

Template controlled synthesis of a coordinated [11]ane-P₂C^{NHC} macrocycle

Oliver Kaufhold, Andreas Stasch, Peter G. Edwards, und F. Ekkehardt Hahn

General: All preparations were carried out under an argon atmosphere using conventional Schlenk techniques. Solvents were dried and degassed by standard methods prior to use. The preparation of 1,2-bis(phosphino)benzene,¹ 1,2-bis(dichlorophosphino)benzene **2**,² and (β -triphenylphosphinimine)ethylenamine **4**³ have been described. *o*-bromofluorobenzene was degassed and dried over a molecular sieve. All other chemicals were used as received. NMR spectra were recorded with a Bruker Avance I 400 NMR spectrometer. IR spectra were measured with a Bruker Vector 22 spectrometer. Electrospray mass spectra were obtained with a Daltronics Micro TOF spectrometer.

Synthesis of 2: Compound **2** was prepared using a modified protocol of the synthesis reported by Kyba.¹ A solution of triphosgene (15.0 g, 50.5 mmol) in CH₂Cl₂ (150 mL) was treated dropwise with a solution of 1,2-bis(phosphino)benzene (3.2 g, 22.5 mmol) in CH₂Cl₂ (50 mL) at -78 °C. The reaction mixture was allowed to warm up to ambient temperature and was stirred at this temperature for 3 d. Compound **2** was obtained as colorless liquid after distillation in vacuo. Yield: 2.8 g (10.0 mmol, 44 %). The ¹H NMR data match those reported.¹ ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 144.6 (d, ¹J_{PC} = 13 Hz, Ar-C_{ipso}), 133.8 (Ar-C_{meta}), 131.1 (d, ²J_{PC} = 9 Hz, Ar-C_{ortho}); ³¹P{¹H} NMR (162.0 MHz, CDCl₃): δ 151.

Synthesis of 3: The reaction has to be carried out at -78 °C. The reactants have to be cooled to this temperature prior to use. A solution of *n*-butyllithium (22.1 mL of a 2.5 M solution, 55.3 mmol) in diethyl ether (100 mL) was treated dropwise with a solution of *o*-bromofluorobenzene (6.3 mL, 57.8 mmol) in diethyl ether (20 mL). After 15 min, a solution of **2** (3.8 g, 12.8 mmol) in diethyl ether (20 mL) was added to the reaction mixture. The

resulting mixture was stirred for 4 h at -78 C and then for 12 h at ambient temperature. Aqueous ammonium chloride (150 mL) was added and the mixture was extracted with diethyl ether ($4 \times 250\text{ mL}$). The solvent of the combined organic phase was removed in vacuo and the residue was dissolved in hot methanol. Compound **3** was isolated by filtration after cooling to $-35\text{ }^{\circ}\text{C}$. The crude product was again dissolved in dichloromethane (10 mL) and purified by passing down a short (2 cm) SiO_2 column. After removal of the solvent compound **3** was isolated as a colourless solid. Yield: 3.2 g (6.2 mmol, 48 %). ^1H NMR (400.1 MHz, CDCl_3 , assignment of signals see Scheme 2): δ 7.33 (m, 2H, Ar-H3), 7.31 (m, 4H, Ar-H7), 7.14 (m, 2H, Ar-H2), 7.04 (m, 4H, Ar-H6), 7.00 (m, 4H, Ar-H8), 6.92 (m, 4H, Ar-H5); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3 , assignment of signals see Scheme 2): δ 164.1 (d, $^1J_{\text{CF}} = 264\text{ Hz}$, Ar-C9), 140.7 (m, Ar-C1), 134.7 (m, Ar-C5), 133.9 (m, Ar-C2), 131.1 (d, $^3J_{\text{CF}} = 8.3\text{ Hz}$, Ar-C7), 129.9 (Ar-C3), 124.4 (d, $^3J_{\text{CP}} = 2.7\text{ Hz}$, Ar-C6), 122.7 (m, Ar-C4), 115.2 (d, $^2J_{\text{CF}} = 23.2\text{ Hz}$, Ar-C8); $^{31}\text{P}\{^1\text{H}\}$ NMR (162.0 MHz, CDCl_3): δ -36 (m). ^{19}F NMR (376.5 MHz, CDCl_3): δ -103 (m); ES-MS (positive ions): m/z (%): 541.0872 (100) (calcd. $[\text{C}_{30}\text{H}_{20}\text{F}_4\text{P}_2 + \text{Na}]^+$ 541.0869), 519.1062 (18) (calcd. $[\text{C}_{30}\text{H}_{20}\text{F}_4\text{P}_2 + \text{H}]^+$ 519.1055).

Synthesis of [1]: Complex [1] was prepared as described for $[\text{ReBr}(\text{CO})_4(\text{NHC})]^{[3]}$ as a colourless solid. Yield: 83 %. ^1H NMR (400.1 MHz, CDCl_3): δ 6.90 (s, br, 2H, NH), 3.72 (s, 4H, $\text{NCH}_2\text{CH}_2\text{N}$); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3): δ 193.6 (NCN), 186.8 (CO), 184.9 (CO), 184.7 (CO), 44.2 ($\text{NCH}_2\text{CH}_2\text{N}$); IR (KBr): ν 3429 (s, NH), 3265 (s, br, NH), 2107 (s, CO), 2016 (s, CO), 1993 (s, br, CO), 1924 (s, br, CO); ES-MS (positive ions): m/z (%): 426.9455 (100) (calcd. $[\text{C}_7\text{H}_6\text{N}_2\text{ClO}_4\text{Re} + \text{Na}]^+$ 426.9457).

Synthesis of [4]Cl: A solution of complex [1] (150 mg, 0.37 mmol) and ligand **3** (250 mg, 0.48 mmol) in acetonitrile (5 mL) was heated under reflux for 6 h. After cooling to ambient temperature the solution was concentrated and diethyl ether (20 mL) was added. Complex [4]Cl precipitated and was isolated by filtration. Yield: 330 mg (0.36 mmol, 98 %). ^1H NMR (400.1 MHz, CD_3CN , assignment of signals see Scheme 2): δ 8.02 (m, 2H, Ar-H4), 7.88 (m, 2H, Ar-H5), 7.67 (m, 2H, Ar-H9), 7.44 (m, 2H, Ar-H15), 7.39 (m, 2H, Ar-H10), 7.32 (m, 2H, Ar-H11), 7.27 (m, 2H, Ar-H8), 7.16 (m, 2H, Ar-H16), 7.10 (m, 2H, Ar-H14), 6.92 (m, 2H, Ar-H17), 6.56 (s, 2H, NH), 3.21 (s, 4H, $\text{NCH}_2\text{CH}_2\text{N}$); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CD_3CN , assignment of signals see Scheme 2): δ 191.0 (dd, $^2J_{\text{CP-trans}} = 50.4\text{ Hz}$, $^2J_{\text{CP-cis}} = 8.2\text{ Hz}$, $\text{CO}_{\text{cis-c1}}$), 190.0 (m, br, $\text{CO}_{\text{trans-c1}}$), 189.8 (t, $^2J_{\text{CP}} = 9.8\text{ Hz}$, C1), 164.5 (d, $^1J_{\text{CF}} = 249\text{ Hz}$, C7), 163.4

(dd, $^1J_{CF} = 247$ Hz, $^2J_{CP} = 4.9$ Hz, C13), 139.2 (dd, $^1J_{CP} = 48.5$ Hz, $^2J_{CP} = 33.4$ Hz, C3), 136.8 (dd, $^2J_{CP} = 14.0$ Hz, $^3J_{CP} = 2.5$ Hz, C4), 136.8 (m, C11), 136.6 (dd, $^3J_{CF} = 9.5$ Hz, $^4J_{CP} = 2.0$ Hz, C9), 134.9 (dd, $^3J_{CF} = 8.5$ Hz, $^4J_{CP} = 1.6$ Hz, C15), 134.8 (dd, $^3J_{CP} = 6.2$ Hz, $^4J_{CP} = 2.2$ Hz, C5), 133.0 (m, C17), 126.5 (dd, $^3J_{CP} = 11.2$ Hz, $^4J_{CF} = 3.0$ Hz, C10), 125.6 (dd, $^3J_{CP} = 8.3$ Hz, $^4J_{CF} = 3.0$ Hz, C16), 122.2 (ddd, $^1J_{CP} = 53$ Hz, $^2J_{CF} = 17$ Hz, $^4J_{CP} = 2.0$ Hz, C12), 118.2 (dd, $^2J_{CF} = 23.8$ Hz, $^3J_{CP} = 3.4$ Hz, C8), 117.3 (ddd, $^1J_{CP} = 45$ Hz, $^2J_{CF} = 16.4$ Hz, $^4J_{CP} = 2.8$ Hz, C6), 117.0 (dd, $^2J_{CF} = 23.0$ Hz, $^3J_{CP} = 3.7$ Hz, C14), 45.9 (C2); $^{31}\text{P}\{\text{H}\}$ NMR (162.0 MHz, CDCl_3): δ 22 (d); ^{19}F NMR (376.5 MHz, CD_3CN): δ -98, -100; IR (KBr): ν 3460 (w, NH), 2043 (s, CO), 1971 (s, CO), 1949 (s, CO); ES-MS (positive ions): m/z (%): 859.0893 (100) (calcd. $[\text{C}_{36}\text{H}_{26}\text{N}_2\text{F}_4\text{O}_3\text{P}_2\text{Re}]^+$ 859.0909).

Synthesis of [5]Cl: A suspension of [4]Cl (280 mg, 0.31 mmol) in THF (5 mL) was treated dropwise with a solution of $\text{KO}t\text{-Bu}$ (12.5 mL of a 0.05 M solution, 0.62 mmol). A clear solution was obtained after the addition. This solution was stirred at ambient temperature for 5 d. The solid formed during this time was isolated by filtration and dissolved in dichloromethane. Remaining solids were separated by filtration. Complex [5]Cl was obtained as a pale yellow solid after removal of the solvent. Yield: 240 mg (0.28 mmol, 91 %). ^1H NMR (400.1 MHz, CD_3CN , assignment of the signals see Scheme 2): δ 7.83 (m, 2H, Ar-H5), 7.81 (m, 2H, Ar-H4), 7.69 (m, 2H, Ar-H13), 7.66 (m, 2H, Ar-H9), 7.63 (m, 2H, Ar-H16), 7.39 (m, 2H, Ar-H14), 7.38 (m, 2H, Ar-H15), 7.37 (m, 2H, Ar-H8), 7.25 (t, 2H, Ar-H10), 6.97 (m, 2H, Ar-H11), 4.61 (m, 2H, N-C(2)H-C(2)H-N), 3.15 (m, 2H, N-C(2)H-C(2)H-N); $^{13}\text{C}\{\text{H}\}$ NMR (100.6 MHz, CD_3CN , assignment of the signals see Scheme 2): δ 193.4 (br, $\text{CO}_{\text{trans-C1}}$), 192.3 (t, $^2J_{CP} = 13.8$ Hz, C1), 191.1 (dm, $^2J_{CP\text{-trans}} = 46.0$, $\text{CO}_{\text{cis-C1}}$), 164.4 (dd, $^1J_{CF} = 249$ Hz, $^2J_{CP} = 5.0$ Hz, C7), 145.8 (d, $^2J_{CP} = 11.8$ Hz, Ar-C17), 139.9 (m, Ar-C3), 136.6 (d, $^3J_{CF} = 9.2$ Hz, Ar-C9), 136.2 (m, Ar-C4), 134.7 (d, $^2J_{CP} = 1.6$ Hz, Ar-C13), 134.6 (m, Ar-C5), 134.3 (m, Ar-C11) 131.2 (d, $^4J_{CP} = 1.6$ Hz, Ar-C15), 127.4 (d, $^3J_{CP} = 8.3$ Hz, Ar-C14), 126.8 (m, Ar-C10), 125.6 (d, $^3J_{CP} = 6.3$ Hz, Ar-C16), 123.8 (dd, $^1J_{CP} = 56.4$ Hz, $^4J_{CF} = 4.9$ Hz, Ar-C12), 117.8 (dd, $^2J_{CF} = 21.9$ Hz, $^3J_{CP} = 4.2$ Hz, Ar-C8), 115.1 (dd, $^1J_{CP} = 54.6$ Hz, $^2J_{CF} = 17.7$ Hz, Ar-C6), 52.4 (NCH₂CH₂N); $^{31}\text{P}\{\text{H}\}$ NMR (162.0 MHz, CD_3CN): δ 16 (d); ^{19}F NMR (376.5 MHz, CD_3CN): δ -97 (m); IR (KBr): ν 2031 (s, CO), 1963 (s, CO), 1937 (s, CO). ES-MS (positive ions): m/z (%): 819.0770 (100) (calcd. $[\text{C}_{36}\text{H}_{24}\text{N}_2\text{F}_2\text{O}_3\text{P}_2\text{Re}]^+$ 819.0784).

X-ray structure determinations. [1]: $C_7H_6N_2ClO_4Re$, $M = 403.79$, colourless crystal, $0.20 \times 0.15 \times 0.08$ mm, $a = 8.852(2)$, $b = 10.297(2)$, $c = 12.389(3)$ Å, $\beta = 107.84(3)^\circ$, $V = 1075.0(4)$ Å³, $\rho_{\text{calc}} = 2.495$ g·cm⁻³, $\mu = 11.547$ mm⁻¹, ω - and ϕ -scans, 3540 measured intensities ($6.4^\circ \leq 2\theta \leq 54.0^\circ$), $\lambda = 0.71073$ Å, $T = 150(2)$ K, semiempirical absorption correction ($0.245 \leq T \leq 0.411$), 2315 observed ($R_{\text{int}} = 0.0249$) and 2070 observed ($I \geq 2\sigma(I)$) intensities, $P2_1/c$, $Z = 4$, $R = 0.0264$, $wR = 0.0596$, refinement of 136 parameters against $|F^2|$ with hydrogen atoms on calculated positions.

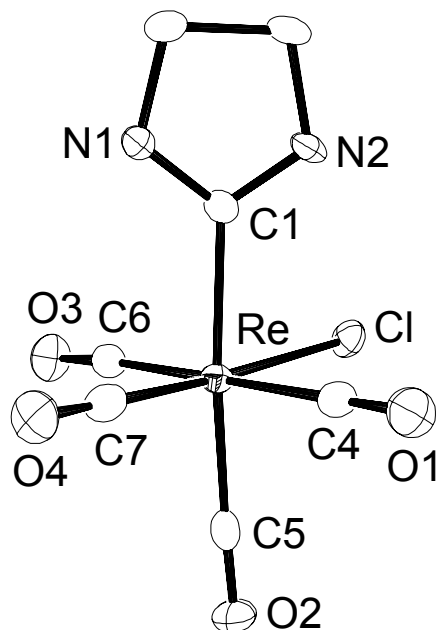


Figure S1. Molecular structure of complex [1]. Selected bond lengths [Å] and bond angles [°]: Re–Cl 2.4960(14), Re–C1 2.175(5), Re–C4 1.995(5), Re–C5 1.978(6), Re–C6 2.011(5), Re–C7 1.915(5), N1–C1 1.321(6), N2–C1 1.314(6); Cl–Re–C1 84.42(13), Cl–Re–C4 88.1(2), Cl–Re–C5 91.1(2), Cl–Re–C6 90.27(2), Cl–Re–C7 176.5(2), C1–Re–C4 88.7(2), C1–Re–C5 175.0(2), C1–Re–C6 92.2(2), C1–Re–C7 92.1(2), Re–C1–N1 126.5(4), Re–C1–N2 125.2(4), N1–C1–N2 108.2(4).

3: $C_{30}H_{20}F_4P_2$, $M = 518.40$, colourless crystal, $0.25 \times 0.20 \times 0.15$ mm, $a = 10.966(2)$, $b = 14.272(3)$, $c = 15.942(3)$ Å, $\beta = 91.88(3)$, $V = 2493.8(9)$ Å³, $\rho_{\text{calc}} = 1.381$ g·cm⁻³, $\mu = 0.222$ mm⁻¹, ω - and ϕ -scans, 8965 measured intensities ($5.9^\circ \leq 2\theta \leq 51.0^\circ$), $\lambda = 0.71073$ Å, $T = 150(2)$ K, semiempirical absorption correction ($0.802 \leq T \leq 0.989$), 4630 independent ($R_{\text{int}} = 0.0419$) and 3481 observed ($I \geq 2\sigma(I)$) intensities, $P2_1/n$, $Z = 4$, $R = 0.0457$, $wR = 0.0950$, refinement of 325 parameters against $|F^2|$ with hydrogen atoms on calculated positions.

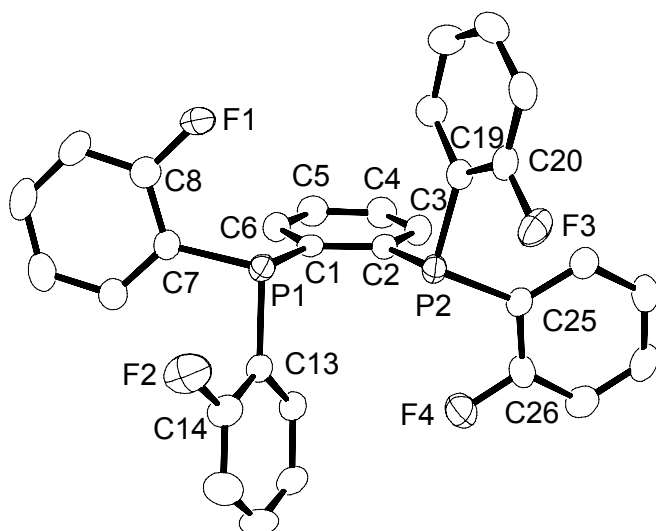


Figure S2. Molecular structure of compound **3**. Selected bond lengths [\AA] and bond angles [$^\circ$]: P1–C1 1.843(2), P1–C7 1.843(2), P1–C13 1.835(2), P2–C2 1.844(2), P2–C19 1.837(2), P2–C25 1.834(2), F1–C8 1.364(3), F2–C14 1.372(3), F3–C20 1.367(3), F4–C26 1.362(3); C1–P1–C7 103.48(10), C1–P1–C13 101.05(10), C7–P1–C13 101.07(10), C2–P2–C19 99.80(11), C2–P2–C25 101.71(10), C19–P2–C25 102.11(10).

[**4**]Cl \cdot 3THF: C₄₈H₅₀N₂ClF₄O₆P₂Re, $M = 1110.49$, colourless crystal, $0.50 \times 0.30 \times 0.30$ mm, $a = 11.201(5)$, $b = 11.800(5)$, $c = 20.504(5)$ \AA , $\alpha = 92.239(5)$, $\beta = 100.058(5)$, $\gamma = 117.123(5)^\circ$, $V = 2353.1(2)$ \AA^3 , $\rho_{\text{calc}} = 1.567$ g \cdot cm⁻³, $\mu = 2.773$ mm⁻¹, ω - and ϕ -scans, 16653 measured intensities ($6.0^\circ \leq 2\theta \leq 52.0^\circ$), $\lambda = 0.71073$ \AA , $T = 150(2)$ K, semiempirical absorption correction ($0.318 \leq T \leq 0.447$), 9183 independent ($R_{\text{int}} = 0.0308$) and 8654 observed intensities ($I \geq 2\sigma(I)$), $P\bar{1}$, $Z = 2$, $R = 0.0399$, $wR = 0.0929$, refinement of 557 parameters against $|F^2|$ with hydrogen atoms on calculated positions. The asymmetric unit contains one molecule of the complex and three molecules of THF. Two THF molecules are disordered.

[**5**]Cl \cdot 3H₂O: C₃₆H₃₀N₂ClF₂O₆P₂Re, $M = 908.21$, light yellow crystal, $0.30 \times 0.20 \times 0.10$ mm, $a = 9.030(5)$, $b = 10.898(5)$, $c = 19.929(5)$ \AA , $\alpha = 75.388(5)$, $\beta = 82.356(5)$, $\gamma = 68.013(5)^\circ$, $V = 1758.1(13)$ \AA^3 , $\rho_{\text{calc}} = 1.716$ g \cdot cm⁻³, $\mu = 3.682$ mm⁻¹, ω - and ϕ -scans, 11370 measured intensities ($6.3^\circ \leq 2\theta \leq 54^\circ$), $\lambda = 0.71073$ \AA , $T = 150(2)$ K, semiempirical absorption correction ($0.541 \leq T \leq 0.696$), 7588 independent ($R_{\text{int}} = 0.0269$) and 6917 observed ($I \geq 2\sigma(I)$) intensities, $P\bar{1}$, $Z = 2$, $R = 0.0298$, $wR = 0.0628$, refinement of 475 parameters against

$|F^2|$ with hydrogen atoms on calculated positions. The asymmetric unit contains a molecule of the complex and three molecules of water.

References

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