Supplementary Information for

P-P Bond Formation via Reductive Dimerization of $[Cp^*Fe(\eta^5\text{-}P_5)]$ by Divalent Samarocenes

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General considerations

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-3} torr) line, or in an argon-filled MBraun glove box. NMR spectra were recorded on a Bruker Avance 400 MHz or a Bruker Avance II 300 MHz NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane (^{1}H NMR) and 85 % phosphoric acid (^{31}P NMR). IR spectra were obtained on a FTIR Spectrometer Bruker IFS 113v. NIR measurements were performed in KBr pellet at room temperature using the FTIR spectrometer Bruker Tensor 37 by means of an NIR lamp, a CaF_2 beamsplitter and a room temperature InGaAs detector. Elemental analyses were carried out with an Elementar vario EL or EL III. The EI mass spectra were recorded at 70 eV on a Varian MAT 711. Ether solvents (THF and Et_2O) and hydrocarbon solvents (toluene, heptane and *n*-pentane) were predried by using an MBraun solvent purification system (SPS-800) and degassed, dried and stored in vacuo over Na/K alloy benzophenone ketyl in resealable flasks prior to use. Deuterated solvents were obtained from Aldrich (99 atom % D) and were degassed, dried and stored in vacuo over Na/K alloy in resealable flasks. HC_5Me_4nPr was commercially available from “DALCHEM” (Nizhny Novgorod, Russia) and used without additional purification. [Cp*Fe(η^5-P_5)][1, 2] and [Cp*$_2$Sm(THF)$_2$][3] were prepared according to literature procedures.

General procedure for ampoule reactions

For the synthesis and recrystallization, two-section ampoules were used. The starting compounds were loaded in one section of the ampoule in an Ar glove box. The section with loading was cooled by liquid nitrogen, and corresponding solvent (typical 10 mL of solvent) was condensed in vacuum to the mixture of starting material. The ampoule was flame sealed. The reaction mixture was slowly warmed up to room temperature and stir for 14 h and heated to 60 °C until the color was definitely changed. In case of the formation of a precipitate it will be separated by decantation of the solution to another section of the ampoule. The concentrated solution was obtained by slow evaporation of the solvent to the empty section of the ampoule. The section with solvent and precipitate was removed by flame sealing. The crystals were obtained by cooling the concentrated solution in a freezer (-11 °C), decantation of the solution to the other end of ampoule and drying by means of cooling the section with the mother liquid. The section with crystals was flame sealed and opened in a glove-box.

[(C_5Me_4*n*Pr)$_2$Sm] Solid K(C_5Me_4*n*Pr) was prepared in a standard manner by treating HC_5Me_4*n*Pr (9.945 g, 60.5 mmol) with K metal (1.903 g, 48.7 mmol) in THF (50 mL) at reflux (ca. 24 h) following by evaporation of the reaction solution, washing of the residual solid with hexane and drying in vacuum. Yield: 6.43 g (65 %).

THF (50 mL) was condensed to a solid mixture of K(C_5Me_4*n*Pr) (1.012 g, 5.00 mmol) and SmI_2 (1.0 g, 2.47 mmol) cooled to –78 °C. The mixture was allowed to warm up to room temperature and then to 60 °C, and stirred for 16 h. The dark purple coloured solution was evaporated to dryness. The residue was recrystallised two times from hot heptane (ca. 20 ml) resulting in dark purple crystals of the solvent-free [(C_5Me_4*n*Pr)$_2$Sm]. Yield: 0.82 g (70 %). MS: m/z 478.21 (100 %). Anal. Calc. for $C_{24}H_{38}Sm$: C, 60.44; H, 8.03. Found: C, 60.31; H, 8.375.

[(Cp*$_2$Sm)$_2$P$_{10}$(FeCp*)$_2$] (1a) Toluene (10 mL) was condensed onto a mixture of [Cp*$_2$Sm(THF)$_2$] (0.113 g, 0.2 mmol) and [Cp*Fe(η^5-P$_5$)] (0.07 g, 0.2 mmol) cooled to –78 °C. The resulting reaction mixture was stirred for 16 h at 60 °C. The mixture was filtered off into a 2-section ampoule to grow crystals by slow evaporation. The dark brown crystals were obtained at ambient temperature. Yield: 0.095 mg, 62 %. MIR (KBr, ν/cm^{-1}): 2961 (m), 2904 (m), 2856 (m), 1476 (w), 1439 (m), 1373 (m), 1020 (s), 574 (m) (Fig. S1). NIR (KBr, ν/cm^{-1}): 9279 (^{6}F$_{9/2}$), 8011 (^{6}F$_{7/2}$), 7284 (^{6}F$_{5/2}$), 6367 (^{6}F$_{1/2}$), 6137 (^{6}H$_{15/2}$) (Fig. S2). Anal. Calc. for **3**, $C_{60}H_{90}P_{10}Sm_2Fe_2$: C, 46.99; H, 5.92. Found: 46.59; H, 5.983.

[((C$_5$Me$_4$*n*Pr)$_2$Sm)$_2$P$_{10}$(FeCp*)$_2$] (1b) Heptane (10 mL) was condensed onto a mixture of [(C$_5$Me$_4$*n*Pr)$_2$Sm] (0.119 g, 0.25 mmol) and [Cp*Fe(η^5-P$_5$)] (0.067 g, 0.2 mmol) cooled to –78 °C. The resulting reaction mixture was stirred for 16 h at 60 °C. The mixture was filtered off into a 2-section ampoule to grow crystals by slow evaporation. The dark brown crystals were obtained at ambient temperature. Yield: 0.078 g, 24 %. MIR (KBr, ν/cm^{-1}): 2955 (m), 2904 (m), 2857 (m), 1477 (w), 1443 (m), 1372 (s), 1019 (s), 581 (m) (Fig. S3). NIR (KBr, ν/cm^{-1}): 8025 (^{6}F$_{7/2}$), 7294 (^{6}F$_{5/2}$), 6371 (^{6}F$_{1/2}$), 6144 (^{6}H$_{15/2}$) (Fig. S4). Anal. Calc. for **3**, $C_{68}H_{106}P_{10}Sm_2Fe_2$: C, 49.63; H, 6.49. Found: 49.10; H, 6.324.

X-ray Crystallographic Studies of 1a and 1b

A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the either -73 °C or -123 °C cold stream of a STOE IPDS 2T diffractometer.

All structures were solved by the Patterson method (SHELXS-97).[4] The remaining non-hydrogen atoms were located from successive difference in Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $(F_o-F_c)^2$, where the weight is defined as $4F_0^2/2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes using the program SHELXL-97.[4] Carbon-bound hydrogen atom positions were calculated. The final values of refinement parameters are given in the note of the main text. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, bond distances and angles have been deposited as supporting information.

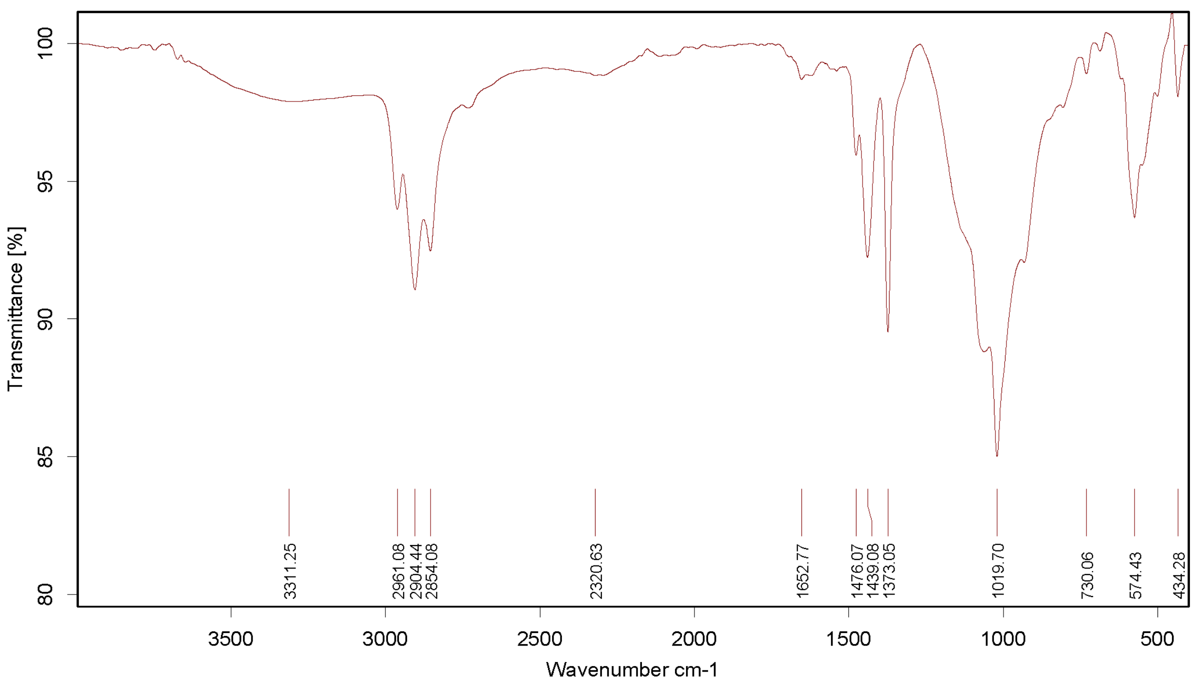

Figure S1. Mid-infrared transmittance measurement of **1a** in KBr pellet (room temperature)

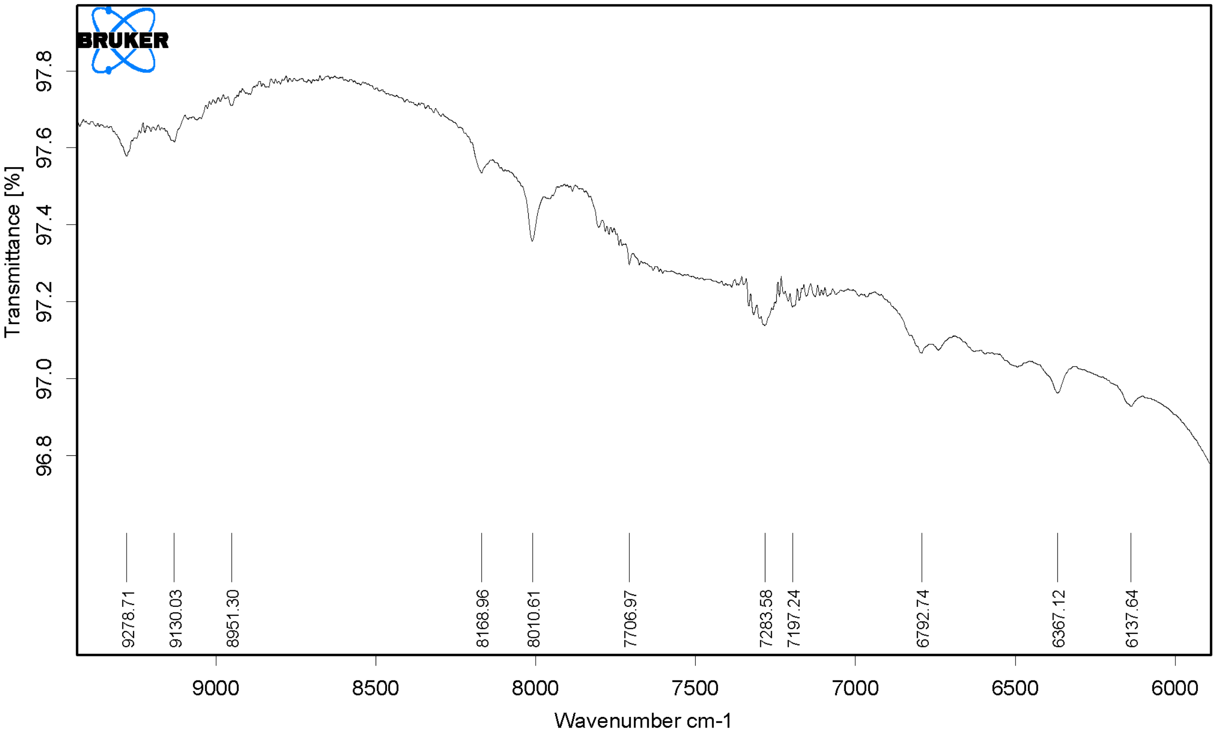

Figure S2. Near infrared transmittance measurement of **1a** in KBr pellet (room temperature)

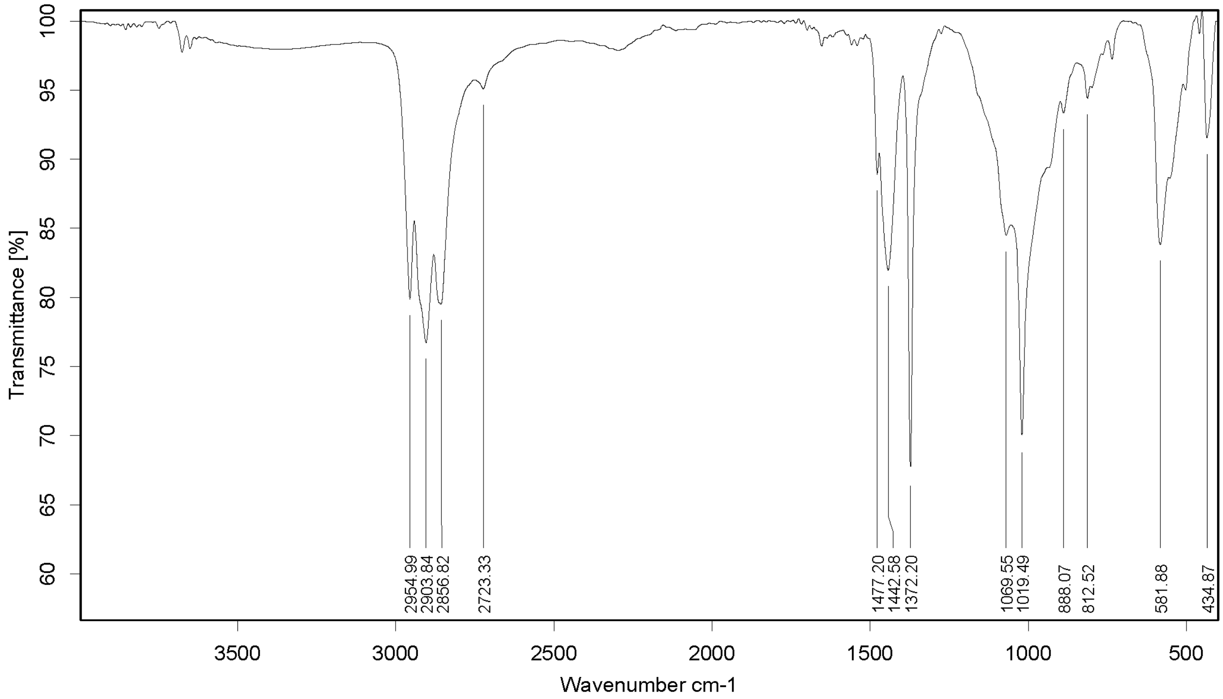

Figure S3. Mid-infrared transmittance measurement of **1b** in KBr pellet (room temperature)

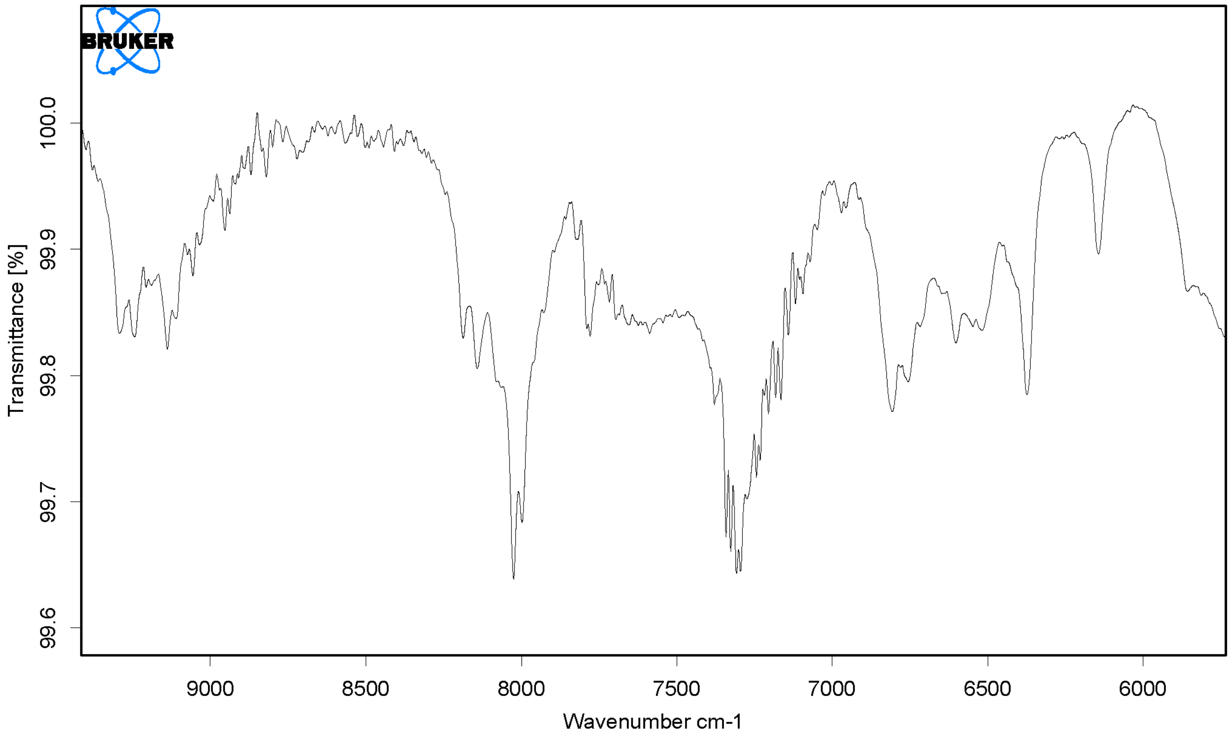

Figure S4. Near infrared transmittance measurement of **1b** in KBr pellet (room temperature)

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