Supporting Information

Determination of coordination modes and estimation of the ^{31}P-^{31}P distances in heterogeneous catalyst by solid state double quantum filtered ^{31}P NMR Spectroscopy

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Supplementary Material (ESI) for Physical Chemistry Chemical Physics

CSA line-shape fitting of [1,2-Bis(diphenylphosphino)ethane] dichloropalladium(II)

The experiment was performed at on a Bruker AVANCEIII spectrometer at a magnetic field strength of 14 T with ^{1}H frequency of 600.13 MHz and 4mm rotor at spinning frequency of 4000 ± 2 Hz. ^{1}H decoupling of 108 kHz was applied. Recycle delay is 55s and the scan number is 100. The pound # in the Fig. S1 denotes the a small amount of ^{31}P signal indirect-coupled with ^{105}Pd present to 22.2% having spin I=5/2 and this signal is not used for the fitting here. The ^{1}J (^{105}Pd,^{31}P) was estimated to be 80Hz. The fitting in Fig. S1 gives out the δ_{CSA1}=-116.73 ppm, η_1=0.777, δ_{CSA2}=-79.53 ppm and η_2=0.788 for a spin-pair. These values were used in SIMPSON simulations in Fig. 2. The home-made fitting program will run the SIMPSON with these CSA parameters and dipolar coupling parameter to simulate the $F_{DQ}^{symm}(d,\tau)$ curve and finally give out the values of the DQ function

$F_{DQ}(t) = AF_{DQ}^{symm}(d,\tau)\exp(-2\tau / T_{\mathrm{d}})$.

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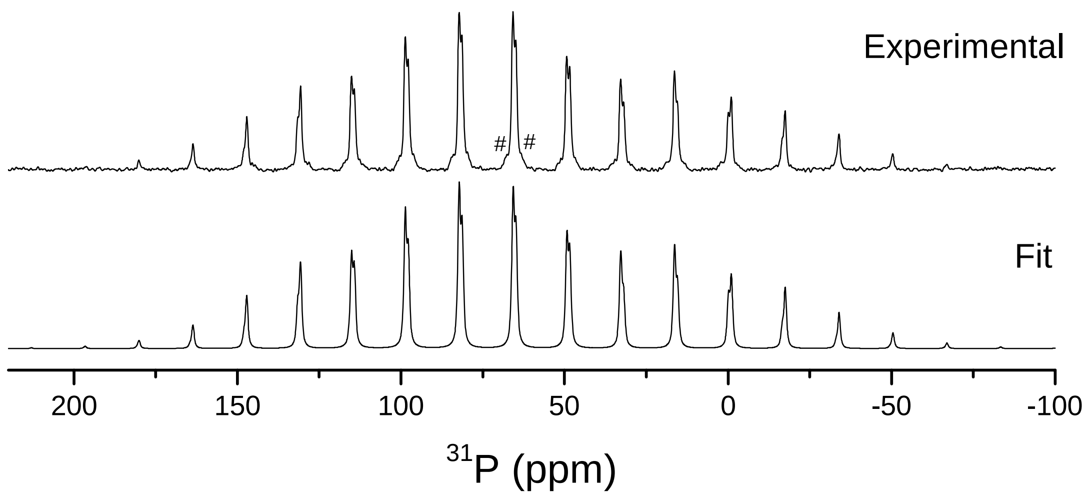

Fig. S1: the fitting of the one-pulse ^{31}P spectrum of [1,2-Bis(diphenylphosphino)ethane] dichloropalladium(II).

The effect of ^{1}J (^{105}Pd,^{31}P)

Palladium system always have a small indirect spin-spin coupling ^{1}J (^{105}Pd,^{31}P) between ^{105}Pd and ^{31}P. Thus we have to consider the effect of ^{1}J (^{105}Pd,^{31}P). The simulation of ^{1}J (^{105}Pd,^{31}P)=0 Hz and ^{1}J (^{105}Pd,^{31}P)=120 Hz for BR2_2^1 are shown in Fig. S2(a) and (b), respectively. Obviously, the introduce of ^{1}J (^{105}Pd,^{31}P) will decrease the signal when the build-up time is long. However, in the real system, there is a strong decay due to T_2 factor and a potential lost due to imperfect decoupling of proton channel. So we could introduce the factor A*exp(-2t/T_d) here, where T_d defines the lost due to T_2 and A the lost due to imperfect decoupling. The Fig. S2(c) and (d) is the result of the mulitiplication of (a) and (b) with the factor A*exp(-2t/T_d) respectively. Now the two curves are more or less overlapped. Meanwhile, only 22.2% ^{105}Pd has an indirect spin-spin coupling with ^{31}P, that means, only small part of ^{31}P should take into account ^{1}J (^{105}Pd,^{31}P) effect (which is obvious in Fig. S1). It should be also mentioned that the quadrupolar coupling constant and the orientation of the EFG tensor have no influence on the build-up curve (overlapped with (a) and (b)). Consequently we could neglect the effect of ^{1}J (^{105}Pd,^{31}P) when dealing with the palladium system.

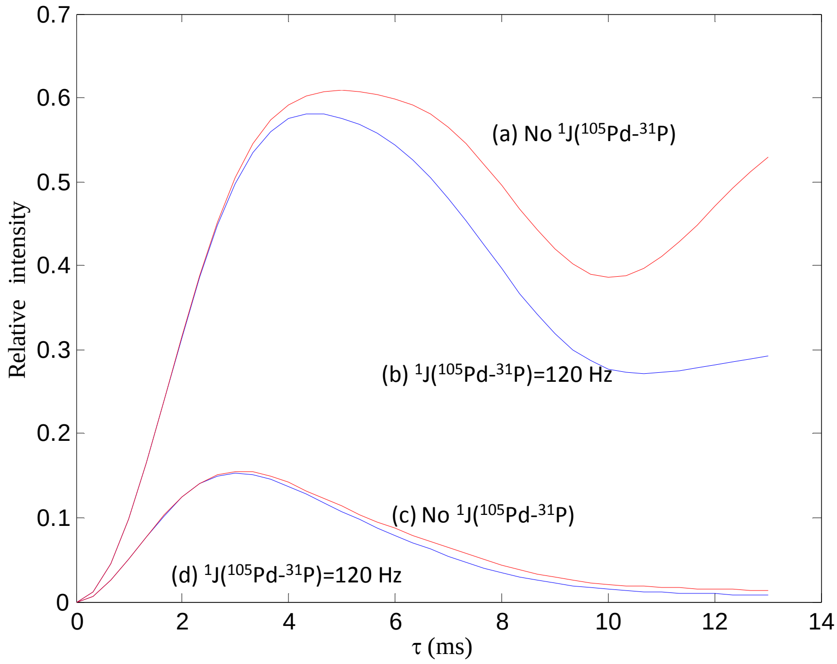

Fig. S2. The build-up curve of BR2_2^1 simluated by SIMPSON. Two identical ^{31}P with δ_{CSA} = 0 were used. The dipolar coupling between two ^{31}P is 616 Hz and the ^{1}J

(^{105}Pd,^{31}P) = 100 Hz. B_0= 14 T. ν_R=12 kHz. The π pulse length of $BR2_2^1$ is 19.25 μs. (c) and (d) is the result of mulitiplication of (a) and (b) with A*exp(-2t/T_d), respectively. A = 0.65 and T_d = 8.0 ms.

The deconvolution of one-pulse experiment of Pd-complex

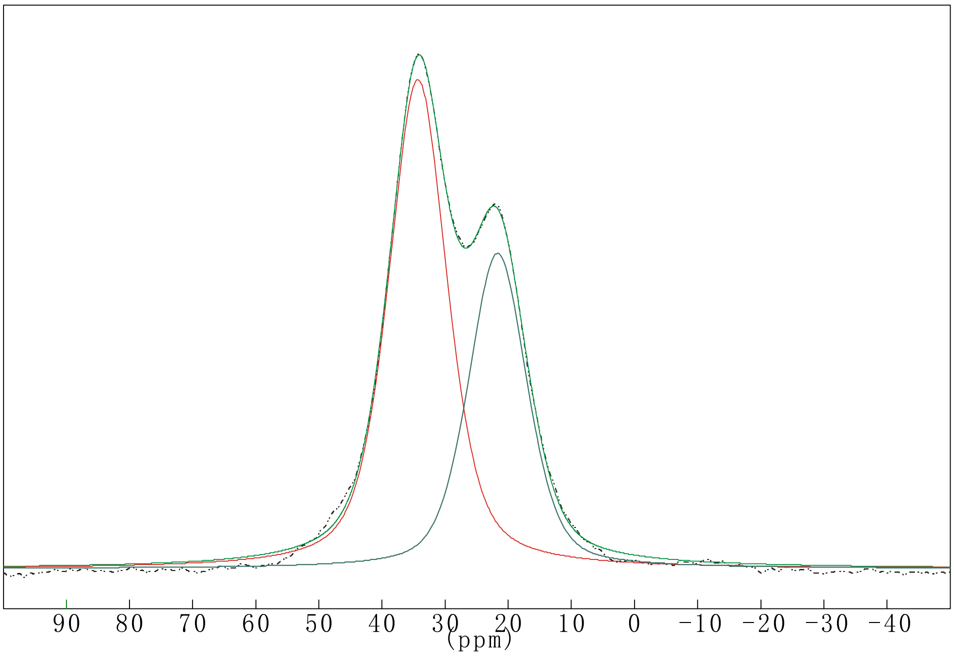

Fig. S3. The deconvolution of one pulse experiment of Pd-complex whose CP version is also shown in Fig. 3b. The black dot line is the experimental data and the green line is the fitting result. A mixture of 60% Gauss and 40% Lorentz line-shape was employed here. The relative proportion of left peak and right peak are 62.8% and 37.2%. Scan number is 1024 and recycle delay is 68 s. B_0=14 T, ν_R=12 kHz.