	3.65387700	4.88246200
H	-2.02029400	3.22454000	3.78946400
H	-0.42970400	2.45160700	3.59607200

C	-3.53098700	2.89228200	0.88883300
H	-2.79608000	2.08059800	1.00775000
H	-3.62414500	3.40492800	1.85952200
H	-4.50954600	2.44090100	0.65332900
C	3.81047100	2.89870900	-3.22996100
H	4.03410100	3.65957200	-3.97940900
C	-1.28428800	5.80898500	3.15548600
H	-1.01258000	6.59669100	2.43700700
H	-2.37186300	5.64507000	3.08530700
H	-1.07146800	6.18808900	4.16848700
C	4.28394300	0.83530100	-2.09582000
H	4.88189200	-0.06329000	-1.93635600
C	0.13088000	3.13847900	-4.84068400
H	0.13940000	4.05857800	-4.23775900
H	1.13110100	3.00471000	-5.28527400
H	-0.58330300	3.28994000	-5.66643900
C	4.61625300	1.77266300	-3.07025600
H	5.49651600	1.62755300	-3.70139400
C	-0.20847700	0.64550600	-4.84318600
H	-0.83559300	0.71184600	-5.74674000
H	0.82318100	0.46473200	-5.18367000
H	-0.53180700	-0.23239800	-4.26440400

Energy = -21090789.13 kJ/mol

3.2 Coordinates of optimised structure 5



Ga	2.48916800	-0.01169900	0.19141000
Ga	-1.21394900	0.07256300	-0.38157900
P	0.82905100	0.19918900	-1.27932300
N	3.24684700	-1.50929500	1.27800900
N	2.47007100	1.47088300	1.73169400
N	-2.69328900	-1.09638700	-0.67969500
N	-2.49169400	1.45981800	-0.01843800
N	4.23167700	0.50546500	-0.64429700
C	-2.71780500	-2.49592400	-0.89027900
C	5.39773500	0.15310600	-0.11309600
C	4.23169400	1.21359300	-1.89624500
C	-0.47735500	3.83348300	-2.59708800
H	-0.49212300	3.63405100	-3.68025500
H	0.31005800	3.20298900	-2.15804500
H	-0.20269400	4.89281700	-2.46149100
C	2.41636800	-3.61209000	-0.56496000
H	2.44780800	-2.55677200	-0.88282000
C	6.67336900	0.68896600	-0.70194700
H	6.80306600	0.32716300	-1.73212000
H	7.54219400	0.38025900	-0.10863000
H	6.64586400	1.78533300	-0.76526800
C	-1.83753800	3.51065900	-1.98287800
H	-2.00948400	2.43260000	-2.11550400
C	2.88983900	4.26346200	-0.56895700
H	2.82577200	4.80767700	0.38656200
H	2.01758100	3.60043800	-0.65487100
H	2.81678400	5.00587100	-1.37962700
C	3.47424800	1.64605800	2.60343000
H	4.32140500	0.95986400	2.51755400
C	2.01431200	-2.57957600	3.13539500
C	5.52964100	-0.74415100	0.96457900
C	4.24955200	2.55612800	-4.35066600
H	4.25388200	3.08037100	-5.30931200
C	2.79024100	-1.81508300	5.44527800

H	2.03317900	-2.36813400	6.02238000
H	3.05224800	-0.92150500	6.03330700
H	3.68594500	-2.45224900	5.38150400
C	-2.97796000	-4.74016900	-0.02274100
H	-3.17898700	-5.41847000	0.81079700
C	-2.23321900	4.41794600	2.22256900
H	-2.38599500	4.67864500	3.27419500
C	-2.94035300	2.07209200	2.81567000
H	-3.09936700	1.13081200	2.26903800
C	4.55905800	-1.60058200	1.51397000
C	2.04224200	-3.61870500	0.90756800
C	4.19663100	3.47365900	-0.66229900
H	4.23733800	2.78820200	0.19655400
C	5.07795600	-2.69664000	2.40750600
H	4.71262200	-2.57404700	3.43720900
H	6.17413300	-2.70205100	2.42001400
H	4.71873300	-3.67922400	2.06953200
C	-7.06309400	2.94822600	-0.01196800
H	-7.48342800	3.94186400	0.16543200
C	-7.37677300	0.60226400	-0.55034500
C	2.27102300	-1.40818200	4.06629800
H	3.04056200	-0.77695200	3.59870400
C	1.31454400	3.32687100	2.69365800
H	0.42906100	3.96577100	2.67760300
C	4.24551300	0.47101700	-3.09959900
C	3.45308700	2.65633500	3.55507500
H	4.29167000	2.76904100	4.24444300
C	1.00009800	-4.75719700	2.78707500
H	0.46225200	-5.62175300	3.18343300
C	1.00231500	-0.56280500	4.19384700
H	0.61908200	-0.26808400	3.20622500
H	1.18842700	0.35147000	4.78022200
H	0.20164200	-1.12956600	4.69507500
C	3.80013500	-4.22415100	-0.80107000

H	4.59888500	-3.66761300	-0.28900000
H	4.04018300	-4.22833100	-1.87613100
H	3.83337100	-5.26788900	-0.44781100
C	-7.42653900	-1.75501400	-1.12883100
H	-7.99337800	-2.65093000	-1.39605500
C	-2.28896700	2.78284500	0.43304900
C	4.23317600	3.27204900	-3.16120300
H	4.22365000	4.36455600	-3.19249300
C	-2.47694100	3.10587100	1.80133000
C	2.40945200	-2.56714200	1.77845400
C	-2.97004100	4.24640800	-2.70534900
H	-2.85645800	5.34027600	-2.62542400
H	-3.95291700	3.97809200	-2.28928300
H	-2.97459400	3.98941800	-3.77660000
C	-3.76161200	0.95210500	-0.19002300
C	-2.48070900	-3.01829500	-2.18205600
C	-6.00770400	-1.85642700	-1.04462400
H	-5.52382500	-2.81354600	-1.25082700
C	-3.27501300	-2.81285700	1.58629500
H	-3.47186500	-1.73649700	1.47755900
C	2.35082000	3.51098600	3.60261100
H	2.30610600	4.31616200	4.34032200
C	-0.98434500	-2.38645600	-4.12635000
H	-0.12126000	-2.25877800	-3.45688100
H	-0.86521400	-1.68368100	-4.96630900
H	-0.95268600	-3.40655400	-4.54351800
C	-8.10456300	-0.57656000	-0.89295300
H	-9.19426100	-0.54026800	-0.97362600
C	-2.47964400	-4.40766700	-2.35194100
H	-2.29703000	-4.82372900	-3.34661800
C	-3.49843700	-2.20076200	-4.32466200
H	-3.60480500	-3.21239600	-4.75017100
H	-3.38831900	-1.49573200	-5.16426700
H	-4.43368300	-1.95740900	-3.79805400

C	1.41626400	2.29283500	1.76803200
H	0.64773200	2.10764700	1.00728500
C	-5.99272700	0.47424300	-0.46284300
C	-4.51776600	-3.43290900	2.22414300
H	-4.38677900	-4.50832000	2.42682500
H	-5.40103700	-3.31292700	1.57928600
H	-4.73568300	-2.94527400	3.18763200
C	-5.10108100	1.54139500	-0.15094000
C	-2.29220500	-2.11379200	-3.38604100
H	-2.24588900	-1.08286700	-3.00520000
C	-7.91346500	1.90157600	-0.30450300
H	-8.99316100	2.06477500	-0.35752900
C	-5.27766100	-0.73333500	-0.70571000
C	-1.89898000	3.78407900	-0.49039600
C	-2.71803600	-5.26622900	-1.28510500
H	-2.71277100	-6.34855500	-1.43881500
C	-3.86451300	-0.38878000	-0.53144200
C	-5.64909000	2.79142000	0.06711200
H	-5.02564800	3.65860400	0.29614300
C	4.25524200	1.16818000	-4.31145400
H	4.26321100	0.60522600	-5.24812300
C	1.36973100	-4.29075600	-1.44436100
H	1.34429100	-5.38236800	-1.29699100
H	1.60358200	-4.11589200	-2.50486600
H	0.36114500	-3.89465100	-1.25638100
C	4.25951400	-1.04843400	-3.13615700
H	4.17731800	-1.40939800	-2.09992700
C	5.57138700	-1.59104300	-3.71101500
H	5.70529400	-1.28367800	-4.76052300
H	5.57688100	-2.69223600	-3.68572800
H	6.45089900	-1.24139000	-3.14935400
C	5.40009700	4.41424100	-0.55993400
H	5.39928900	5.15943600	-1.37080000
H	6.35813400	3.87473300	-0.61204300

H	5.37722700	4.96687300	0.39279900
C	-2.05407900	-2.96598100	2.49263900
H	-2.23422500	-2.50106200	3.47616400
H	-1.15990200	-2.49860700	2.05179200
H	-1.81549000	-4.02789500	2.66143500
C	4.22452600	2.62560700	-1.92140800
C	-2.99144900	-3.36016000	0.19736900
C	3.06108700	-1.60132700	-3.90852200
H	2.11610400	-1.24441500	-3.47205700
H	3.06293800	-2.70244900	-3.88159000
H	3.08868700	-1.30126200	-4.96814800
C	-1.87695400	1.80919000	3.88207500
H	-0.92681700	1.48717100	3.43315800
H	-2.20693200	1.01655200	4.57262200
H	-1.67593900	2.70987600	4.48588500
C	1.31837300	-3.69150700	3.61805100
H	1.01395900	-3.71901200	4.66679200
C	-1.64806700	5.07624700	-0.01475600
H	-1.34292500	5.85376100	-0.72062800
C	-1.80922000	5.39788800	1.32876100
H	-1.62367200	6.41776900	1.67639200
C	-4.26985000	2.45807400	3.46711600
H	-4.17821000	3.38456200	4.05764300
H	-4.60562100	1.66284700	4.15154900
H	-5.05771600	2.60923500	2.71596600
C	1.34049200	-4.70457700	1.44164800
H	1.05121900	-5.52654500	0.78516400
H	6.55046700	-0.92290400	1.29837300

Energy = -18846522.74 kJ/mol

4. EPR Spectroscopy

Continuous wave electron paramagnetic resonance (CW-EPR) of the samples under photolysis leads to small fractional mole percent of spin concentration from the overall sample concentration of the analytes **2a**−**c**, shown in Figures S29−S32. For example, EPR signals of 64−80 μM in Figure S30 represent found in sample **2b** represent only 1.3 mole percent of the 5 mM total molecular concentration prior to photolysis. In addition to low mole percent of spin signals, inconsistency in the shape of these signals and complex photolytic changes in the time course, lead to some uncertainty as to the role of the species represented by the signals, beyond contributing generally to the absence of NMR features. An isotropic EPR simulation, shown in Figure S30c, of the signal from a concentrated **2b** sample of 4 mM spin concentration (nearly identical to 55 μM spin concentration) employed $g = 2.0022$, $A\{\text{Ga,N,P,H}\} = \{45.8,15.68,32.6,1.45\}$ / MHz with number of equivalent hyperfine couplings of $n = \{1,2,1,8\}$, respectively. However, intensities are up to a factor of two greater in the simulation edges, characteristic asymmetry is absent, and the g-factor is not indicative of Ga and P character in the molecular wavefunction, given their large contribution in hyperfine coupling. DFT calculations of candidate structure hyperfine interaction values, such as from the photolysis of CO form PCO moiety and breaking of the P=P bond of **3** diverged in derived, simulated EPR spectral shape and g-value. Low temperature photolysis failed to produce characteristic phosphinidene triplet state signals near 1250 mT and 9.7 GHz.[13b] Future work to isolate and study the radicals with advanced EPR methods may elucidate their structure and any mechanistic role more clearly.

CW-EPR was collected in the Centre for Advanced ESR (CAESR) in the Inorganic Chemistry Laboratory of the Department of Chemistry of the University of Oxford. The X-band (9.1-9.9 GHz) spectrometer was an EMXmicro with a Premium bridge and 0.64 T, 6-inch electromagnet. The Xenon control software was version 1.1b.159. Spin quantitation of the CW-EPR signals involved use of the hardware calibration of the resonator, a Bruker BioSpin ER-4122-SHQE-W1 cylindrical mode TE011, with a Q-value of about 6500−8800 for the samples studied. Sample tubes were custom 3.8 mm O.D. clear fuse quartz, with a J. Young tap added by the university glassblower. Resulting spin quantitation has been found to be accurate within 10% with these tubes and hardware determination. Photolysis involved a Schott KL2500LED broadband white light source set to 680 mW measured by an Ophir 3A thermopile detector head.

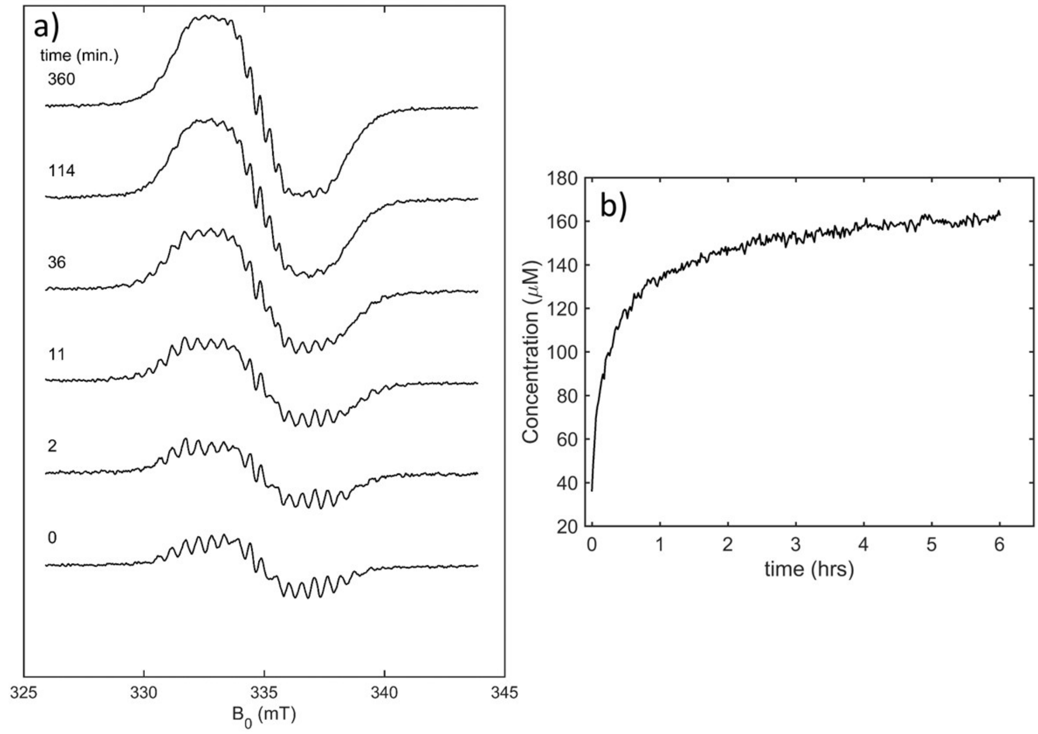


Figure S29. Time course of room temperature X-band CW-EPR (a.u.) of the **2a** sample dissolved in pyridine, at selected time points as indicated in panel a) and the concentration dependence of the entire signal as a function of time in panel b). The initial **2a** concentration was 20 mM. The signal evolves from a prior radical to one unresolved in features. The microwave frequency was 9.3877 GHz, and modulation amplitude of 0.1 mT.

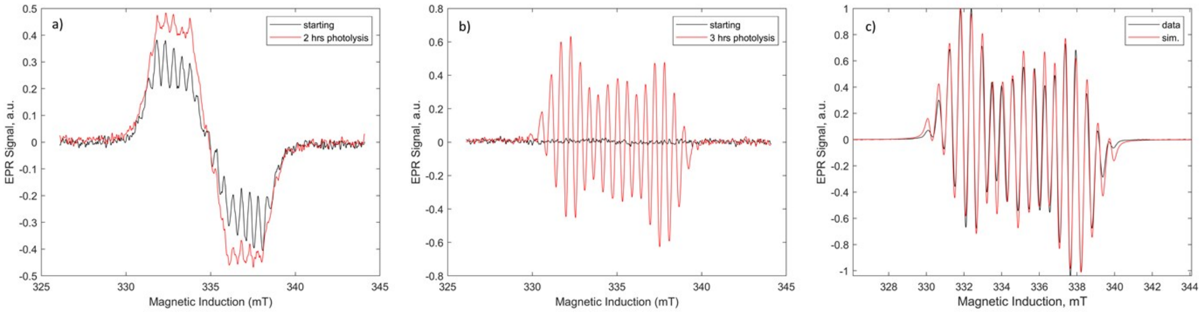


Figure 30. X-band CW-EPR of starting and photolysis points of two samples of **2b**. The panel a) had a **2b** concentration of 5 mM and the spin concentration increase from 45 to 65 µM over the course of two hours. A second sample, of a 20 mM solution, in panel b) had no EPR signal as dissolved, and spin concentration was 20 µM at 3 hrs, though increasing overnight to 125 µM. An EPR simulation of **2b** is shown in panel c, as discussed in supplemental ESR text. For panels a&b, the microwave frequency was 9.384 GHz, modulation amplitude was 0.1 mT, and microwave power of 1 mW. For panel c), the microwave frequency was 9.3884 GHz, modulation amplitude of 0.05 mT, and microwave power of 0.1 mW.

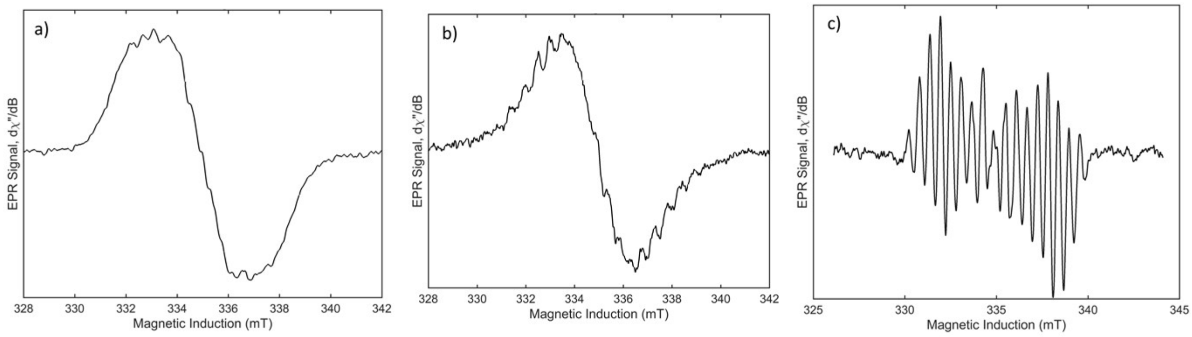


Figure 31. X-band CW-EPR of two samples of crystalline **2c**. The first at 20 mM, as dissolved in panel a) leading to 80 µM spin concentration and after subsequent heating in panel b) for 10 min. at 50 deg., gave 64 µM spin concentration. A second at crystalline **2c** sample had no EPR signal as dissolved, *not shown*, and a very weak EPR signal in the photolytic time course peaking at 1.5 µM spin concentration at 2.2 hours of photolysis, generated from a 5 mM solution of **2c**. The sum total of all time periods of the second sample is shown in panel c). For

panels a & b, the microwave frequency was 9.3869 GHz, modulation amplitude was 0.05 mT, and microwave power of 0.1 mW. For panel c), the microwave frequency was 9.3878 GHz, modulation amplitude of 0.1 mT, and a microwave power of 1 mW.

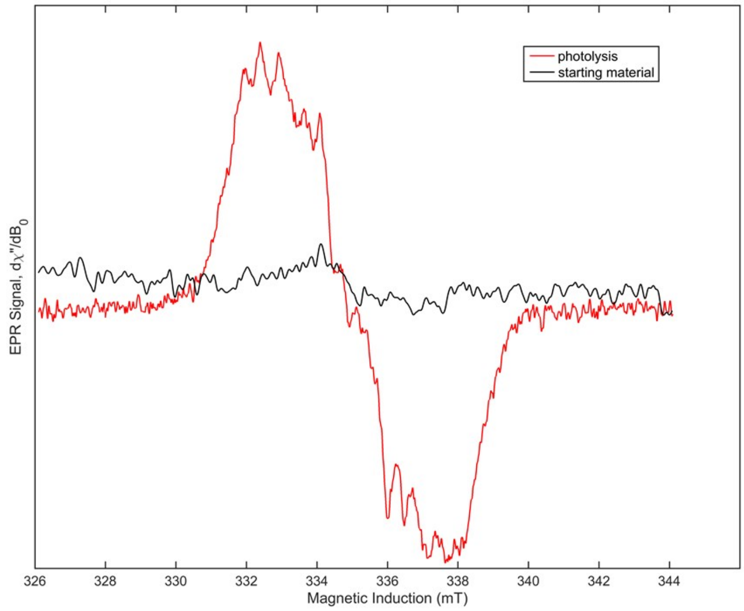


Figure 32. X-band CW-EPR of the photolysis product of **2b** in the presence of trimethylphosphine, leading to a spin concentration of 68 uM, from an initial concentration of **2b** of 5 mM. The microwave frequency was 9.38845 GHz, , modulation amplitude of 0.1 mT, microwave power of 1 mW, and a field offset of 0.1 mT was applied.modulation amplitude of 0.05 mT, and a microwave power of 0.1 mW.

5. References

[1] I. L. Fedushkin, A. A. Skatova, V. A. Dodonov, V. A. Chudakova, N. L. Bazyakina, A. V. Piskunov, S. V. Demeshko and G. K. Fukin, *Inorg. Chem.*, 2014, **53**, 5159–5170.

[2] D. Heift, Z. Benko and H. Grützmacher, *Dalton Trans.*, 2014, **43**, 831–840.

[3] M. Hans, J. Lorkowski, A. Demonceau and L. Delaude, *Beilstein J. Org. Chem.*, 2015, **11**, 2318–2325.

[4] X. Bantreil and S. P. Nolan, *Nat. Protoc.*, 2011, **6**, 69–77.

[5] *CrysAlisPro*, Agilent Technologies, Version 1.171.35.8.

[6] (a) G. M. Sheldrick in SHELXL97, *Programs for Crystal Structure Analysis (Release 97-2)*, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998; (b) G. M. Sheldrick, *Acta Crystallogr. Sect. A* 1990, **46**, 467−473; (c) G. M. Sheldrick, *Acta Crystallogr. Sect. A* 2008, **64**, 112−122.

[7] C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158−6169.

[8] (a) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297−3305; (b) F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057−1065

[9] (a) A. Schaefer, H. Horn, and R. Ahlrichs, *J. Chem. Phys.*, 1992, **97**, 2571−2577; (b) A. Schaefer, C. Huber, and R. Ahlrichs, *J. Chem. Phys.*, 1994, **100**, 5829−5835.

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

L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[11] 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).

[12] G. A. Petersson and M. A. Al-Laham, *J. Chem. Phys.*, 1991, **94**, 6081–6090.

[13] a) D. W. N. Wilson, A. Hinz and J. M. Goicoechea, *Angew. Chem. Int. Ed.*, 2018, **57**, 2188–2193. b) D. W. N. Wilson, M. P. Franco, W. K. Myers, J. E. McGrady and J. M. Goicoechea, *Chem. Sci.*, 2020, **11**, 862–869.