## **Electronic Supporting Information (ESI)**

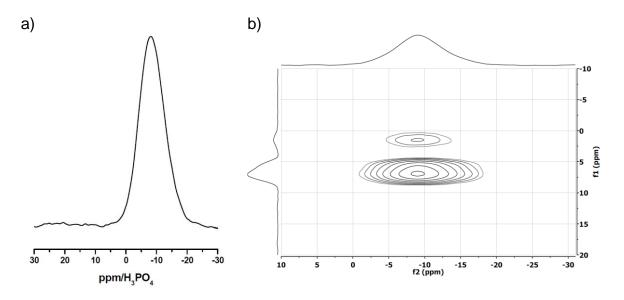
## <sup>31</sup>P-Solid-State NMR Characterization and Catalytic Hydrogenation Tests of Novel heterogeneous Iridium- and Palladium-Catalysts

<sup>1</sup>Torsten Gutmann, <sup>1</sup>Safaa Alkhagani, <sup>1</sup>Niels Rothermel, <sup>2</sup>Hans-Heinrich Limbach, <sup>1</sup>Hergen Breitzke, <sup>1</sup>Gerd Buntkowsky\*

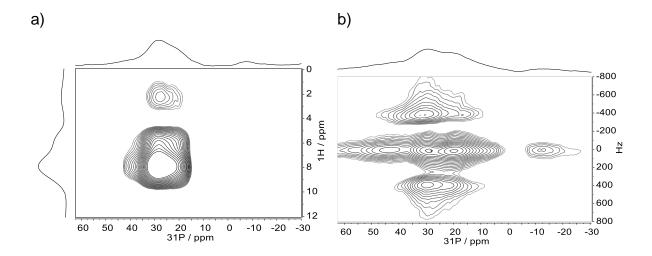
<sup>1</sup>Technische Universität Darmstadt, Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Alarich-Weiss-Str. 8, D-64287 Darmstadt, Germany eMail: gerd.buntkowsky@chemie.tu-darmstadt.de

> <sup>2</sup>Freie Universität Berlin, FB Biologie, Chemie, Pharmazie, Takustr. 3, D-14195 Berlin, Germany

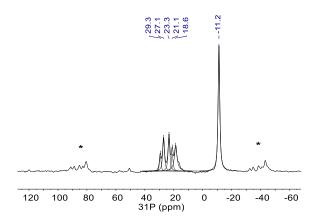
Dedicated to Prof. Kev Salikhov on the occasion of his 80th birthday.



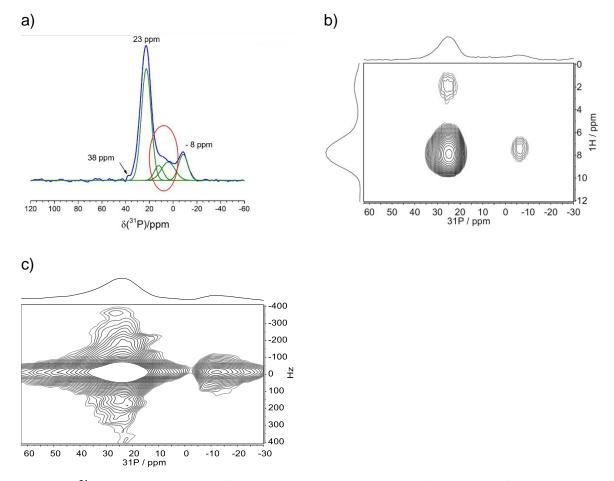
**Figure S1.** a) <sup>31</sup>P CP-MAS NMR spectrum of **Si-PB** at 10 KHz spinning. b) Two-dimensional <sup>31</sup>P-<sup>1</sup>H HETCOR of the **Si-PB** structure. f1 is the <sup>1</sup>H dimension, f2 is the <sup>31</sup>P dimension. The splitting in the f1-dimension proves that the phosphorous is part of the polymeric shell (adapted from ref. <sup>38</sup>).



**Figure S2:** 2D spectra of a **Si-PB-Rh** sample for comparison: a)  $^{31}P^{-1}H$  HETCOR with (f1)  $^{1}H$  spectrum and (f2). b)  $^{31}P$  spectrum *J*-resolved  $^{31}P^{-31}P$  with (f1) *J* coupling in Hz and (f2)  $^{31}P$  1D spectrum. (spectrum refers to ref. 38)



**Figure S3:**  $^{31}P$  CP-MAS spectrum of the neat IrCl(PPh<sub>3</sub>)<sub>3</sub> measured at 10 kHz spinning rate. *Note:* Spinning side bands are marked with asterisks.



**Figure S4:** <sup>31</sup>P CP-MAS spectrum of **Si-PB-Ir** synthesized at 85 °C. (a) 2D spectra for **Si-PB-Ir** sample synthesized at 85 °C: <sup>31</sup>P-<sup>1</sup>H HETCOR with (f1) <sup>1</sup>H spectrum and (f2) <sup>31</sup>P spectrum (b), and <sup>31</sup>P *J*-resolved spectra (f1) *J*-coupling in Hz and (f2) <sup>31</sup>P 1D spectrum (c).

*Note:* Spectra were recorded at 10 kHz spinning. The spectrum (a) was measured employing an additional TOSS sequence  $^{67}$  to suppress the spinning sidebands.