Supporting Information

Probing the Surface Heterogeneity of Silica by 1D and INADEQUATE ^{31}P NMR Solid State NMR Spestroscopy of PMe_3-Au(I) adducts

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General procedure. All experiments were carried out under dry and oxygen free Ar using either standard Schlenk or glove-box techniques for organometallic synthesis. For the syntheses and the treatments of the surface species, reactions were carried out using high vacuum lines (10^{-5} mbar) and glove-box techniques. Silica (Aerosil, 200 $m^2.g^{-1}$) was compacted with distilled water, calcined at 500 °C under air for 2 h and treated under vacuum (10^{-5} mbar) at 500 °C for 12 h and then at 700 °C for 4 h to give$SiO_{2-(700)}$. Pentane was distilled from NaK under N_2. $(Me_3Si)_2NAuPMe_3$ was prepared according to literature procedures.[1] Elemental analyses were performed at MikroanalytischesLaborPascher.

Direct reflectance infrared Fourier transform spectroscopy (DRIFT). DRIFT spectra were recorded on a Thermo Electron Corporation Nicolet F6700 apparatus. Typically, 64 scans were accumulated for each spectrum (resolution 2 cm^{-1}). The reflectance measurements were refined according to the Kubelka-Munk theory for enhanced resolution.

Solid State Nuclear Magnetic Resonance Spectroscopy. All spectra were recorded on a Bruker AVANCE spectrometer operating at ^{1}H, ^{13}C and ^{31}P Larmor frequencies of 500.13, 125.76 and 202.47 MHz, respectively. The samples were introduced in a zirconia rotor in the glove box and tightly closed. Chemical shifts are reported in ppm downfield from liquid

$SiMe_4$ (0 ppm) for ^1H and ^{13}C NMR, and from $Na_2HPO_4,2H_2O$ (6.6 ppm) for ^{31}P spectra, respectively. Spectra were obtained using a 4 mm MAS double resonance ($X–^1H$) probe at a spinning frequency of 10 kHz. 1D refocused zfr-INADEQUATE spectra[2] were obtained using a 4 mm MAS double resonance ($^{31}P–^1H$) probe at a spinning frequency of 12.5 kHz (the length of the echo period (tau-pi-tau) was experimentally optimized). The proton 90° pulse was 2.5 μs. Ramped cross-polarization[3] using a contact time of 5 ms was used to transfer the magnetization from protons to phosphorus. SPINAL-64 proton decoupling[4] was applied during evolution and acquisition periods at a RF field of 100 kHz. Carbon 90°and 180° pulse lengths of 2.5 and 5 μs, respectively, were used. Unless otherwise stated, the τ delay was set to 3 ms.The time of double quantum coherence evolution was 3 μs. The recycle delay was 2 s.

Preparation of $\{Au(PMe_3)/SiO_2\}_X$ (X = 0.5, 0.75, 1 and 2) by impregnation of X equiv. of $(Me_3Si)_2NAuPMe_3$onto $SiO_{2-(700)}$.

Representative procedure. A mixture of **$(Me_3Si)_2NAuPMe_3$**(120 mg, 0.27 mmol, 2.1 equiv.) and $SiO_{2-(700)}$ (510 mg, 0.13 mmolSiOH) in pentane (8 mL) was stirred at 25 °C for 3 h. The reaction mixture was filtered-off. The solid washed three times with pentane (8 mL), and finally dried under vacuum (10^{-5} mbar) at 25 °C for 1 h to yield **$\{Au(PMe_3)/SiO_2\}_2$.**

Reaction of $\{Au(PMe_3)/SiO_2\}_X$ with PMe_3. Representative procedure for$\{Au(PMe_3)/SiO_2\}_{1.0}$.(140 mg, 21 μmol) was contacted with an excess of PMe_3under vapor pressure at25 °C for 1 h. The sample was treated 8 h under vacuum (10^{-5}mbar) at 25 °C and stored in the glove box.

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