

Carbene insertion into a P-H bond: Parent phosphinidene-carbene adducts from PH₃ and bis(phosphinidene) mercury complexes

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S1. Materials and methods

All reactions were carried out under argon using either standard Schlenk techniques or an argon-filled glove box. Solvents were purified using an Innovative Technology PureSolv MD 7 solvent purification system. Deuterated solvents were purchased from Cambridge Isotope Laboratories. THF- d_8 and C_6D_6 were distilled from sodium benzophenone, whereas CD_2Cl_2 was dried over 4 Å molecular sieves before use. All reagents were used as received from commercial suppliers unless otherwise stated. The compounds $[^{Dipp}NHC-H]-[Cl]$ (**5a**),¹ $[^{Dipp}NHC^*-H]-[Cl]$ (**5b**),² $(TMS)_3P$,³ $^{Dipp}NHC=PH$ (**7a**)⁴ and the aggregate compound $\{[Na(OtBu)]_x[Na(PH_2)]\}$ ($x \approx 2.5$)⁵ were synthesized following literature procedures. The exact stoichiometry of the latter was determined by integration of the 1H -NMR signals to be $x = 2.5$. Reactions involving PH_3 gas were carried out in a setup and following a procedure described by Pringle and co-workers⁶ and PH_3 electronic grade, > 99.9995 % was used.

NMR spectra were recorded on Bruker 300 MHz and 500 MHz spectrometers. All 1H and ^{13}C chemical shifts are reported in ppm relative to $SiMe_4$ using the 1H and ^{13}C shifts of the solvent as an internal standard. ^{31}P -NMR shifts are reported relative to 85% H_3PO_4 .

Elemental analyses were performed at the microanalysis laboratory of ETH Zürich. Elemental analysis of the mercury complexes could not be carried out due to the incompatibility of the equipment with mercury. As an alternative method of bulk characterization, powder X-ray diffraction patterns of these complexes were recorded and compared to patterns calculated from the single crystal data.

S2. X-ray diffraction studies

X-ray single crystal diffraction studies were performed on a Bruker X8 APEX2 or an Oxford XCalibur S diffractometer, both equipped with a molybdenum X-ray tube ($\lambda = 0.7107 \text{ \AA}$). Preliminary data was collected to determine the crystal system.

Powder X-ray diffraction patterns were recorded on a *STOE* Stadi P diffractometer equipped with a germanium monochromator and $CuK_{\alpha 1}$ radiation (operated at 35 mA, 35 kV). Powder spectra were simulated using: *STOE* WinXPow, version 3.0.1.13.

Table 1: Crystal data and structure refinement details.

| Compound | [^{Dipp}NHC*-H]-[PH₂] (6b) | DippNHC=PH (7b) |
|---|---|--|
| Empirical formula | C ₂₇ H ₄₁ N ₂ P | C ₂₇ H ₃₉ N ₂ P |
| Formula weight | 424.59 | 422.57 |
| Temperature/K | 105.7(3) | 173.0 |
| Crystal system | orthorhombic | orthorhombic |
| Space group | Pbca | Pnma |
| a/Å | 12.1771(3) | 11.8631(6) |
| b/Å | 16.0504(3) | 20.2676(9) |
| c/Å | 26.4131(5) | 10.9214(5) |
| α/° | 90.00 | 90 |
| β/° | 90.00 | 90 |
| γ/° | 90.00 | 90 |
| Volume/Å ³ | 5162.35(19) | 2625.9(2) |
| Z | 8 | 4 |
| ρ _{calc} /g/cm ³ | 1.093 | 1.069 |
| μ/mm ⁻¹ | 0.122 | 0.119 |
| F(000) | 1856.0 | 920.0 |
| Crystal size/mm ³ | 0.16 × 0.16 × 0.1 | 0.23 × 0.15 × 0.1 |
| Radiation | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) |
| 2θ range for data collection/° | 5.94 to 52.74 | 4.02 to 55.876 |
| Reflections collected | 38487 | 42885 |
| Independent reflections | 5270 | 3242 |
| Data/restraints/parameters | 5270/0/287 | 3242/0/175 |
| Goodness-of-fit on F ² | 1.111 | 1.021 |
| Final R indexes [I ≥ 2σ (I)] | R ₁ = 0.0545, wR ₂ = 0.1275 | R ₁ = 0.0476, wR ₂ = 0.1236 |
| Final R indexes [all data] | R ₁ = 0.0633, wR ₂ = 0.1323 | R ₁ = 0.0645, wR ₂ = 0.1364 |
| Largest diff. peak/hole / e Å ⁻³ | 0.38/-0.39 | 0.41/-0.27 |
| Compound | [(^{Dipp}NHC=P)₂Hg] (8a) | [(^{Dipp}NHC*=P)₂Hg] (8b) |
| Empirical formula | C ₅₄ H ₇₂ HgN ₄ P ₂ | C ₂₇ H ₃₈ Hg _{0.5} N ₂ P |
| Formula weight | 1039.69 | 521.86 |
| Temperature/K | 100(2) | 106.22(15) |
| Crystal system | triclinic | triclinic |
| Space group | P-1 | P-1 |
| a/Å | 10.4911(8) | 10.7696(5) |
| b/Å | 11.1172(8) | 11.0160(10) |
| c/Å | 12.5446(9) | 12.2625(6) |
| α/° | 103.202(2) | 103.816(6) |
| β/° | 112.596(2) | 110.797(5) |
| γ/° | 95.847(2) | 96.922(6) |
| Volume/Å ³ | 1285.49(16) | 1286.44(15) |
| Z | 1 | 2 |
| ρ _{calc} /g/cm ³ | 1.338 | 1.347 |
| μ/mm ⁻¹ | 3.093 | 3.091 |
| F(000) | 534.0 | 538.0 |
| Crystal size/mm ³ | 0.3 × 0.14 × 0.03 | 0.16 × 0.12 × 0.08 |
| Radiation | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) |
| 2θ range for data collection/° | 4.48 to 58.26 | 5.72 to 52.74 |
| Reflections collected | 49394 | 10844 |
| Independent reflections | 6911 | 5259 |
| Data/restraints/parameters | 6911/0/285 | 5259/0/285 |
| Goodness-of-fit on F ² | 1.078 | 1.044 |
| Final R indexes [I ≥ 2σ (I)] | R ₁ = 0.0215, wR ₂ = 0.0495 | R ₁ = 0.0513, wR ₂ = 0.1132 |
| Final R indexes [all data] | R ₁ = 0.0216, wR ₂ = 0.0496 | R ₁ = 0.0524, wR ₂ = 0.1139 |
| Largest diff. peak/hole / e Å ⁻³ | 1.29/-0.50 | 4.59/-3.19 |

Table 2: Comparison of selected bond lengths and angles of the free carbenes DippNHC^2 and DippNHC^* ,⁷ the phosphanyl-phosphinidene $[\text{DippNHC-H}]\text{-[PH}_2\text{]}$ (**6b**), the carbene-phosphinidene adducts DippNHC=PH (**7a**),⁴ $\text{DippNHC}^*=\text{PH}$ (**7b**), $\text{Li}(\text{DippNHC}=\text{PH})$,⁸ $\text{DippNHC}=\text{P}(\text{TMS})$ ⁸ and $\text{MesNHC}^*=\text{PPh}$,⁹ the PCl_3 -adduct DippNHC-PCl_3 ,⁸ the NHC-stabilized diphosphorus $(\text{DippNHC}=\text{P})_2$,¹⁰ the bis(phosphinidene) mercury(II) complexes $[(\text{DippNHC}=\text{P})_2\text{Hg}]$ (**8a**) and $[(\text{DippNHC}^*=\text{P})_2\text{Hg}]$ (**8b**) and the phosphinidene transition metal complexes $[(\text{DippNHC}=\text{P})\text{Ru}(\text{L}^1)(\text{Cl})]$ ¹¹ and $[(\text{DippNHC}=\text{P})\text{Rh}(\text{L}^2)(\text{Cl})]$.¹¹ $\text{L}^1 = \eta^6\text{-}p\text{-cymene}$, $\text{L}^2 = \eta^5\text{-C}_5\text{Me}_5$. ^a Bond length given in Å. ^b Bond angle given in °.

| Compound | C1–P1 ^a | C1–N1 ^a | C1–N2 ^a | M1–P1 ^a | N1–C1–N2 ^b |
|---|--------------------|--------------------|--------------------|--------------------|-----------------------|
| DippNHC | | 1.367 | | | 101.4 |
| DippNHC* | | 1.346(2) | 1.347(2) | | 105.0(1) |
| $[\text{DippNHC-H}]\text{-[PH}_2\text{]}$ (6b) | 1.885(2) | 1.454(2) | 1.456(2) | | 101.5(5) |
| $\text{DippNHC}=\text{PH}$ (7a) | 1.752(1) | 1.374(1) | 1.373(1) | | 104.3(1) |
| $\text{DippNHC}^*=\text{PH}$ (7b) | 1.743(2) | 1.357 (2) | | | 107.4(2) |
| $\text{Li}(\text{DippNHC}=\text{PH})$ | 1.763(2) | 1.362(3) | 1.366(3) | | 103.7(2) |
| $\text{DippNHC}=\text{P}(\text{TMS})$ | 1.774(1) | 1.379(2) | 1.378 (2) | | 103.8(1) |
| $\text{MesNHC}^*=\text{PPh}$ | 1.746(4) | 1.352(1) | 1.378(5) | | 107.4(3) |
| $\text{DippNHC}\rightarrow\text{PCl}_3$ | 1.87(1) | 1.356(3) | 1.349(3) | | 106.0(2) |
| $(\text{DippNHC}=\text{P})_2$ | 1.750(2) | 1.393(2) | 1.387(2) | | 103.1(1) |
| $[(\text{DippNHC}=\text{P})_2\text{Hg}]$ (8a) | 1.755(2) | 1.384(2) | 1.384(2) | 2.399(1) | 103.6(1) |
| $[(\text{DippNHC}^*=\text{P})_2\text{Hg}]$ (8b) | 1.754(6) | 1.380(7) | 1.384(7) | 2.407(1) | 106.5(5) |
| $[(\text{DippNHC}=\text{P})\text{Ru}(\text{L}^1)(\text{Cl})]$ | 1.824(2) | 1.363(3) | 1.360(3) | 2.201(1) | 105.5(2) |
| $[(\text{DippNHC}=\text{P})\text{Rh}(\text{L}^2)(\text{Cl})]$ | 1.822(6) | 1.354 | 1.365 | 2.354(2) | 104.9(5) |

Table 3: Comparison of selected bond lengths and angles of the bis(phosphinidene) mercury(II) complexes $[(\text{DippNHC}=\text{P})_2\text{Hg}]$ (**8a**) and $[(\text{DippNHC}^*=\text{P})_2\text{Hg}]$ (**8b**), the bis(phosphane) mercury(II) complexes $[\text{Hg}(\text{PCy}_3)_2](\text{ClO}_4)_2$,¹² $[\text{Hg}(\text{P}(2,4,6\text{-Trimethoxyphenyl})_3)_2](\text{Hg}_2\text{Cl}_4)$ ¹³ and $[\text{Hg}(\text{PBn}_3)_2](\text{BF}_4)_2$ ¹⁴ and the bis(phosphido) mercury(II) complexes $[\text{Hg}(\text{P}(\text{tBu})_2)_2]$ ¹⁵ and $[\text{Hg}(\text{P}(\text{TMS})_2)_2]$.¹⁶ ^a Bond length given in Å. ^b Bond angle given in °.

| Compound | P1–Hg1 ^a | P2–Hg1 ^a | P1–Hg1–P2 ^b |
|--|---------------------|---------------------|------------------------|
| $[(\text{DippNHC}=\text{P})_2\text{Hg}]$ (8a) | 2.399 (1) | | 180 |
| $[(\text{DippNHC}^*=\text{P})_2\text{Hg}]$ (8b) | 2.407 (1) | | 180 |
| $[\text{Hg}(\text{PCy}_3)_2](\text{ClO}_4)_2$ | 2.445 | 2.444 | 170.733 |
| $[\text{Hg}(\text{P}(2,4,6\text{-Trimethoxyphenyl})_3)_2](\text{Hg}_2\text{Cl}_4)$ | 2.388 | | 166.513 |
| $[\text{Hg}(\text{PBn}_3)_2](\text{BF}_4)_2$ | 2.403 | | 180 |
| $[\text{Hg}(\text{P}(\text{tBu})_2)_2]\{$ | 2.442 | 2.451 | 177.478 |
| $[\text{Hg}(\text{P}(\text{TMS})_2)_2]$ | 2.410 | 2.402 | 175.863 |

S3. Synthetic procedures

Synthesis of [DippNHC*-H]-[PH₂] (**6b**) from PH₃

Caution! PH₃ gas is highly toxic and explosive. It should be handled with extreme care.

A three-necked 50 mL flask was equipped with a magnetic stirrer, a gas inlet for N₂ and PH₃ admission and a gas outlet connected to a bleach trap. The gas inlet was equipped with a sintered-glass frit attached to the bottom to ensure fine dispersion of the gas. The flask was charged with a suspension of [DippNHC*-H]-[Cl] (**5b**, 214 mg, 0.50 mmol, 1.25 eq) and sodium *tert*-butoxide (38 mg, 0.40 mmol, 1 eq) in THF (22 mL). N₂ was passed through the suspension for 90 min to ensure elimination of dioxygen from the system. PH₃ gas was passed through the suspension for 4 h at a minimum rate and N₂ was then bubbled again through the solution for 16 h to ensure complete elimination of PH₃. Volatiles were removed under reduced pressure from the yellow suspension and the product extracted with *n*-hexane (3x 5 mL). Removal of the solvent under reduced pressure and recrystallization from *n*-hexane yielded **6b** as a pale yellow, crystalline solid (109 mg, 0.257 mmol, 64%). Single crystals suitable for X-ray diffraction were obtained from a saturated *n*-hexane solution at -30 °C. **Mp** 123–125 °C (from *n*-hexane). **Analysis** Found: C, 76.7; H, 9.8; N, 6.5. Calc. for C₂₇H₄₁N₂P: C, 76.4; H, 9.7; N, 6.6. **¹H-NMR** (300 MHz, C₆D₆): δ = 7.25 – 7.01 (m, 6H, *Ar*), 6.00 (dt, ²J_{PH} = 14.9 Hz, ³J_{HH} = 3.0 Hz, 1H, *PCH*), 4.09 (sept, ³J_{HH} = 6.9 Hz, 2H, *CH*(CH₃)₂), 3.75 – 3.61 (m, 2H, *H₂C-CH₂*), 3.51 – 3.42 (m, 2H, *H₂C-CH₂*), 3.39 (sept, ³J_{HH} = 6.9 Hz, 2H, *CH*(CH₃)₂), 2.48 (dd, ¹J_{PH} = 187.0 Hz, ³J_{HH} = 3.0 Hz, 2H, *PH₂*), 1.37 (d, ³J_{HH} = 6.9 Hz, 6H, *CH*(CH₃)₂), 1.27 (d, ³J_{HH} = 6.9 Hz, 6H, *CH*(CH₃)₂), 1.23 (d, ³J_{HH} = 6.9 Hz, 6H, *CH*(CH₃)₂), 1.20 (d, ³J_{HH} = 6.9 Hz, 6H, *CH*(CH₃)₂). **¹³C{¹H}-NMR** (126 MHz, C₆D₆): δ = 151.2 (s, *Ar*), 149.7 (s, *Ar*), 139.2 (s, *Ar*), 124.7 (s, *Ar*), 76.7 (d, ¹J_{PC} = 10.0 Hz, *CHP*), 52.8 (s, *H₂C-CH₂*), 28.9 (s, *CH*(CH₃)₂), 28.6 (s, *CH*(CH₃)₂), 28.5 (s, *CH*(CH₃)₂), 26.2 (s, *CH*(CH₃)₂), 25.2 (s, *CH*(CH₃)₂), 24.6 (s, *CH*(CH₃)₂), 23.7 (s, *CH*(CH₃)₂) ppm. **³¹P{¹H}-NMR** (C₆D₆, 101 MHz): δ = -139.7 (s) ppm. **³¹P-NMR** (C₆D₆, 101 MHz): δ = -139.7 (td, ¹J_{PH} = 187.0, ²J_{PH} = 14.9 Hz) ppm.

Alternative synthesis of [DippNHC*-H]-[PH₂] (**6b**) from Na(PH₂)

A 10 mL round bottom flask was charged with [DippNHC*-H]-[Cl] (**5b**, 1.00 g, 2.34 mmol, 1 eq) and NaPH₂(NaOtBu)_{2.8}(dme)_{0.7} (0.91 g, 2.34 mmol, 1 eq). THF (2 mL) was added and the suspension stirred at 20 °C for 15 min. Volatiles were removed under reduced pressure and the work-up carried out as described above (0.80 g, 1.88 mmol, 80 %).

Synthesis of the DippNHC*=PH (**7b**) from **6b**

To a solution of [DippNHC*-H]-[PH₂] (**6b**, 420 mg, 1.00 mmol, 1 eq) in THF (5 mL) was added 9,10-Phenanthrenequinone (210 mg, 1.00 mmol, 1 eq). The dark blue solution was refluxed for 5 h,

before the volatiles were removed under reduced pressure. The product was separated from the hydroquinone by repeated recrystallization from cold *n*-hexane. $\text{DippNHC}^*=\text{PH}$ (**7b**) was isolated as a clear, needle-shaped, crystalline material (325 mg, 0.770 mmol, 77 %). Single crystals suitable for X-ray diffraction were obtained from a slowly evaporating *n*-hexane solution.

Mp 195–196 °C (from *n*-hexane). **Analysis** Found: C, 76.8; H, 9.5; N, 6.4. Calc. for $\text{C}_{27}\text{H}_{39}\text{N}_2\text{P}$: C, 76.7; H, 9.3; N, 6.6. **$^1\text{H-NMR}$** (300 MHz, C_6D_6): $\delta = 7.22\text{--}7.04$ (m, 6H, *Ar*), 3.41 (t, $^3J_{\text{HH}} = 4.6$ Hz, 4H, $\text{H}_2\text{C-CH}_2$), 3.31–3.11 (m, 4H, $\text{CH}(\text{CH}_3)_2$), 1.82 (d, $^1J_{\text{PH}} = 163.5$ Hz, 1H, *P-H*), 1.51 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.41 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.19 (d, $^3J_{\text{HH}} = 7.0$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$) ppm. **$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$** (75 MHz, C_6D_6): $\delta = 195.1$ (d, $^1J_{\text{PC}} = 72.6$ Hz, $\text{C}=\text{P}$), 148.6 (s, ipso-C), 136.8 (s, ortho-C), 135.7 (s, ortho-C), 129.6 (s, para-C), 129.3 (s, meta-C), 52.0 (s, $\text{H}_2\text{C-CH}_2$), 51.2 (s, $\text{H}_2\text{C-CH}_2$), 29.1 (s, $\text{CH}(\text{CH}_3)_2$), 25.1 (s, $\text{CH}(\text{CH}_3)_2$), 25.0 (s, $\text{CH}(\text{CH}_3)_2$), 24.8 (s, $\text{CH}(\text{CH}_3)_2$) ppm. **$^{31}\text{P}\{^1\text{H}\}\text{-NMR}$** (THF, 101 MHz): $\delta = -116.7$ (s) ppm. **$^{31}\text{P-NMR}$** (THF, 101 MHz): $\delta = -116.7$ (d, $^1J_{\text{PH}} = 163.6$ Hz) ppm.

Alternative synthesis of $\text{DippNHC}^*=\text{PH}$ (**7b**) from $(\text{TMS})_3\text{P}_7$

A suspension of $[\text{DippNHC}^*\text{-H}]\text{-[Cl]}$ (**5b**, 854 mg, 2.0 mmol, 1 eq) and $(\text{TMS})_3\text{P}_7$ (900 mg, 2.05 mmol, 1.025 eq) in THF (10 mL) was stirred for 20 h at 20 °C. Volatiles were removed from the red suspension under reduced pressure and the product extracted into *n*-hexane (3x 5 mL) and recrystallized from cold *n*-hexane (603 mg, 1.43 mmol, 71 %).

Synthesis of $[(\text{DippNHC}=\text{P})_2\text{Hg}]$ (**8a**)

A solution of $\text{DippNHC}=\text{PH}$ (**7a**, 421 mg, 1.0 mmol, 1 eq) and DBU (0.30 mL, 2.0 mmol, 2 eq) in THF (5 mL) was stirred for 10 min. HgCl_2 (150 mg, 0.55 mmol, 0.55 eq) was added slowly over 10 min to the stirring solution. After stirring for another 5 min at 20 °C, volatiles were removed from the yellow suspension. The yellow residue was extracted with toluene (3x 2 mL) and filtered over a G4 glass frit. Cooling off the concentrated toluene solution to –30 °C afforded **8a** as a yellow crystalline solid (385 mg, 0.37 mmol, 74 %). Single crystals suitable for X-ray diffraction were obtained from a concentrated toluene solution at –30 °C.

Mp 252–255 °C (decomposition, from toluene). **$^1\text{H-NMR}$** (300 MHz, C_6D_6): $\delta = 7.27\text{--}7.05$ (m, 12H, *Ar*), 6.14 (s, 4H, $\text{HC}=\text{CH}$), 3.00 (sept, $^3J_{\text{HH}} = 6.9$ Hz, 8H, $\text{CH}(\text{CH}_3)_2$), 1.53 (d, $^3J_{\text{HH}} = 6.9$ Hz, 24H, $\text{CH}(\text{CH}_3)_2$), 1.10 (d, $^3J_{\text{HH}} = 6.9$ Hz, 24H, $\text{CH}(\text{CH}_3)_2$). **$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$** (75 MHz, C_6D_6): $\delta = 146.7$ (s, ipso-C), 135.8 (s, ortho-C), 130.4 (s, para-C), 125.1 (s, meta-C), 119.2 (s, $\text{HC}=\text{CH}$), 28.7 (s, $\text{CH}(\text{CH}_3)_2$), 24.4 (s, $\text{CH}(\text{CH}_3)_2$), 23.6 (s, $\text{CH}(\text{CH}_3)_2$). **$^{13}\text{C-HMBC-NMR}$** (126 MHz, C_6D_6): $\delta = 181.8$ (br. d, $^1J_{\text{PC}} = 128$ Hz, CP) ppm. **$^{31}\text{P}\{^1\text{H}\}\text{-NMR}$** (THF, 101 MHz): $\delta = -56.0$ (s) ppm.

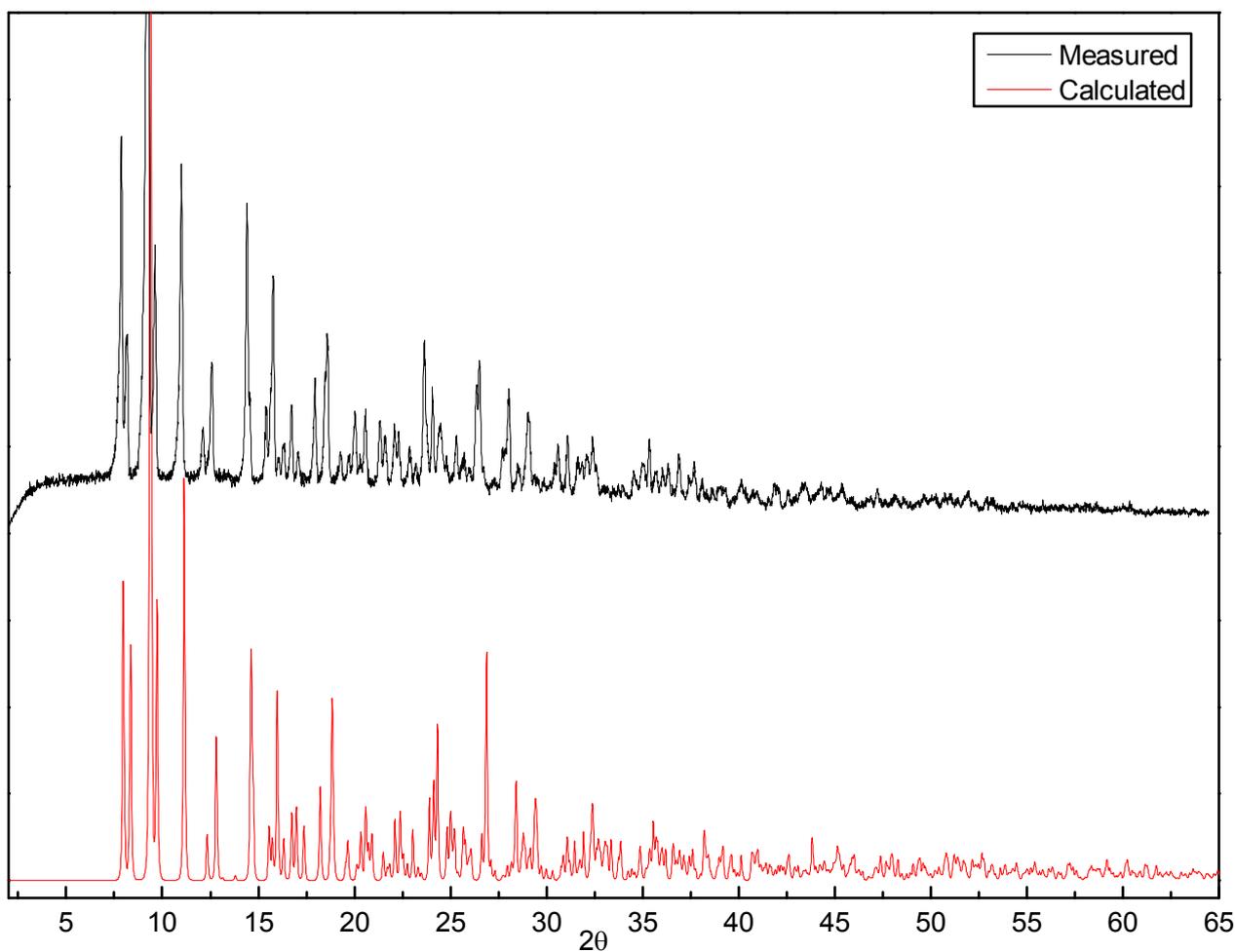


Figure 1: Measured and calculated powder X-ray diffraction pattern of $[(\text{DippNHC}=\text{P})_2\text{Hg}]$ (**8a**).

Synthesis of $[(\text{DippNHC}^*=\text{P})_2\text{Hg}]$ (**8b**)

A solution of $\text{DippNHC}=\text{PH}$ (**7b**, 422 mg, 1.0 mmol, 1 eq) and DBU (0.30 mL, 2.0 mmol, 2 eq) in THF (5 mL) was stirred for 10 min before HgCl_2 (150 mg, 0.55 mmol, 0.55 eq) was added. After stirring for 5 min, the volatiles were removed under reduced pressure. The yellow residue was washed with *n*-hexane (3x 3 mL), the product extracted with toluene (3x 2 mL) and recrystallized from toluene to yield **8b** as a pale yellow, crystalline solid (318 mg, 0.304 mmol, 61 %). Single crystals suitable for X-ray diffraction were obtained from a concentrated toluene solution at -30 °C.

Mp 265–267 °C (decomposition, from toluene). **$^1\text{H-NMR}$** (300 MHz, C_6D_6): δ = 7.26 – 7.00 (m, 12H, *Ar*), 3.44 (s, 8H, $\text{H}_2\text{C}-\text{CH}_2$), 3.19 (hept, $^3J_{\text{HH}} = 6.1$ Hz, 8H, $\text{CH}(\text{CH}_3)_2$), 1.55 (d, $^3J_{\text{HH}} = 6.7$ Hz, 24H, $\text{CH}(\text{CH}_3)_2$), 1.18 (d, $^3J_{\text{HH}} = 6.9$ Hz, 24H, $\text{CH}(\text{CH}_3)_2$). **$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$** (75 MHz, C_6D_6): δ = 147.7 (s, ipso-C), 137.5 (s, ortho-C), 129.6 (s, para-C), 125.1 (s, meta-C), 51.7 (s, $\text{H}_2\text{C}-\text{CH}_2$), 28.7 (s, $\text{CH}(\text{CH}_3)_2$), 24.9 (s, $\text{CH}(\text{CH}_3)_2$), 24.6 (s, $\text{CH}(\text{CH}_3)_2$). **$^{13}\text{C-HMBC-NMR}$** (126 MHz, C_6D_6): δ = 197 (br. d, $^1J_{\text{PC}} = 256$ Hz, CP) ppm. **$^{31}\text{P}\{^1\text{H}\}\text{-NMR}$** (THF, 121 MHz): δ = -32.5 (s) ppm.

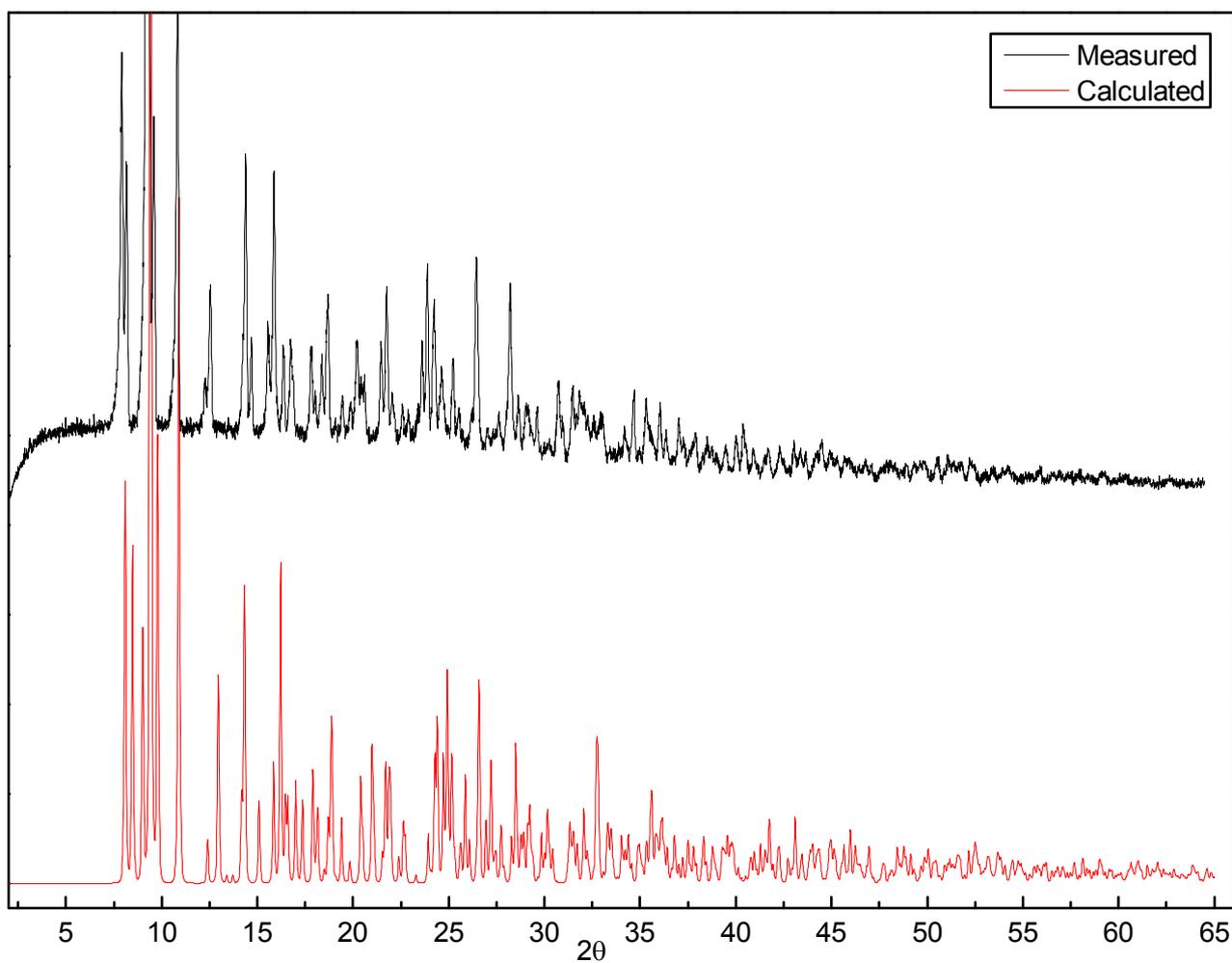


Figure 2: Measured and calculated powder X-ray diffraction pattern of $[(\text{DippNHC}^*=\text{P})_2\text{Hg}]$ (**8b**).

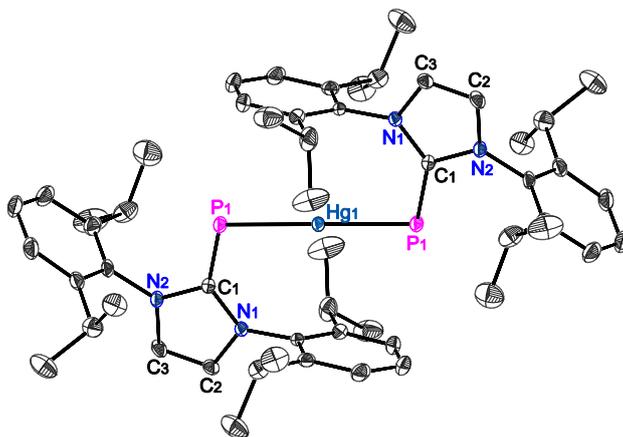


Figure 3: ORTEP plot of $[(\text{DippNHC}=\text{P})_2\text{Hg}]$ (**8a**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at 50% probability.

S4. References

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