

Phosphaguanidines as scaffolds for the synthesis of multi-metallic complexes containing metal-functionalized phosphines

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General Considerations

All manipulations were carried out under dry nitrogen using standard Schlenk-line and cannula techniques, or in a conventional nitrogen-filled glovebox. Solvents were dried over appropriate drying agent and degassed prior to use. NMR spectra were recorded using a Bruker Avance DPX 300 MHz spectrometer at 300.1 (^1H), 75.4 ($^{13}\text{C}\{^1\text{H}\}$) and 121.4 ($^{31}\text{P}\{^1\text{H}\}$) or a Bruker AMX 500 MHz spectrometer at 500.1 (^1H) and 125.7 ($^{13}\text{C}\{^1\text{H}\}$) MHz, from samples at 25 °C in [$^2\text{H}_6$]-benzene, unless otherwise stated. Coupling constants are quoted in Hz. Proton and carbon chemical shifts were referenced internally to residual solvent resonances. Elemental analyses were performed by S. Boyer at London Metropolitan University. The compounds $\text{Ph}_2\text{PC}\{\text{N}^i\text{Pr}\}\{\text{NH}^i\text{Pr}\}$ (**I-H**),¹ $\text{Cy}_2\text{PC}\{\text{N}^i\text{Pr}\}\{\text{NH}^i\text{Pr}\}$ (**II-H**),² $\text{Al}(\text{Ph}_2\text{PC}\{\text{N}^i\text{Pr}\}_2)\text{Me}_2$ (**3**),³ and $\text{PtMe}_2(\text{cod})$ ⁴ were made according to our earlier published procedures.

*Synthesis of $\text{PtMe}_2(\text{I-H})_2$ (**1**)*

A solution of **I-H** (0.72 g, 2 mmol) in THF (20 mL) was added to $\text{PtMe}_2(\text{cod})$ (0.33 g, 1.00 mmol) in THF (20 mL) at ambient temperature. The resulting cream/grey suspension was stirred for 16 h prior to removal of volatiles in vacuo. Crystallization by slow cooling of a hot (~70 °C) saturated toluene solution to ambient temperature yielded colorless crystals of **1**. Yield 0.80 g, 95 %. Anal. Calc. for $\text{C}_{40}\text{H}_{56}\text{N}_4\text{P}_2\text{Pt}$ (849.93): C 56.53, H 6.64, N 6.59 %; Found: C 56.60, H 6.58, N 6.55 %. ^1H NMR: δ 7.25-6.80 (m, 20H, C_6H_5), 4.86

(br m, 2H, CHMe₂), 4.46 (br d, *J* = 7, 2H NH), 4.40 (sept, *J* = 7, 2H, CHMe₂), 1.48 (m, 6H, PtMe₂), 1.28 (d, *J* = 7, 12H, CHMe₂) 1.23 (d, *J* = 7, 12H, CHMe₂). ¹³C NMR: δ 145.7 (m, PCN₂), 135.1 (d, *J* = 11, *J* = 14, *o*-C₆H₅) 133.2 (m, *i*-C₆H₅), 128.9 (*m*-C₆H₅), 133.2 (d, *J* = 5, *p*-C₆H₅), 51.3 (d, *J* = 22, CHMe₂), 43.5 (CHMe₂), 25.1 (CHMe₂), 22.5 (CHMe₂), 5.4 (m, PtMe₂). ³¹P NMR: δ 22.8 (*J* = 1800).

Synthesis of PtMe₂(II-H)₂ (2)

A solution of II-H (0.10 g, 0.31 mmol) in toluene (10 mL) was added to a suspension of PtMe₂(COD) (0.04 g, 0.15 mmol) in toluene (10 mL) at ambient temperature. The resulting cream/grey suspension was stirred for 16 h prior to removal of volatiles in vacuo. Crystallization by slow cooling of a hot (~70 °C) saturated toluene solution to ambient temperature yielded colorless crystals of **2**. Yield 0.15 g, 55 %. Anal. Calc. for C₄₀H₈₀N₄P₂Pt (874.11): C 54.96, H 9.22, N 6.41 %; Found: C 54.86, H 9.17, N 6.38. ¹H NMR: δ 5.39 (br d, *J* = 8, 2H, NH), 4.00 (sept, *J* = 7, 2H, CHMe₂), 3.82 (m, 2H, CHMe₂), 2.50 - 0.96 (m, 44H, Cy + 6H, PtMe₂), 1.30 (d, *J* = 7, 12H, CHMe₂), 1.08 (d, *J* = 7, 12H, CHMe₂). ¹³C NMR: δ 146.4 (m, PCN₂), 48.3 (CH), 46.5 (CH), 35.6 (CH), 30.0 (CH₂), 27.8 (CH₂), 27.2 (CH₂), 25.8 (CHMe₂), 24.8 (CHMe₂), 8.9 (m, PtMe₂). ³¹P NMR: δ 43.8 (*J* = 1692).

*Synthesis of $\text{PtMe}_2\{\text{Al}(\text{I})\text{Me}_2\}_2$ (**3**)*

A solution of AlMe_3 (0.5 mL of a 2.0 M in toluene, 1.0 mmol) was added *via* syringe to a solution of **1** (0.43 g, 0.5 mmol) in toluene. The mixture was allowed to stir at room temperature for 8 h before being concentrated and cooled to -30°C , affording colourless crystals of **3**. ^1H NMR, ^{31}P NMR spectroscopy and mass spectrometry identified the crystals as the previously reported compound, $\text{PtMe}_2\{\text{Al}(\text{I})\text{Me}_2\}_2$.⁵

*Synthesis of $\text{CuBr}(\text{I-H})_2$ (**4**)*

A solution of **I-H** (0.62 g, 2.0 mmol) in THF (20 mL) was added to a slurry of CuBr (0.14 g, 1.0 mmol) in THF (20 mL) and allowed to stir for 8 hrs. Volatiles were removed from the resulting colourless solution and crystallization from toluene afforded colourless crystals of $\text{CuBr}(\text{I-H})_2$. Yield 0.42 g (55%). Anal. Calc. for $\text{C}_{38}\text{H}_{50}\text{N}_4\text{BrCuP}_2$ (768.23): C 59.41, H 6.56, N 7.29 %; Found: C 59.66, H 6.34, N 7.11 %. ^1H NMR: δ 7.78 (br s, 8H, C_6H_5), 7.03-6.94 (br, m, 12H, C_6H_5), 4.48 (br m, 2H, CHMe_2), 4.34 (m, 2H, CHMe_2), 4.09 (br d, $J = 6$, 2H, NH), 1.17 (d, $J = 6$, 12H, CHMe_2), 0.99 (d, $J = 6$, 12H, CHMe_2). ^{13}C NMR: δ *, 134.4 (d, $J = 12$, $i\text{-C}_6\text{H}_5$), 131.5 (d, $J = 14$, $o\text{-C}_6\text{H}_5$), 130.3 ($m\text{-C}_6\text{H}_5$), 129.2 ($p\text{-C}_6\text{H}_5$), 53.3 (d, $J = 25$, CHMe_2), 43.6 (CHMe_2), 25.3 (CHMe_2), 22.4 (CHMe_2). ^{31}P NMR (C_6D_6 , 298 K) δ -15.1 (br).

(* the resonance corresponding to PCN_2 could not be located, due to the inherent low intensity associated with this resonance and the proximity to the quadrupolar copper center).

Synthesis of $\text{CuBr}\{\text{Al}(\text{I})\text{Me}_2\}_2$ (**5**)

Compound **5** was prepared using the procedure described for **3** using the following quantities: **4** (0.77g, 1.0 mmol), AlMe_3 (1.0 mL of a 2.0 M solution in hexane, 2.0 mmol), resulting in yellow needles of **5**. Yield 0.65 g (74 %). Anal. Calc. for $\text{C}_{42}\text{H}_{60}\text{Al}_2\text{BrCuN}_4\text{P}_2$ (880.31): C 57.30, H 6.87, N 6.36 %; Found C 56.93, H 7.08, N 6.15 %. ^1H NMR (C_6D_6 , 298 K) δ 7.67 (br s, 8H, C_6H_5), 6.97 (br m, 12H, C_6H_5), 3.82 (m, 4H, CHMe_2), 0.89 (d, $J = 6$, 24H, CHMe_2), -0.16 (s, 6H, AlMe_2). ^{13}C NMR (C_6D_6 , 298 K) δ *, 133.4 (d, $J = 20$, $o\text{-C}_6\text{H}_5$) 130.7 (br s, $m\text{-C}_6\text{H}_5$) 129.8 (br s, $p\text{-C}_6\text{H}_5$), 46.6 (d, $J = 11$, CHMe_2), 25.4 (s, CHMe_2), -9.3 (br s, AlMe_2). ^{31}P NMR (C_6D_6 , 298 K) δ -18.4 (br).

(* the resonances corresponding to PCN_2 and $i\text{-C}_6\text{H}_5$ could not be located, due to the inherent low intensity associated with this resonance and the proximity to the quadrupolar copper center).

References

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