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Solvent-free mechanochemical synthesis of two Pt complexes: *cis*-$(Ph_3P)_2PtCl_2$ and *cis*-$(Ph_3P)_2PtCO_3$†

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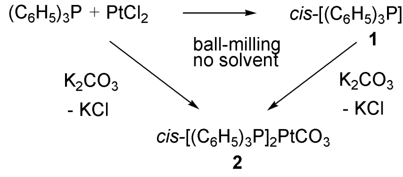
***Cis*-$(Ph_3P)_2PtCl_2$ and *cis*-$(Ph_3P)_2PtCO_3$ were prepared mechanochemically from solid reactants in the absence of a solvent; *cis*-$(Ph_3P)_2PtCl_2$ was obtained in 98% yield after ball-milling of polycrystalline $PtCl_2$ and Ph_3P; the mechanically induced solid-state reaction of *cis*-$(Ph_3P)_2PtCl_2$ with an excess of anhydrous K_2CO_3 produced *cis*-$(Ph_3P)_2PtCO_3$ in 70% yield; the formation of transition metal complexes as a result of mechanochemical solvent-free reactions has been confirmed by means of solid-state ^{31}P MAS NMR spectroscopy, X-ray powder diffraction and differential thermal analysis.**

Mechanochemical transformations of transition metal complexes containing organic molecules as ligands have been reported in a number of recent publications.[1,2] In all known cases, however, mechanical treatment of the reactants was followed by a subsequent heating and/or the processed samples were dissolved in appropriate solvents for characterization. Consequently, reports[1,2] provide little, if any, evidence to confirm that observed reactions occur during mechanical processing and not as the result of a successive treatment. The latter was demonstrated in experiments with chromium acetylacetonate, which did not form during ball-milling of $CrCl_3$ and $NaO_2C_5H_7$, but it was obtained after heating of the mechanically processed mixture of chromium trichloride and sodium acetylacetonate in a vacuum.[2]

Recently we demonstrated that high energy mechanical processing triggers a variety of efficient organic reactions in the solid-state without a solvent.[3] This was made possible by the means of a unique experimental approach, where solid-state ^{31}P magic angle spinning nuclear magnetic resonance (^{31}P MAS NMR) spectroscopy, X-ray powder diffraction, and differential thermal analysis (DTA) were combined to investigate both chemical and physical events that occur in organic materials during mechanical processing. Here we show that the same *modus operandi* can be extended towards different classes of molecular solids, for example metal coordination compounds. For the first time, two platinum complexes — *cis*-bis(triphenylphosphine)platinum(II) dichloride **1** and *cis*-bis(triphenylphosphine)platinum(II) carbonate **2** — were prepared from solid reactants during ball-milling in a solvent-free environment, as depicted in Scheme 1.

Complex **1** is usually prepared in solution by ligand substitution in platinum (II) compounds or by oxidative addition of chlorine to $(Ph_3P)_4Pt$.[4,5] It also forms when $PtCl_2$ reacts with molten Ph_3P. In addition to **1**, the reaction in the melt produces at least 20% of *trans*-bis(triphenylphosphine)platinum(II) dichloride as a by-product.[5] Carbonate **2** is often synthesized in solution by ligand exchange between **1** and Ag_2CO_3.[6] The latter has been proven to be the only metal carbonate effective in this transformation. To the best of our knowledge, mechanochemical solvent-free synthesis of Pt-complexes was not reported in the literature before.



Scheme 1

Ball-milling of crystalline $PtCl_2$ with two molar equivalents of Ph_3P at rt for 1 h produces an X-ray amorphous powder†. Its solid-state ^{31}P MAS NMR spectrum, shown in Fig. 1a, is in excellent agreement with the previously reported solid-state NMR data of pure crystalline **1**,[7–9] indicating the formation of compound **1** during mechanical processing.

The differential thermal analysis of the ball-milled powder confirms the completion of this reaction because no endothermic events due to the melting of Ph_3P have been observed.† Endothermic anomaly in the DTA trace of the mechanically processed sample (onset at 280 °C) agrees well with melting and decomposition of pure **1**.[5,10]† The DTA trace of the mechanochemically prepared complex **1** contains two additional exothermic effects between 104 and 180 °C, which are absent in the crystalline *cis*-$(Ph_3P)_2PCl_2$. The origin of these anomalies was studied using *in-situ* high temperature X-ray powder diffraction,† which revealed crystallization of the ball-milled amorphous sample between 100 °C and 180 °C. It is worth noting that similar exothermic events were also observed in the DTA trace of the pure crystalline *cis*-$(Ph_3P)_2PCl_2$ ball-milled for 2 h. Hence, the exothermic anomalies in the DTA trace of

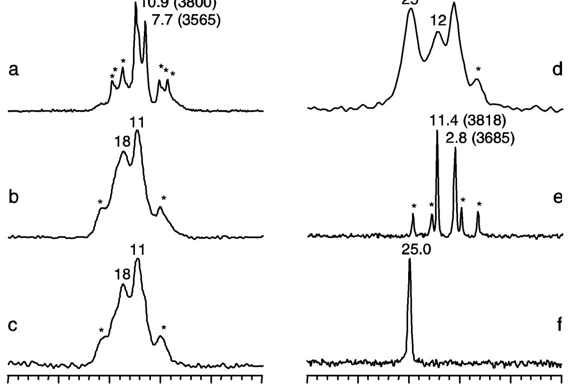


Fig. 1 Solid-state ^{31}P MAS NMR spectra: powders obtained during ball-milling of Ph_3P with $PtCl_2$ for 1 h {lit. for **1**: $\delta^{31}P/J_{Pt-P}$ (ppm/Hz) = 12.5/3727, 10.9/3910, 7.8/3596[7] and 12.6/3750, 7.8/3580[8]} (a), and 2 h (b); crystalline **1** ball-milled for 2 h (c); reaction mixture formed during ball-milling of **1** with 2.5 equiv. of K_2CO_3. The broad peak at $\delta^{31}P$ = 25 ppm includes both the signal of Ph_3PO and the resonance signals due to ^{195}Pt–^{31}P interactions in complex **2** (d); crystalline complex **2** (e), and Ph_3PO (f). The values of the isotropic chemical shifts (ppm) and the coupling constants (Hz, in parenthesis) are shown at the corresponding peaks. The phosphorus resonances are accompanied by doublets due to Pt–P *J* coupling, denoted by asterisks, with intensities consistent with the natural abundance of ^{195}Pt (33.8%).

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† Electronic supplementary information (ESI) available: differential thermal analysis data, X-ray diffraction data. See http://www.rsc.org/suppdata/cc/b2/b203694k/

the mechanochemically prepared complex **1** represent amorphous to crystalline transitions in the powder, which are exothermic processes.

Pure complex **1**, identical to that described in the literature,[5,8,11] was obtained in 98% yield after dissolution of the ball-milled powder in CH_2Cl_2, filtration and evaporation of the solvent in a vacuum.[9] According to the conventional ^{31}P NMR spectroscopy in $CDCl_3$, compound **1** was the only product of the mechanochemical reaction, *i.e.* no triphenylphosphine oxide or other phosphorus containing species were detected.

Ball-milling of $PtCl_2$ with two molar equivalents of Ph_3P for 2 h results in the same product **1** (98% yield). On the other hand, prolonged mechanical treatment has a significant effect on the shape of the solid-state ^{31}P MAS NMR spectrum of the resulting powder, which however, remains in excellent agreement with the spectrum of pure **1** ball-milled at the same experimental conditions (Figs. 1b and c). It is worth noting that this observation is in line with the previous reports about the extreme sensitivity of solid-state ^{31}P NMR spectra of Pt(II) complexes to the crystallinity of the samples.[7,8]

The mechanical processing of **1** with 2.5 equiv. of anhydrous K_2CO_3 produced a powder mixture containing complex **2**, crystalline KCl (identified by X-ray powder diffraction†) and minor amounts of Ph_3PO plus unidentified Pt-specie(s) as side-products.[9] According to the conventional ^{31}P NMR spectra of the samples extracted from the milling equipment during the mechanochemical experiment, the complete transformation of the starting complex **1** into the reaction products requires 6.5 h of ball-milling. The solid-state ^{31}P MAS NMR spectrum of the mechanochemically prepared sample and the spectra of the pure crystalline **2** and Ph_3PO are shown in Figs.1d–f. Once again, the solid-state NMR spectroscopy clearly indicates the formation of the carbonate **2** during mechanical processing prior to any further treatment.

The ball-milled powder was dissolved in CH_2Cl_2, filtered and the complex **2** was then isolated by precipitation with diethyl ether in 70% yield. The conventional NMR and IR spectra, and the melting point of the thus obtained compound **2**[9] were identical with literature data reported for *cis*-$(Ph_3P)_2PtCO_3$.[6,12]

Carbonate **2** also forms as a major product during ball-milling of the mixture of $PtCl_2$, Ph_3P and anhydrous K_2CO_3 without a solvent (Scheme 1). Apparently, this transformation is a two-stage process involving the intermediate formation of complex **1**, which was detected in the ball-milled powder using conventional ^{31}P NMR spectroscopy. Contrary to the previous reaction, this transformation did not result in a complete consumption of **1** even after mechanical treatment for 14 h.

We found no evidence that the studied reactions proceed in the absence of the mechanical treatment. At least two different scenarios could explain the role of mechanical energy in the transformations described above. First, the reactions may occur in the melt, which possibly forms locally and momentarily in the areas where the balls collide with the walls of the reaction vial and with one another. Previously, we showed that the local temperature in a material during mechanical processing at the experimental conditions identical to those used in the current study does not exceed 110 °C.[3] Thus, it is unlikely that complex **2** forms as a result of a liquid-state reaction between high-melting complex **1** (mp 193 °C) and anhydrous K_2CO_3 (mp 891 °C). On the other hand, the possibility of the reaction between the transient Ph_3P liquid (mp 79–82 °C) and solid $PtCl_2$ (mp 581 °C) could not be entirely excluded. However, since one of the major products of the reaction between $PtCl_2$ and molten Ph_3P — *trans*-$(Ph_3P)_2PtCl_2$[5] — does not form in a detectable amount in the mechanochemical process, this mechanism is rather doubtful.

The second scenario reflects the occurrence of truly solid-state mechanochemical transformations. The available experimental data suggest that mechanical processing enables interactions of reacting centers in the solid state by first breaking the crystallinity of the reactants and second by providing the mass transfer in the absence of a solvent. Our experiments on the ball-milling of pure $PtCl_2$ and **1**, both of which lose crystallinity and become essentially amorphous powders during mechanical processing, support this assumption.‡

In summary, we showed that platinum (II) complexes can be prepared in high yields during mechanically induced solid-state reactions at solvent-free conditions. The completion of the reactions during ball-milling has been confirmed directly using a combination of solid-state ^{31}P MAS NMR spectroscopy, X-ray powder diffraction and DTA. The mechanochemical technique appears to be a convenient and extremely efficient experimental tool, which opens a pathway to new processes where chemical transformations are performed in an environmentally benign manner.

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Notes and references

‡ $PtCl_2$, anhydrous K_2CO_3 and Ph_3P were purchased from Alfa Aesar, Fisher or Aldrich. Solid-state ^{31}P MAS NMR spectra were collected on a Chemagnetics Infinity 400 MHz system using relaxation delay of 45 s, 20 kHz MAS and ^{1}H decoupling of 30 kHz. ^{1}H and ^{31}P NMR spectra in $CDCl_3$ were performed on Varian VXR-300 and 400 spectrometers. Chemical shifts are reported with respect to an 85% solution of H_3PO_4 in water (^{31}P) or TMS (^{1}H). Ball-milling was performed as described in ref. 3.

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9 Mechanochemically prepared platinum complexes. **1**: yield 98%; solid-state ^{31}P MAS NMR: δ^{31}P/$J_{\text{Pt-P}}$ (ppm/Hz): 12.5/3765, 10.6/3850, 7.8/3600; liquid-state NMR ($CDCl_3$): δ^{31}P/$J_{\text{Pt-P}}$ (ppm/Hz): 15.3/3672; δ^1H (ppm): 7.52–7.47 (m, 2H, Ph), 7.35–7.32 (m, 1H, Ph), 7.19–7.16 (m, 2H, Ph); mp 298–303 °C (decomp.); **2**: yield 70%; solid-state ^{31}P MAS NMR: δ^{31}P/$J_{\text{Pt-P}}$ (ppm/Hz): 11.4/3818, 2.8/3685; liquid-state NMR ($CDCl_3$): δ^{31}P/$J_{\text{Pt-P}}$ (ppm/Hz): 7.2/3704; δ^1H (ppm/Hz): 7.42–7.33 (m, 3H, Ph), 7.22–7.18 (m, 2H, Ph); IR (KBr): 1672(CO), 1629 (CO); mp 193–195 °C (decomp.). The amount of Ph_3PO formed as a side-product in **2** was ~20% as estimated from the liquid-state ^{31}P NMR (corrected for T_1 of the reaction products).

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