

Supporting Information for:

Synthesis and coordination behaviour of a novel 1,2,3-triphosphaferrocene

Shining Deng,^a Christoph Schwarzmaier,^a Christiane Eichhorn,^b Otto Scherer,^b
Gotthelf Wolmershäuser,^b Manfred Zabel,^a and Manfred Scheer^{*a}

^aInstitute of Inorganic Chemistry, University of Regensburg, D-93040 Regensburg, Germany.
Institute of Inorganic Chemistry, University of Kaiserslautern, D-67663 Kaiserslautern,
Germany.

Contents

S1. Experimental section and analytical characterisation

S2. Crystallographic details

S1. Experimental Section and analytical characterisation

General remarks:

All manipulations were performed under an atmosphere of dry nitrogen using standard glovebox and Schlenk techniques. Solvents were purified and degassed by standard procedures. The starting material **1** was prepared according to our published methods.¹ The phenylacetylene was received from Aldrich and used after distillation. Solution NMR spectra were recorded on a Bruker AVANCE 400 spectrometer. Mass spectra were performed using ThermoQuest Finnigan TSQ 7000 (ESI-MS) or a Finnigan MAT 95 (FD-MS and EI-MS). The C, H, N analyses are measured on an Elementar Vario EL III apparatus.

Synthesis of [Cp^{'''}Fe(η⁵-P₃C₂PhH)] (2): PhC≡CH (0.9 g, 8.8 mmol) was added to a solution of [Cp^{'''}(CO)₂Fe]₂(μ,η¹:η¹-P₄) (**1**) (1.8 g, 2.2 mmol) in toluene (200 ml) at room temperature. The reaction mixture was heated under reflux for 18 h. After removal of all volatile material in vacuum, the residue was dissolved in dichloromethane (10 ml) and transferred onto silica gel. Chromatographic work-up on a silica gel column (40 x 2.5 cm) eluting with hexane/toluene (20:1) give a red fraction of the oily compound **2** (150 mg; 14%), and afterwards a green fraction of the crystalline compound **3** (480 mg, 43.6%).

[Cp^{'''}Fe(η⁵-P₃C₂PhH)] (2): ¹H NMR (C₆D₆, RT, 400.13 MHz): δ = 1.09 (s, 9H), 1.12 (s, 9H), 1.41 (s, 9 H), 4.00 (d, 1H, Cp^{'''}, *J*(H,H) = 2.24 Hz), 4.19 (d, 1H, Cp^{'''}; *J*(H,H) = 2.24 Hz), 6.24 (ddd, 1H, P₃C₂-ring), 7.07 (m, 3H, C₆H₅), 7.80 (m, 2H, C₆H₅) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , RT, 161.98 MHz, ABM spin system): $\delta(\text{P}_\text{A}) = 51.7$ (dd), $\delta(\text{P}_\text{B}) = 48.9$ (dd), $\delta(\text{P}_\text{M}) = 15.2$ (dd), $J(\text{P}_\text{A}, \text{P}_\text{M}) = 427.1$ Hz, $J(\text{P}_\text{M}, \text{P}_\text{B}) = 399.6$ Hz, $^2J(\text{P}_\text{A}, \text{P}_\text{B}) = 4.4$ Hz.

^{31}P NMR (C_6D_6 , RT, 161.98 MHz, ABM spin system): $\delta(\text{P}_\text{A}) = 51.7$ (ddd), $\delta(\text{P}_\text{B}) = 48.9$ (ddd), $\delta(\text{P}_\text{M}) = 15.2$ (ddd), $^2J(\text{P}_\text{B}, \text{H}_\text{a}) = 40.1$, $^3J(\text{P}_\text{M}, \text{H}_\text{a}) = 10.8$, $^4J(\text{P}_\text{A}, \text{H}_\text{a}) = 4.5$ Hz.

EI-MS (70 eV): $m/z = 484$ [$\text{Cp}^*\text{Fe}(\text{P}_3\text{C}_2\text{PhH})$] $^+$ (65%), 452 [$\text{Cp}^*\text{Fe}(\text{P}_2\text{C}_2\text{PhH})$] $^+$ (8.2%), 377 [$\text{Cp}^*\text{Fe}(\text{P}_2\text{C}_2\text{H}_2)$] $^+$ (15%).

[$\text{Cp}^*\text{Fe}(\eta^5\text{-PC}_4\text{Ph}_2\text{H}_2)$] (3**):** ^1H NMR (C_6D_6 , RT, 400.13 MHz): $\delta = 1.12$ (s, 9H), 1.32 (s, 9H), 1.56 (s, 9H), 3.62 (s, 1H, Cp *), 3.77 (s, 1H, Cp *), 4.65 (d, 1H, PC $_4$ -ring; $J(\text{P}, \text{H}) = 36.1$ Hz), 6.15 (d, 1H, PC $_4$ -ring; $J(\text{P}, \text{H}) = 4.5$ Hz), 7.26 (m, 6H, C $_6\text{H}_5$), 7.77 (m, 4H, C $_6\text{H}_5$) ppm.

^{31}P NMR (C_6D_6 , RT, 161.98 MHz): $\delta = -64.1$ (dd) ppm, ($^2J(\text{P}, \text{H}) = 35.6$ Hz; $^4J(\text{P}, \text{H}) = 4.9$ Hz).

EI-MS (70 eV): $m/z = 524$ [$\text{Cp}^*\text{Fe}(\text{PC}_4\text{Ph}_2\text{H}_2)$] $^+$ (28%), 493 [$\text{Cp}^*\text{Fe}(\text{C}_4\text{Ph}_2\text{H}_2)$] $^+$ (100%), 421[(C $_5\text{H}_3$ ^tBuⁱPr)Fe(PC $_4\text{Ph}_2\text{H}_2)$] $^+$ (4.8%). Found: C, 75.01; H, 7.90. C $_{33}\text{H}_{41}\text{FeP}$ requires C, 75.42; H, 8.06%.

Synthesis of [$\{\text{Cp}^*\text{Fe}(\eta^5\text{-}\eta^1\text{-P}_3\text{C}_2\text{PhH})\}_4(\mu\text{-CuBr})_4(\text{CH}_3\text{CN})_2$] $_\infty$ (5**):** A solution of CuBr (30 mg 0.21 mmol) in CH $_3\text{CN}$ (8 ml) was layered onto a solution of [$\text{Cp}^*\text{Fe}(\eta^5\text{-P}_3\text{C}_2\text{PhH})$] (50 mg, 0.10 mmol) in 8 ml CH $_2\text{Cl}_2$. After complete diffusion of two layers at room temperature, the mixture was concentrated under reduced pressure to about one half of the original volume (ca. 8 ml) and the concentrate was then layered with 8 ml of pentane. After one week, red plate crystals were obtained on the wall of the Schlenktube (15 mg, 38.6%). Found: C, 39.62; H, 4.43; N, 1.41. C $_{54}\text{H}_{76}\text{Br}_4\text{Cu}_4\text{Fe}_2\text{N}_2\text{P}_6$ requires C, 39.92; H, 4.72; N 1.72%.

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD $_2\text{Cl}_2$; reaction mixture), 27 °C, 161.98 MHz, ABM spin system): $\delta(\text{P}_\text{A}) = 40.5$, $\delta(\text{P}_\text{B}) = 37.8$, $\delta(\text{P}_\text{M}) = 0.2$ ppm, $J(\text{P}_\text{A}, \text{P}_\text{M}) = 436.4$ Hz, $J(\text{P}_\text{M}, \text{P}_\text{B}) = 425.7$ Hz.

ESI-MS (CH $_3\text{CN}$, RT): $m/z = 1319$ [$\{\text{Cp}^*\text{Fe}(\text{P}_3\text{C}_2\text{PhH})\}_2\text{Cu}_3\text{Br}_2$] $^+$ (5.7%), 1175 [$\{\text{Cp}^*\text{Fe}(\text{P}_3\text{C}_2\text{PhH})\}_2\text{Cu}_2\text{Br}$] $^+$ (6%), 1031 [$\{\text{Cp}^*\text{Fe}(\text{P}_3\text{C}_2\text{PhH})\}_2\text{Cu}$] $^+$ (20%), 588 [$\{\text{Cp}^*\text{Fe}(\text{P}_3\text{C}_2\text{PhH})\}_2\text{CuCH}_3\text{CN}$] $^+$ (100%).

S2. Crystallographic details

Crystal structure analysis: The crystal structure analysis of **3** was performed on a STOE IPDS diffractometer with image plate detector using MoK $_\alpha$ radiation ($\lambda = 0.71073$ Å), whereas the crystal structure analysis of **5** was performed on an Oxford Diffraction Gemini Ultra diffractometer with CuK $_\alpha$ radiation ($\lambda = 1.54184$). The structures were solved by direct methods with the program SHELXS-97, and full matrix least squares refinement on F^2 in SHELXL-97 was performed with anisotropic displacements for non-H atoms.² Hydrogen

atoms at the carbon atoms were located in idealised positions and refined isotropically according to the riding model. Crystal data for **3**: C₃₃H₄₁FeP, $M = 524.48$, orthorhombic space group $Pbca$, $a = 10.5821(7)$, $b = 16.6027(8)$, $c = 33.0952(18)$ Å, $V = 5814.5(6)$ Å³, $T = 293(2)$ K, $Z = 8$, $\mu(\text{Mo-K}\alpha) = 0.592$ mm⁻¹, 64880 reflections measured, 5529 unique ($R_{\text{int}} = 0.1183$) which were used in all calculations. The final $R_1 [I > 2\sigma(I)]$ was 0.0400. Crystal data for **5**: C₅₄ H₇₆ Br₄ Cu₄ Fe₂ N₂ P₆ · 1.5 CH₂Cl₂, $M = 1751.88$, triclinic space group $P\bar{1}$, $a = 15.1002(10)$, $b = 15.5709(11)$, $c = 16.3950(12)$ Å, $\alpha = 110.545(7)$, $\beta = 94.432(6)$, $\gamma = 104.171(6)^\circ$, $V = 3442.8(5)$ Å³, $T = 123(1)$ K, $Z = 2$, $\mu(\text{Cu-K}\alpha) = 10.019$ mm⁻¹, 25040 reflections measured, 10799 unique ($R_{\text{int}} = 0.0389$) which were used in all calculations. The final $R_1 [I > 2\sigma(I)]$ was 0.0366.

References

-
- 1 O. J. Scherer, T. Hilt, G. Wolmershäuser, *Organometallics* 1998, **17**, 4110-4112.
 - 2 (a) G. M. Sheldrick, *SHELXS-97*, University of Göttingen, Göttingen, Germany, 1996;
(b) G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Göttingen, Germany, 1997.