Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information (SI)

Adsorption of Solid Phosphines on Silica and Implications for Catalysts on Oxide Surfaces

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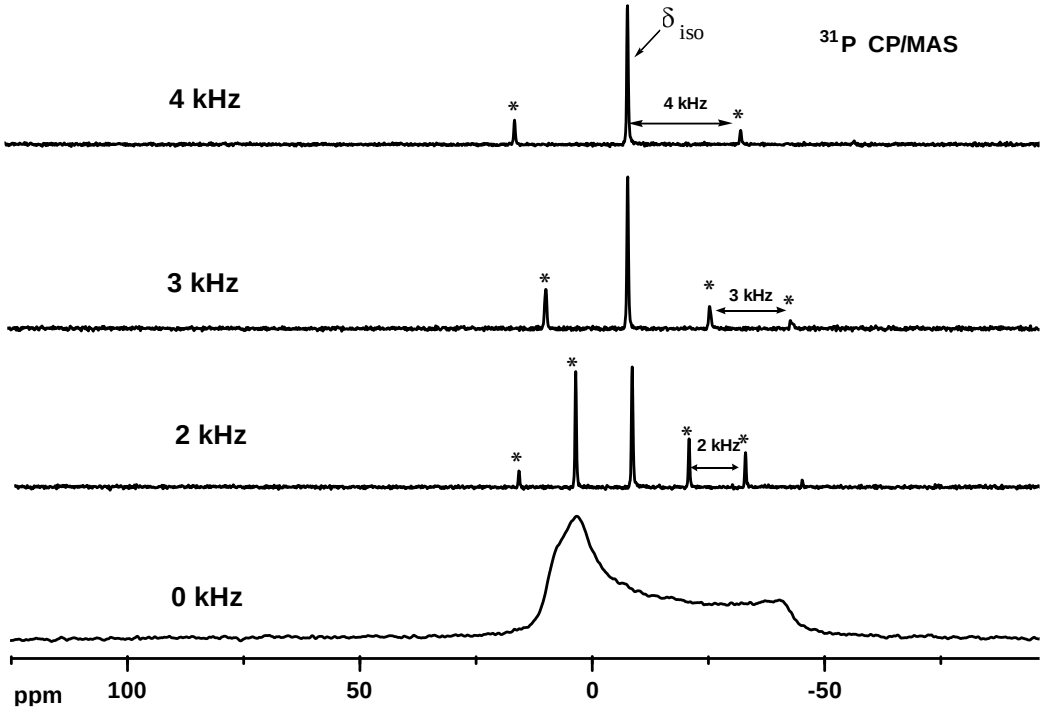

Figure S1. ^{31}P CP/MAS NMR spectra of polycrystalline PPh_3 at 4 kHz, 3 kHz and 2 kHz spinning speeds and the corresponding wideline spectrum without spinning (bottom). Asterisks denote the rotational sidebands.

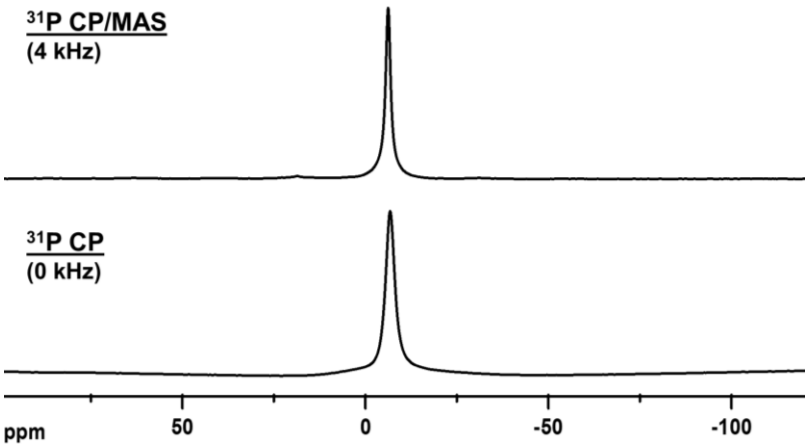

Figure S2. ^{31}P CP/MAS NMR spectrum of PPh_3 adsorbed on silica (**1a**) in a monolayer (206 molecules per 100 nm^2 of surface area) at 4 kHz spinning speed (top) and ^{31}P CP wideline spectrum (bottom).

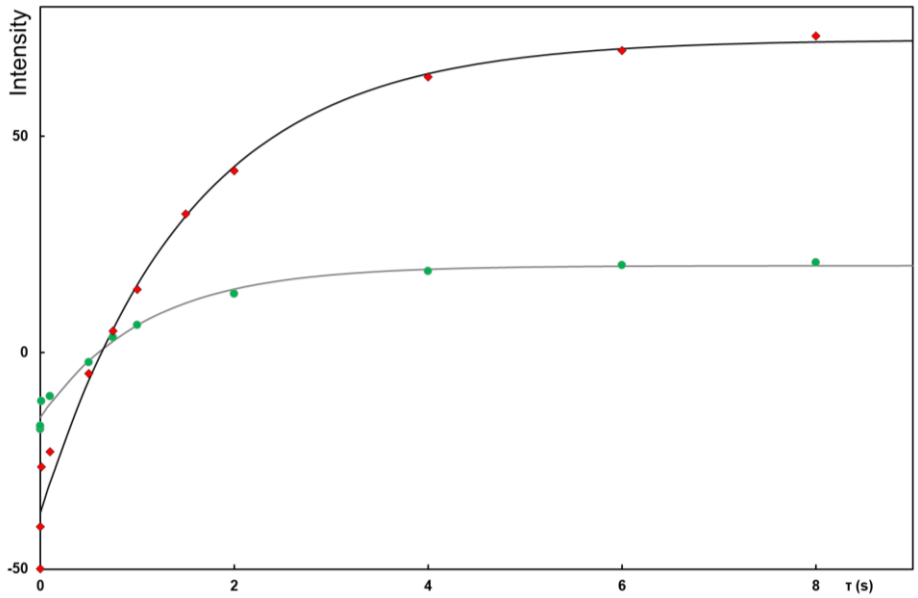

Figure S3. ^{31}P NMR signal intensities for PPh_3 adsorbed on silica (green symbols 0.1 g, red symbols 0.4 g per g of silica) when using a standard Bruker inversion recovery pulse sequence (t1ir1d) at 293 K with MAS (10 kHz). The inversion recovery data was fitted using the stretched exponential function $I(t)=A(1-Be^{(-\tau/T)})$ in the program LabPlot. The values of specific parameters for each fit can be found in Table S1 and the spectra are displayed in Figure S4.

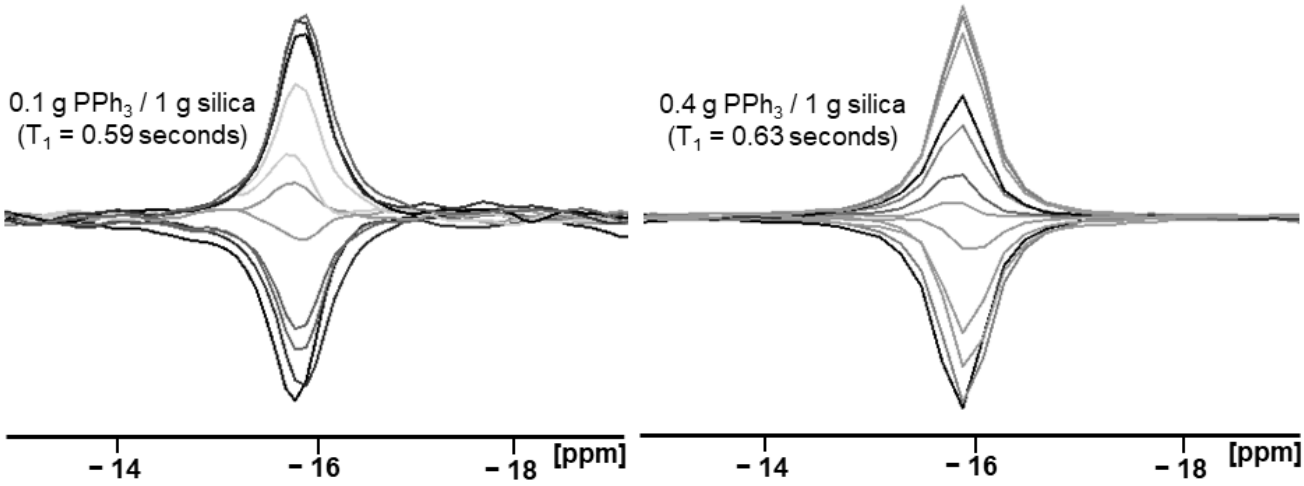

Figure S4. ^{31}P NMR spectra acquired with the standard Bruker inversion recovery pulse sequence (t1ir1d) at 293 K with MAS (10 kHz) for two samples of PPh_3 adsorbed on dried silica at different concentrations.

Table S1. Equation parameters with % uncertainty for the fit obtained from T_1 time experiments (Figure S3 and Figure S4). The inversion recovery data was fitted using the stretched exponential function $I(t) = A(1-Be^{(-\tau/T)})$ in the program LabPlot. I(t) represents arbitrary intensities measured with the TopSpin software and τ is the delay time.

Parameter (% uncertainty)	**0.1 g PPh_3 per g of SiO_2**	**0.4 g PPh_3 per g of SiO_2**
A	20.1371 (5.8)	72.3582 (6.0)
B	1.73934 (3.9)	1.51027 (3.7)
T	1.07103 (11.5)	1.5208 (11.9)

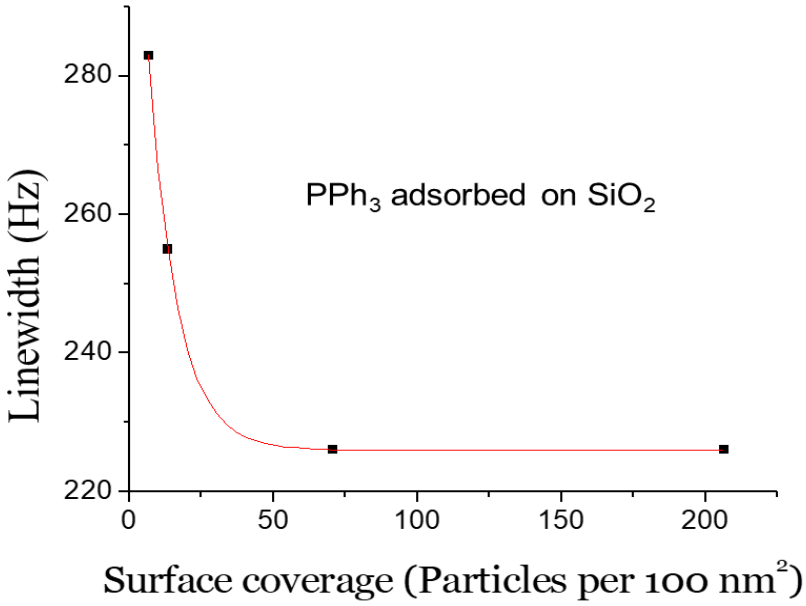

Figure S5. Correlation between ^{31}P signal linewidth and surface coverage of PPh_3 on silica.

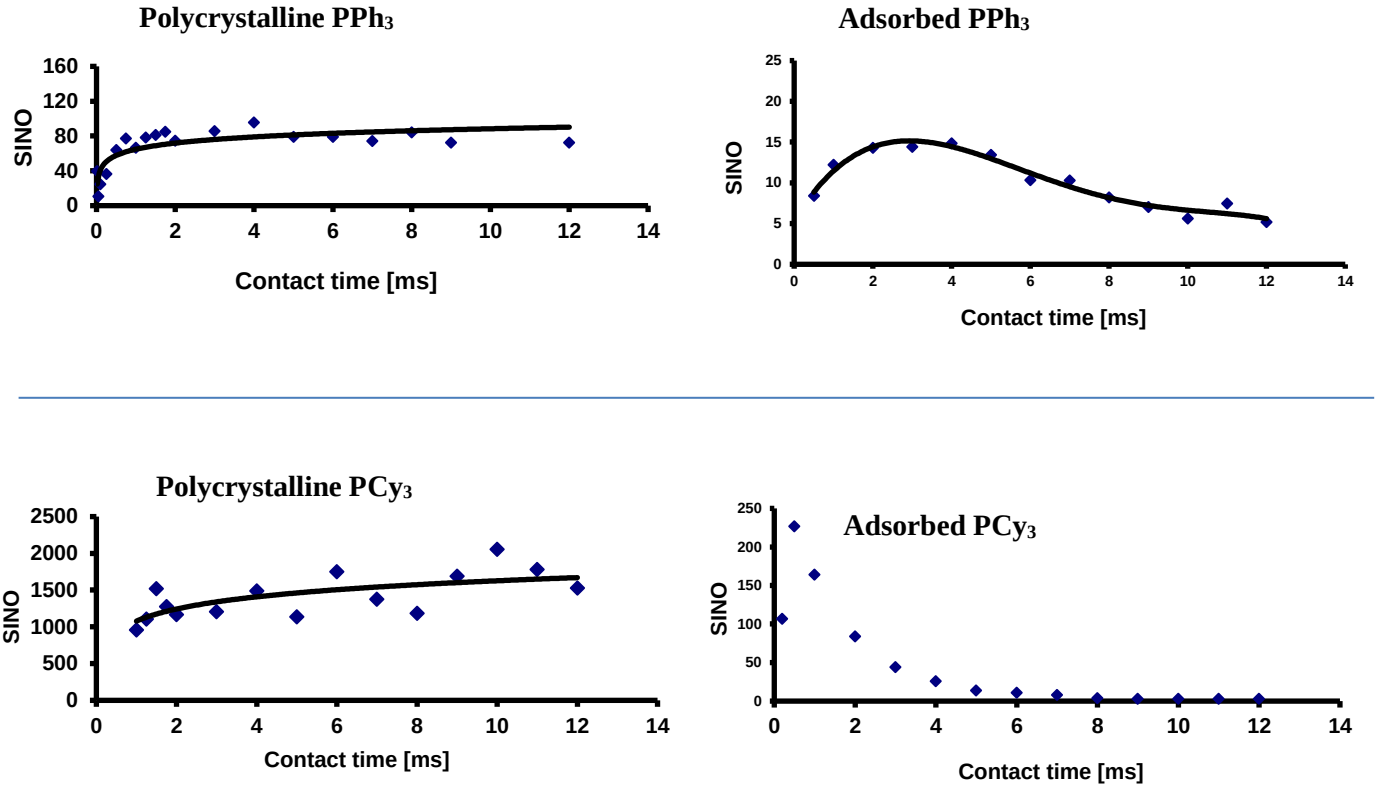

Figure S6. ^{31}P CP/MAS signal intensities (SINO) at different contact times for polycrystalline PPh_3 (top, left) and PCy_3 (bottom, left) and surface-adsorbed PPh_3 (top, right) and PCy_3 (bottom, right).

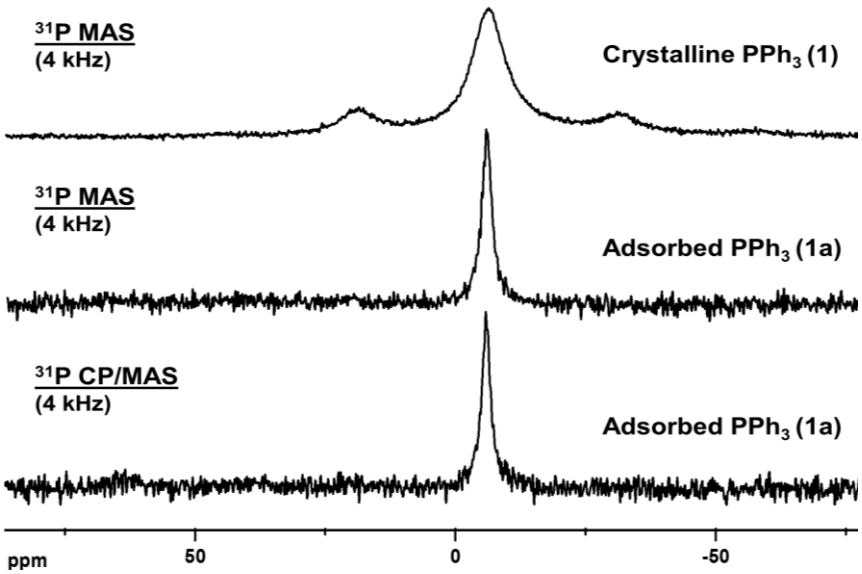

Figure S7. ^{31}P MAS spectra of polycrystalline (**1**) and adsorbed PPh_3 (**1a**), measured with a single pulse sequence without proton decoupling (top two spectra), and ^{31}P CP/MAS spectrum of adsorbed PPh_3 (bottom) at 4 kHz.

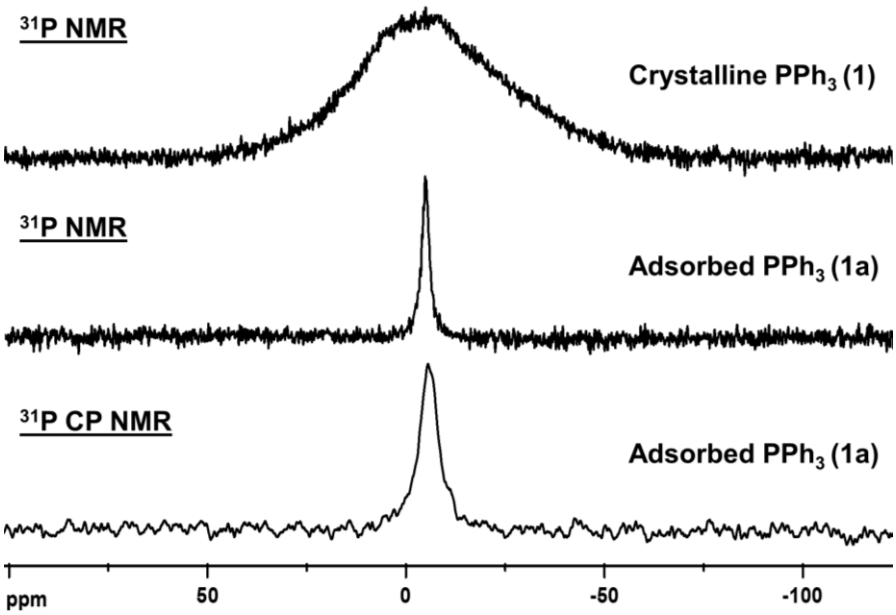

Figure S8. ^{31}P Wideline (no sample spinning) NMR spectra of polycrystalline PPh_3 (**1**, top) and surface-adsorbed PPh_3 (**1a**, middle), recorded without ^{1}H high-power decoupling, and ^{31}P CP spectrum of surface-adsorbed PPh_3 (**1a**, bottom, with high-power ^{1}H decoupling).

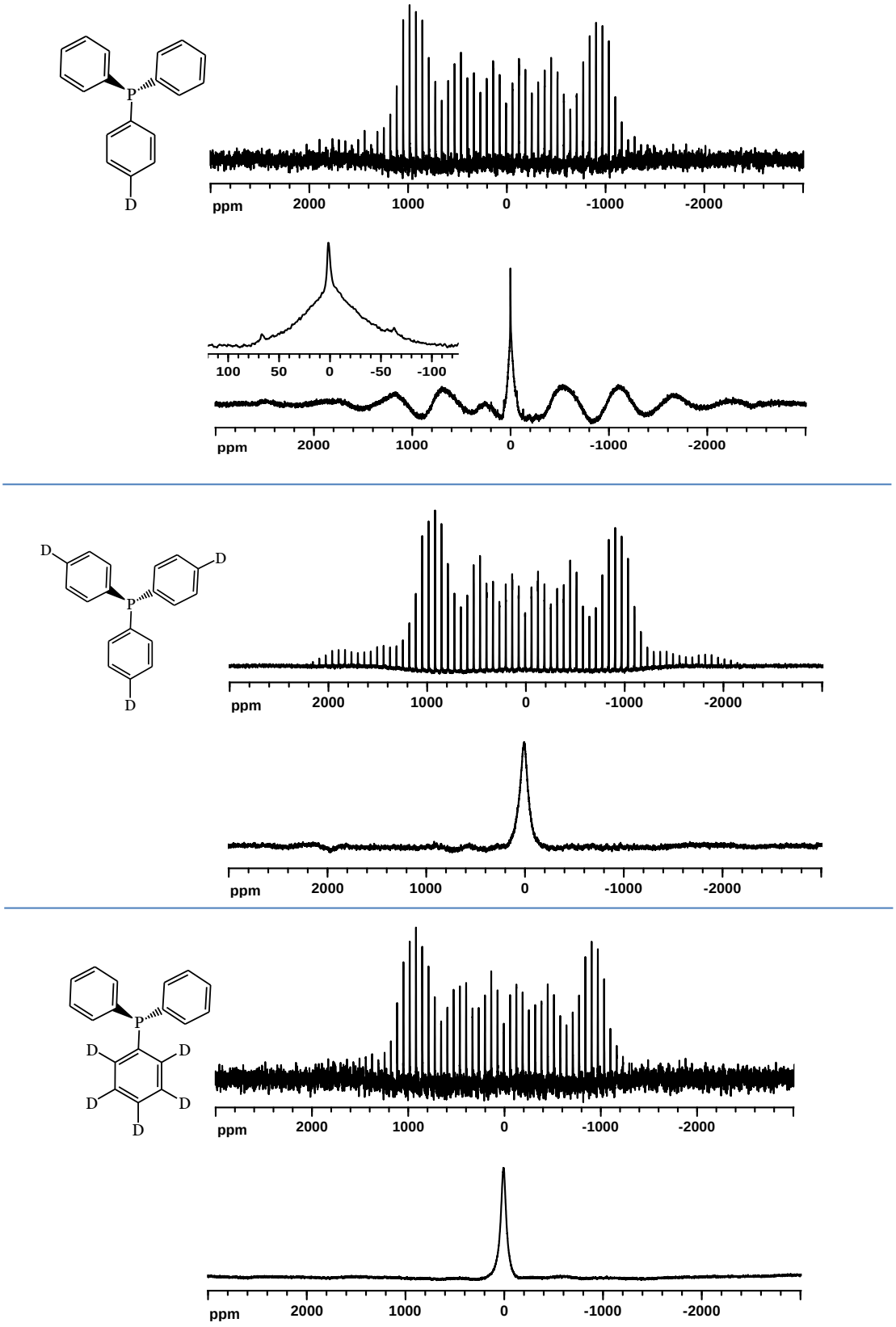

Figure S9. ^{2}H CP/MAS NMR spectra of the shown polycrystalline deuterated phosphines (top each) and ^{2}H{^{1}H} MAS spectra of the silica-adsorbed deuterated phosphines (bottom each). The spinning speed was 4 kHz for all measurements. None of the ^{2}H CP/MAS spectra of the adsorbed deuterated phosphines showed any signals. No baseline correction was applied.

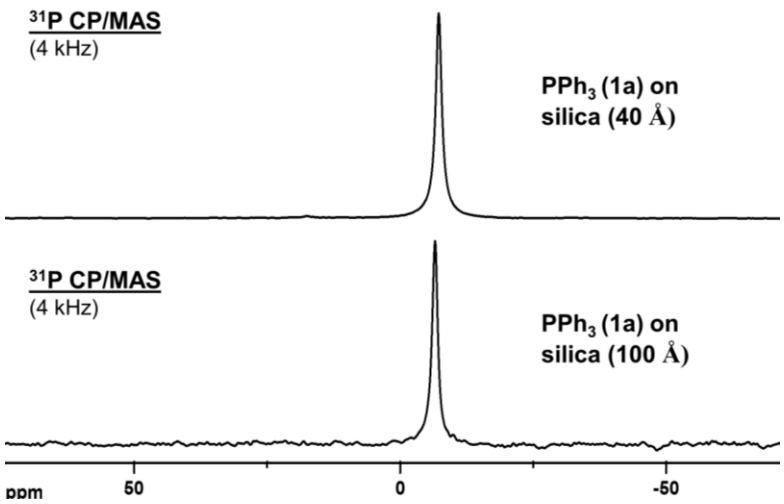

Figure S10. ^{31}P CP/MAS spectra of surface-adsorbed PPh_3 (**1a**) on silica with 40 Å (top) and silica with 100 Å (bottom) average pore diameter at 4 kHz. Surface coverages see Table S2.

Table S2. Adsorption of 601 mg of **1** on 1 g each of rigorously dried silicas with 40 Å and 100 Å average pore diameters.

Average Pore Diameter of Silica	Surface coverage of 1a (molecules per 100 nm^2)	δ(^{31}P) of the adsorbed PPh_3 [ppm]	Linewidth [Hz]
40 Å	202	–6	230
100 Å	169	–6	200

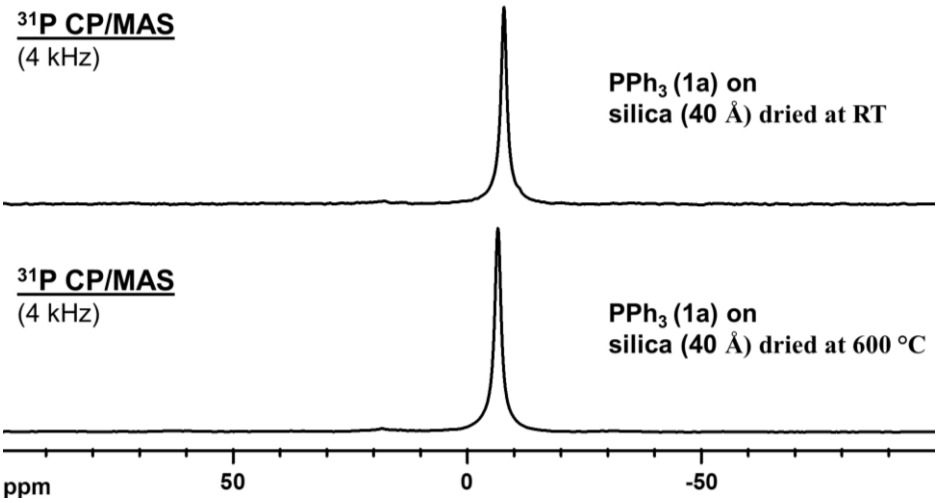

Figure S11. ^{31}P CP/MAS spectra of surface-adsorbed PPh_3 on silica that had been dried at RT (top) and at 600 °C (bottom). The rotational frequency was 4 kHz for both spectra and 592 mg have been adsorbed on 1 g of silica, corresponding to 199 molecules of **1a** on 100 nm^2 of surface area.

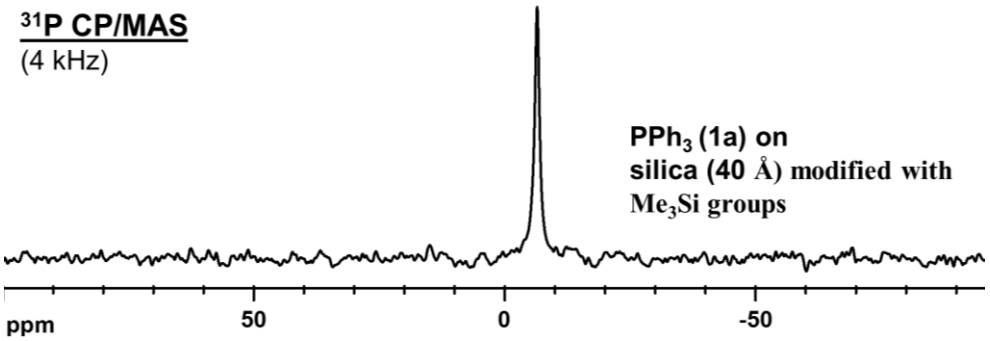

Figure S12. ^{31}P CP/MAS spectra of surface-adsorbed PPh_3 on Me_3Si-modified silica at 4 kHz. The surface coverage is 61 mg of **1a** per 1 g of modified silica.

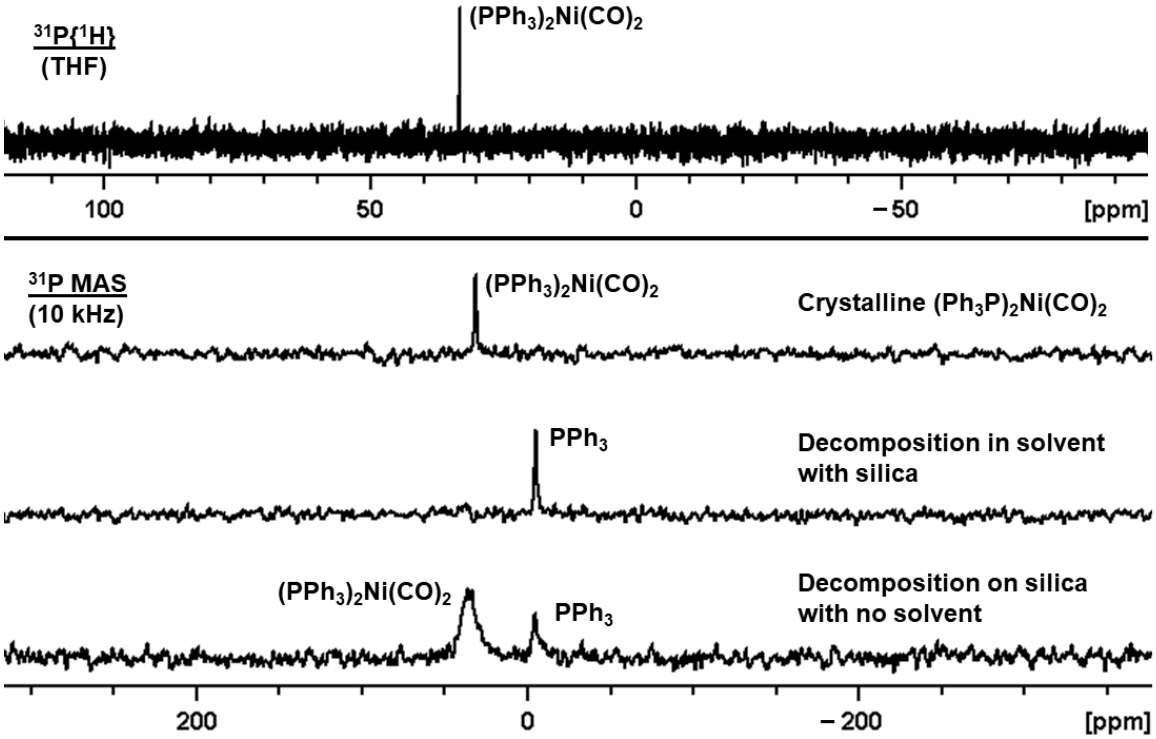

Figure S13. ^{31}P NMR spectrum of a solution of $(PPh_3)_2Ni(CO)_2$ (**3**) in THF after heating to 50 °C for 3 h (top), proton high-power decoupled ^{31}P MAS spectra (10 kHz) of polycrystalline $(PPh_3)_2Ni(CO)_2$ (**3**, second from top), **3** heated in the presence of silica in THF to 50 °C for 3h (second from bottom), and **3** applied to silica and heated without solvent for 3 h (bottom).

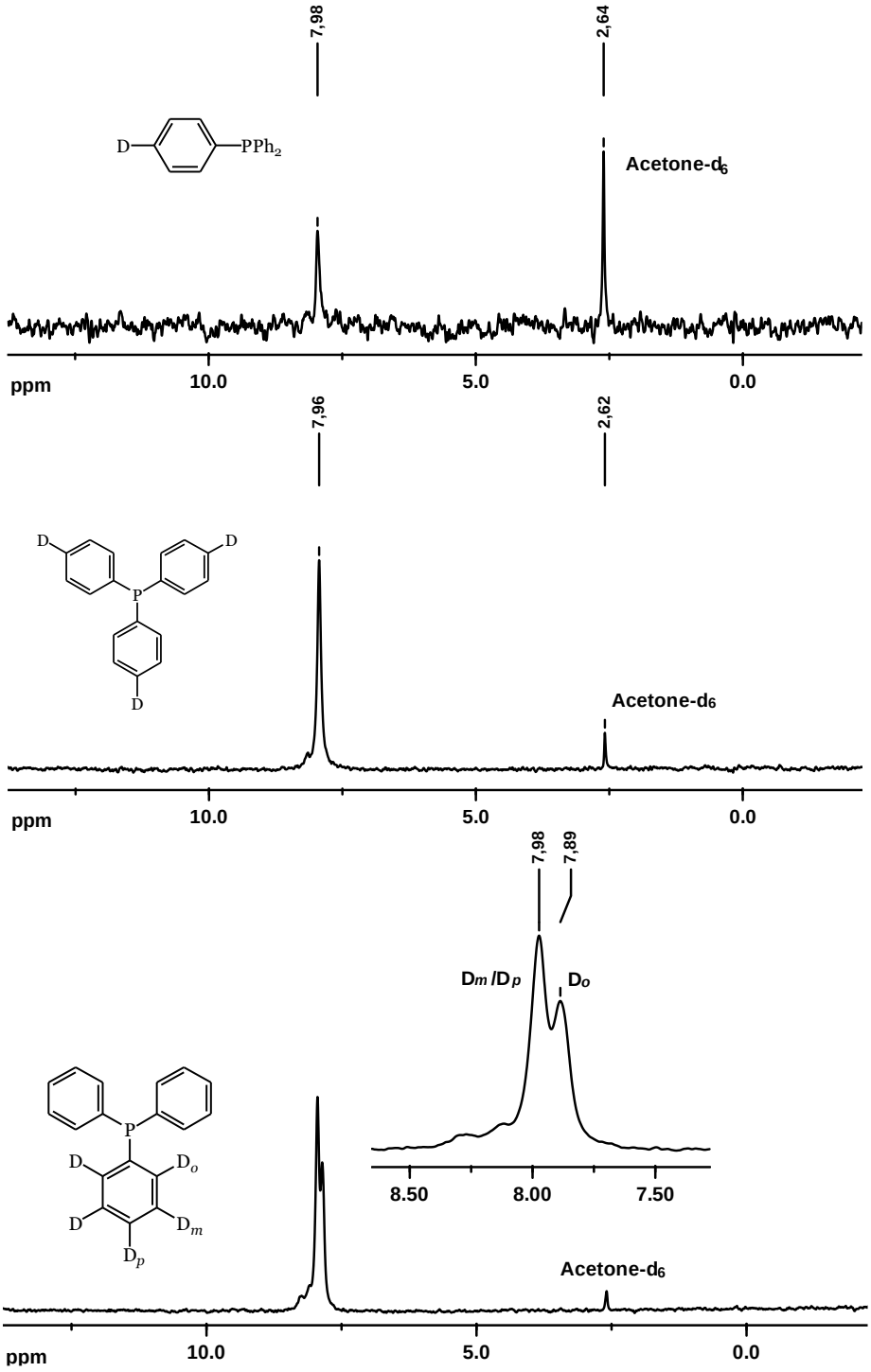

Figure S14. ^{2}H NMR spectra of **1-*d*$_1$** (top), **1-*d*$_3$** (middle), and **1-*d*$_5$** (bottom), with acetone-d_6 as chemical shift reference.