Assembly of Hybrid Organic–Organometallic Materials through Mechanochemical Acid–Base Reactions

Dario Braga,*[a] Lucia Maini,[a] Marco Polito,[a] Laurent Mirolo,[a] and Fabrizia Grepioni*[b]

Abstract: Manual grinding of the organometallic complex [Fe(η^5-C_5H_4COOH)$_2$] with a number of solid bases, namely 1,4-diazabicyclo[2.2.2]octane, $C_6H_{12}N_2$, 1,4-phenylenediamine, *p*-(NH_2)$_2$$C_6H_4$, piperazine, HN($C_2H_4$)$_2$NH, *trans*-1,4-cyclohexanediamine, *p*-(NH_2)$_2$$C_6H_{10}$, and guanidinium carbonate [(NH_2)$_3$C]$_2$[CO_3], generates quantitatively the corresponding adducts, [$HC_6H_{12}N_2$][Fe(η^5-C_5H_4COOH)(η^5-C_5H_4COO)] (**1**), [$HC_6H_8N_2$][Fe(η^5-C_5H_4COOH)(η^5-C_5H_4COO)] (**2**), [$H_2C_4H_{10}N_2$][Fe(η^5-C_5H_4COO)$_2$] (**3**), [$H_2C_6H_{14}N_2$][Fe(η^5-C_5H_4COO)$_2$]$\cdot$2H_2O, (**4**$\cdot$2H_2O), and [C(NH_2)$_3$]$_2$[Fe(η^5-C_5H_4COO)$_2$]$\cdot$2H_2O, (**5**$\cdot$2H_2O), respectively. Crystallization from methanol in the presence of seeds of the ground sample allows the growth of single crystals of these adducts; therefore we were able to determine the structures of the adducts by single-crystal X-ray diffraction. This information was used in turn to identify and characterize the polycrystalline materials obtained by the grinding process. In the case of [$HC_6N_2H_{12}$][Fe(η^5-C_5H_4COOH)(η^5-C_5H_4COO)] (**1**), the base can be removed by mild treatment regenerating the starting dicarboxylic acid, while in all other cases decomposition is observed. The solid–solid processes described herein imply molecular diffusion through the lattice, breaking and reassembling of hydrogen-bonded networks, and proton transfer from acid to base.

Keywords: crystal engineering · hydrogen bonds · mechanochemistry · organic–organometallic hybrids · solid phase synthesis

Introduction

There is a growing interest in the exploitation of solvent-free reactions because, inter alia, of environmental and sustainability issues.[1] Reactions between two solid reactants to yield a solid product are prototypical solvent-free reactions.[2] Such reactions, also known as mechanochemical reactions if activated by grinding or milling, have been known for a long time.[3] Under the impetus of crystal engineering,[4] that is, the bottom-up construction of molecular materials starting from molecular or ionic building blocks, these "less conventional" synthetic procedures are beginning to be reinvestigated as viable routes for the preparation of novel molecular aggregates.[5] Solvent-free molecular reactions are also attractive under the topochemical viewpoint,[6] often offering alternative preparative routes to molecular materials.

Mechanically activated reactions have been exploited mainly with inorganic solids[7] (alloying, milling of soft metals with ceramics, activation of minerals for catalysis, extraction, preparation of cements), while very little has been done with molecular systems.[5, 6] Besides being advantageous for the absence of solvents, solid–solid reactions often lead to very pure products and require very simple equipment to be carried out. The main disadvantage is inherent to the characterization of the (usually polycrystalline) reaction product, in particular when complex supramolecular systems are involved. As a matter of fact, the product nature (let alone its detailed structural features) is often difficult to determine in the absence of single crystals suitable for X-ray diffraction. In spite of the enormous progress, ab initio structural determination from powder diffraction data[8] it is still far from being applicable to complex supramolecular systems. On the other hand, the utilization of mechanochemical (grinding) methods appears to be in contradiction with the very idea of obtaining single crystals, since they are usually grown to a suitable size from solution or by sublimation. Moreover, crystallization from solution does not necessarily lead to the same product as obtained by grinding.[9a] This is a particularly noticeable when crystallization from solution is under kinetic control, thus favoring crystallization of those species that nucleate first and form less soluble nuclei.

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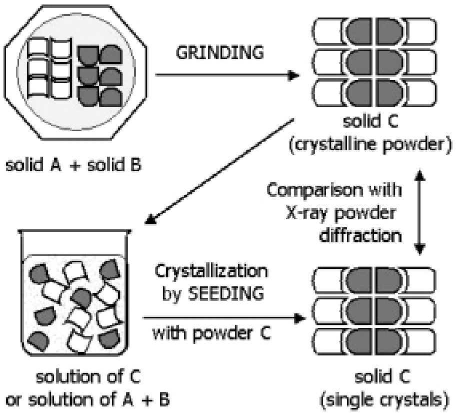
The problem can be circumvented if the crystal nucleation step can be *instructed* on how to generate the desired product. This can be achieved through *seeding*, that is, by using preformed micro crystals of the desired phase in order to grow the desired material to crystals of suitable size.[9b] One needs to be wary of the fact that, in order for the controlled growth by seeding to be successful, it is necessary not to dissolve the material entirely: nuclei must remain undissolved for the crystallization process to proceed towards the desired phase.[10] It is important to appreciate that by means of this *trick* it is often possible to avoid kinetic control over the crystallization process, which often leads to formation of kinetically favored over thermodynamic products. Seeding procedures are commonly employed in pharmaceutical industries to make sure that the desired crystal form is always obtained from a preparative process.[11] The use of a *seeding* procedure often allows preparation of single crystals of suitable size, which, in turn, can be used to confirm, a posteriori, that the same phase obtained from solution crystallization and that yielded by solid – solid mixing processes has been obtained by comparing calculated and observed powder diffraction patterns. Similar methods have been used previously[12] to determine the structure of other polycrystalline products obtained by "nonsolution" methods (grinding, dehydration, thermal treatment). The process described above is pictured in Scheme 1.



Scheme 1. The solid yielded by the mechanochemical process is compared by means of X-ray powder diffraction with the solids obtained by crystallization through *seeding* of a solution of the ground powder or of A and B powders. The crystallization process allows preparation of single crystals that, after crystal structure determination, can be used to obtain calculated diffraction patterns.

In our group organometallic building blocks have been utilized to prepare novel molecular crystalline materials and exploit the variable valence, spin and charge states of coordination complexes.[13] Interesting results have been obtained also in the cases of solid – gas reactions.[14]

In this paper we report that mechanochemical treatment of the organometallic complex $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ with a number of solid bases, namely, 1,4-diazabicyclo[2.2.2]octane $[C_6H_{12}N_2]$, 1,4-phenylenediamine, $[p\text{-}(NH_2)_2C_6H_4$, $C_6H_8N_2]$, piperazine $[HN(C_2H_4)_2NH$, $C_4H_{10}N_2]$, *trans*-1,4-cyclohexanediamine, $[p\text{-}(NH_2)_2C_6H_{10}$, $C_6H_{14}N_2]$, and guanidinium carbonate $[(NH_2)_3C]_2[CO_3]$, generates quantitatively the 1:1 adducts $[HC_6H_{12}N_2][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ (**1**), $[HC_6H_8N_2][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ (**2**), $[H_2C_4H_{10}N_2][Fe(\eta^5\text{-}C_5H_4COO)_2]$ (**3**), and the two hydrated species $[H_2C_6H_{14}N_2][Fe(\eta^5\text{-}C_5H_4COO)_2]\cdot 2H_2O$ (**4**$\cdot 2H_2O$) and $[C(NH_2)_3]_2[Fe(\eta^5\text{-}C_5H_4COO)_2]\cdot 2H_2O$ (**5**$\cdot 2H_2O$), respectively. These solid – solid reactions do not seem to occur through the formation of eutectic phases. Structural characterization (see below) allows us to see that the formation of the hybrid organic – organometallic materials implies proton transfer from the acid to the base, breaking and forming of strong hydrogen-bonding interactions, and severe structural rearrangements.

Compound **1** can also be obtained in a heterophase process through uptake by the diacid $Fe(\eta^5\text{-}C_5H_4COOH)_2$ of vapours of 1,4-diazabicyclo[2.2.2]octane, which is easily sublimed at room temperature. Formation of the solid adduct **1** in the solid – gas process is, however, much slower than in the case of mechanical treatment. Interestingly though, the diacid $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ can be regenerated if the base is sublimed off solid **1** by thermal treatment at approximately 235 °C.

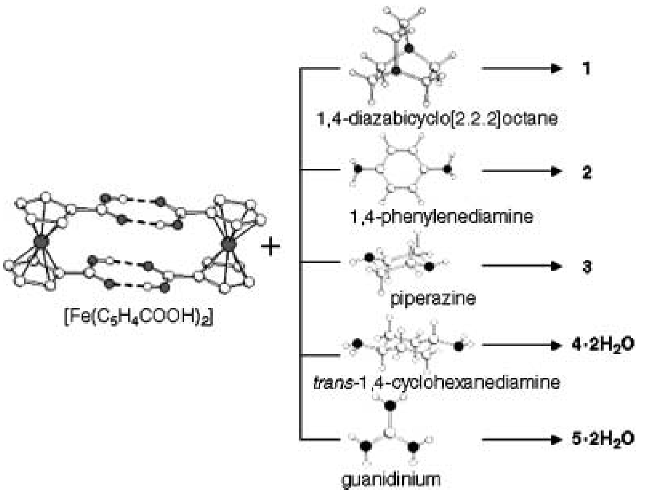
Results and Discussion

All mechanochemical preparations were carried out by manual grinding in an agata mortar of equimolar quantities of the two solid materials (see Experimental Section). After grinding, the polycrystalline material was used as such for powder diffraction experiments. We performed two separate experiments in which 1) equimolar quantities of acid and base were dissolved in methanol and the solvent was allowed to evaporate at room temperature and 2) small portions of the ground samples were dissolved in the minimum amount of solvent, in order to act as seeds and allow growth of single crystals suitable for X-ray diffraction experiments. By comparison with the diffractograms measured on the raw reactants, it was possible to ascertain whether the starting materials had been completely converted into products. In all cases discussed in this paper, except in the case of the adduct with cyclohexanediamine, the structures of the compounds obtained mechanochemically are the same as those obtained from solution crystallization.

In the case of compound **4** with cyclohexanediamine, the product of the grinding process is anhydrous, whereas from solution only the hydrated form **4**$\cdot 2H_2O$ is obtained. Even though seeding was not successful in this case, de-hydration of the hydrated compound **4**$\cdot 2H_2O$ yields the anhydrous phase **4** quantitatively. In the case of compound **5**, both grinding and crystallization from solution only yielded the di-hydrated phase **5**$\cdot 2H_2O$. Further details will be provided in the following.

Grinding of the diacid $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ with the various bases in stoichiometric amounts other than 1:1 (i.e., 1:2 and 2:1) does not appear to lead to formation of different compounds, rather a mixture of the 1:1 products and of unreacted base or acid (as ascertained by X-ray powder diffraction) was invariably observed.

In order to assist the reader, a schematic representation of the structures of the reactants is reported in Scheme 2, together with the numbering scheme.



Scheme 2. Schematic representation of the structures of the reactants.

Beside the interest in the mechanochemical experiments (which, to the best of the author's knowledge, have not been applied before to organometallic species), the preparation of hybrid organic–organometallic compounds by solvent-free methods is relevant from the crystal engineering point of view. As it will be apparent in the following, all adduct formations imply profound modifications of the hydrogen-bonding motifs, with breaking of O–H···O hydrogen bonds between the organometallic complexes and formation of $^{(-)}$O···H–N$^{(+)}$ and/or O–H···N interactions within the adducts. It is interesting to note that dissolution of the adducts in methanol and subsequent crystallization does not lead (with the exception of compound **4**, see above) to different assemblies. Methanol (99.8%) was used in all crystallizations because of the lower solubility of the products.

Hydrogen-bonding structural parameters for the five compounds discussed herein are grouped in Table 1. A word of caution is in order, the comparison of calculated and measured X-ray diffractograms does guarantee that the compounds obtained by the two routes (solid–solid reaction and recrystallization from solvent) possess the same structural features, but cannot be used confidently to state that the same proton-transfer process has taken place. It is well known not only that O–H···N and $^{(-)}$O···H–N$^{(+)}$ interactions, associated to acid–base proton transfer, can be in competition, but also that proton transfer along the O···N hydrogen bond in the solid state depends on the temperature.[15]

We will first describe the solid-state structures as obtained from single crystals and then proceed with the characterization of the mechanochemical product. Importantly, the structure determination by single-crystal X-ray diffraction also allowed us to establish unambiguously whether mono- or di-deprotonation had occurred. In fact, while compounds **1** and **2** contain the monoanion [Fe(η^5-C$_5$H$_4$COOH)(η^5-C$_5$H$_4$COO)]$^-$ (and may form inter-anionic $^{(-)}$O–H···O$^{(-)}$ as well as O–H···N and $^{(-)}$O···H–N$^{(+)}$ interactions), compounds **3**, **4**·2H$_2$O, and **5**·2H$_2$O contain the fully deprotonated dianion [Fe(η^5-C$_5$H$_4$COO)$_2$]$^{2-}$, which can only accept hydrogen-bond donation from the base or solvent molecules. In the case of **5**·2H$_2$O this also requires the presence of two guanidinium cations. The preparation and structure of compounds **1** and **2** have been reported in a preliminary communication.[16]

Table 1. Relevant hydrogen-bonding distances [Å] for compounds **1**, **2**, **3**, **4**·2H$_2$O, and **5**·2H$_2$O.

Compound	OH···O	NH···O	CH···O
1		N(1)···O(3) 2.580(7)	C(13)···O(1) 3.447(9)
		N(2)···O(2) 2.560(8)	C(15)···O(1) 3.391(9)
			C(16)···O(1) 3.134(9)
			C(17)···O(4) 3.185(9)
			C(18)···O(4) 3.268(9)
2	O(1)···O(3) 2.509(7)	N(2)···O(2) 2.936(9)	C(18)···O(3) 3.343(7)
		N(1)···O(2) 2.964(8)	
		N(1)···O(1) 2.810(8)	
		N(2)···O(4) 2.925(8)	
3		N(1)···O(1) 2.650(8)	C(3)···O(1) 3.294(7)
		N(1)···O(2) 2.726(9)	C(7)···O(2) 3.311(9)
			C(8)···O(2) 3.395(9)
4·2H$_2$O	O(3)···O(1) 2.804(3)	N(1)···O(2) 2.779(3)	C(7)···O(1) 3.364(4)
	O(3)···O(1) 2.791(3)	N(1)···O(2) 2.831(3)	
		N(1)···O(3) 2.780(4)	
5·2H$_2$O	O(3)···O(1) 2.749(4)	N(1)···O(3) 2.891(5)	
	O(3)···O(2) 2.785(4)	N(1)···O(1) 2.850(5)	
		N(2)···O(1) 2.906(5)	
		N(2)···O(3) 2.928(5)	
		N(3)···O(2) 2.972(5)	
		N(3)···O(2) 2.862(5)	

Structure and mechanochemical preparation of [HC$_6$H$_{12}$N$_2$][Fe(η^5-C$_5$H$_4$COOH)(η^5-C$_5$H$_4$COO)] (1): Figure 1 shows that, upon acid–base reaction and crystallization, the C$_6$H$_{12}$N$_2$ molecules act as bridges between acid sandwich molecules in a *transoid* conformation. This is a useful observation, since both polymorphic forms of the neutral diacid[17] contain hydrogen-bonded dimers in which the –COOH groups are, by necessity, in *cisoid* (eclipsed) conformation. This difference is not so much relevant when considering the acid–base reaction in solution (where one can expect that the proton transfer is mediated by the solvent molecules and the dimers are already broken with formation of solvate diacid molecule) inasmuch as for the solid-state process. In the solid–solid reaction the molecules of the base have to diffuse through the crystal and generate a thoroughly different hydrogen-bonded network. Formation of [HC$_6$H$_{12}$N$_2$][Fe(η^5-C$_5$H$_4$COOH)(η^5-C$_5$H$_4$COO)] implies a

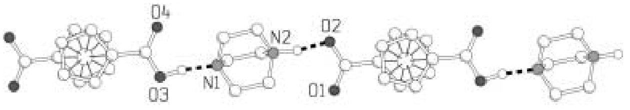


Figure 1. Stucture of compound **1** in which the [HC$_6$H$_{12}$N$_2$]$^+$ ions act as bridges between acid sandwich molecular anions in *transoid* conformation (H$_{CH}$ atoms not shown for clarity).

rather dramatic change in the supramolecular arrangement of the components: the twin cyclic carboxylic rings in the diacid dimer are opened up, and molecules of $C_6H_{12}N_2$ are inserted in between $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ molecules with formation of O–H···N hydrogen-bonding interactions. The process is accompanied by a conformational change from *cis* to *trans* of the carboxylic groups on the five-membered rings, which are rotated by 180° around the molecular axis passing through the iron center.

It is worth mentioning here that compound **1** has been recently reported also by other authors as a part of a comprehensive study of the use of the diacid as a building block in supramolecular chemistry.[18] Our data fit very well with those reported, except for the location of the hydrogen atoms along the O···N hydrogen bonds.[18] In our determination, the hydrogen atoms are ordered and indicate that the base forms two different interactions in the chain, that is, an O–H···N and an $^{(-)}$O···H–N$^{(+)}$ interaction (N(1)···O(3) 2.580(7) and N(2)···O(2) 2.560(8) Å, respectively). As shown in Figure 1, no disorder is observed in our case and the chain can be described (on the basis of the single-crystal X-ray structure) as alternate $[HC_6H_{12}N_2]^+$ and $[Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]^-$ ions, joined by alternate neutral O–H···N and charge-assisted $^{(-)}$O···H–N$^{(+)}$ hydrogen-bonding interactions.

Finally, it should be mentioned that it has been possible to prepare compound **1** in a gas-phase reaction by exploiting the relatively high vapour pressure of solid $C_6H_{12}N_2$. The process is fully reversible as shown by thermal treatment of the product and thermogravimetric measurements (see below).

Figure 2 shows a comparison between the X-ray powder diffractogram of the ground polycrystalline product and that calculated on the basis of the structure determined by single-crystal X-ray diffraction. Even though the crystallinity of the $[HC_6H_{12}N_2][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ sample obtained from grinding is not high, all significant peaks can be easily recognized. Note that peaks attributable to the starting materials, namely monoclinic $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ and solid $C_6H_{12}N_2$ (also provided for comparison) are absent.

As for the reverse process, thermogravimetric measurements indicate that, on heating at about 235 °C, $[HC_6H_{12}N_2][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ loses 1 mole of $C_6H_{12}N_2$. No decomposition is observed and the nature of the final product, that is, $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$, has again been confirmed by powder diffraction. Note also that mixing the two solids in stoichiometric ratios other than 1:1 (e.g., 1:2 and 2:1) leads to formation of solid mixtures with diffraction peaks corresponding to the unreacted excess reagent in addition to the peaks of **1**. It is also worth noting that mechanical grinding, vapour uptake, and crystallization from solution all lead to formation of the same product. Whether the first process can be described as a true solid – solid reaction or implies the occurrence of an intermediate liquid phase cannot be stated with confidence at present and will require further studies.

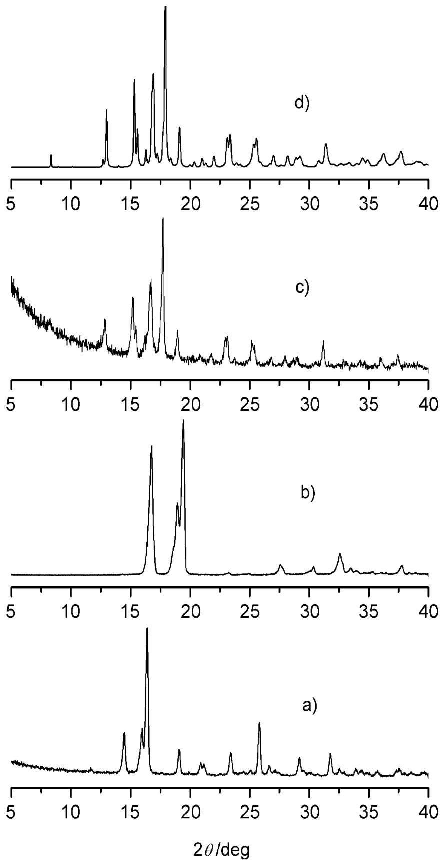


Figure 2. Comparison between the X-ray powder diffractogram of the ground polycrystalline product **1** (c) and that calculated on the basis of the structure determined by single-crystal X-ray diffraction (d). Powder patterns of the starting materials, $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ (a) and 1,4-diazabicyclo[2.2.2]octane (b), are also provided for comparison.

Structure and mechanochemical preparation of $[HC_6H_8N_2][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ (2):

Grinding of $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ with 1,4-phenylenediamine in 1:1 ratio leads to quantitative formation of the salt $[HC_6H_8N_2][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ (**2**). As in the $C_6H_{12}N_2$ case, both recrystallization from solution of the ground sample and direct reaction of the reagents in solution allowed the growth of single crystals of the same species as obtained from the solid – solid process.

The supramolecular arrangement in crystalline **2** is shown in Figure 3. In contrast to the case of **1**, in which chains are

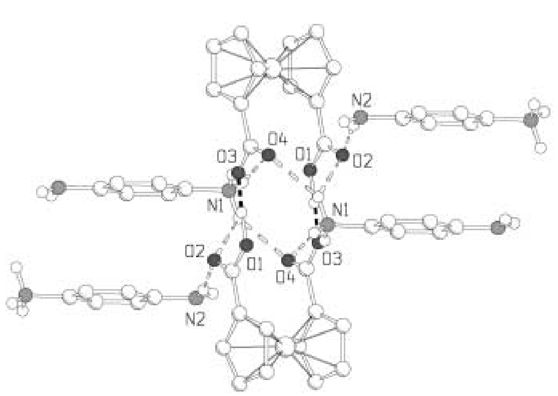


Figure 3. The supramolecular arrangement in crystalline **2** shows the presence of a super-dianion, composed of two units joined by an $^{(-)}$O–H···O$^{(-)}$ interaction (2.509(7) Å), whose outermost oxygen atoms form $^{(-)}$O···H–N$^{(+)}$ interactions with the cations (H_{CH} atoms not shown for clarity).

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characterized by alternating cations and anions, the structure of **2** retains, in a sense, the dimeric structure of the parent neutral diacid (see Scheme 2). Proton removal generates a *supramolecular dianion* composed of two units joined by an O–H···O interaction (2.509(7) Å) (see Figure 3). The outermost oxygen atoms form $^{(-)}$O···H–N$^{(+)}$ interactions with the cations. Proton transfer from the acid to the base, with formation of charge assisted $^{(-)}$O···H–N$^{(+)}$ hydrogen-bonding interactions, could be established unequivocally. The dimeric unit in **2** is reminiscent of the dimer formed by the cobalticinium zwitterion [Co(η^5-C_5H_4COOH)(η^5-C_5H_4COO)] in many of its crystals with alkali salts.[19]

The comparison between the X-ray powder diffractogram measured on the ground polycrystalline product **2** and that calculated on the basis of the structure determined by single-crystal X-ray diffraction is shown in Figure 4.

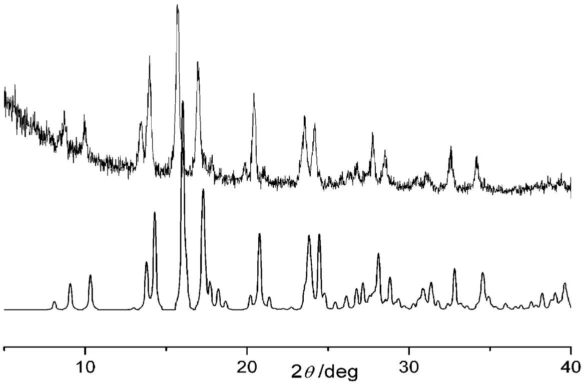

Figure 4. Comparison between (top) the X-ray powder diffractogram measured on a sample of **2** obtained by grinding and (bottom) that calculated on the basis of the structure determined by single-crystal X-ray diffraction.

Structure and mechanochemical preparation of [$H_2C_4H_{10}N_2$][Fe(η^5-C_5H_4COO)$_2$] (3): Compound **3** differs from **1** and **2** because the acid is completely deprotonated by reaction with the piperazine. The supramolecular packing is shown in Figure 5. One can see how each dication is bound to four surrounding dianions through $^{(-)}$O···H–N$^{(+)}$ hydrogen bonds (in the range 2.810(8)–2.925(8) Å). The comparison between the X-ray powder diffractogram measured on the ground polycrystalline product **3** and that calculated on the basis of the structure determined by single-crystal X-ray diffraction is shown in Figure 6.

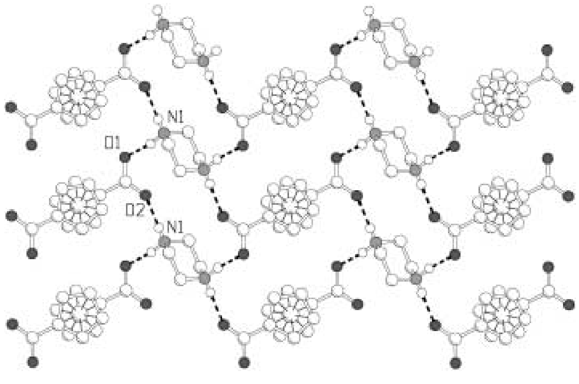

Figure 5. The supramolecular packing in compound **3**: each dication is bound to four surrounding dianions through $^{(-)}$O···H–N$^{(+)}$ hydrogen bonds (O···N range 2.810(8)–2.925(8) Å; H_{CH} atoms not shown for clarity).

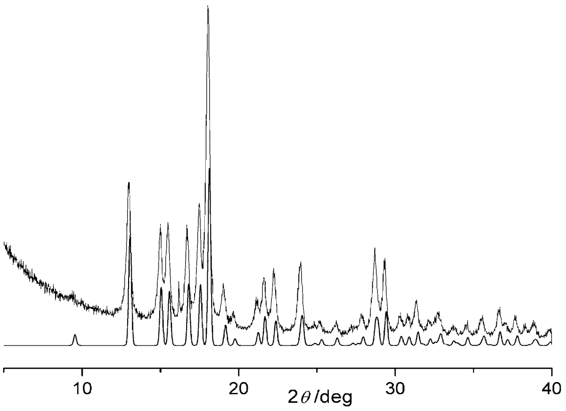

Figure 6. Comparison between (top) the X-ray powder diffractogram measured on a sample of **3** obtained by grinding and (bottom) that calculated on the basis of the structure determined by single-crystal X-ray diffraction.

Mechanochemical preparation of [$H_2C_6H_{14}N_2$][Fe(η^5-C_5H_4COO)$_2$] (4) and structure of the dihydrated form [$H_2C_6H_{14}N_2$][Fe(η^5-C_5H_4COO)$_2$]·2H_2O (4·2H_2O): Compound **4**·2H_2O contains a dianion [Fe(η^5-C_5H_4COO)$_2$]$^{2-}$ and two water molecules besides the protonated cyclohexanediamine molecule (Figure 7). Each nitrogen atom is capable of donating three hydrogen bonds. In fact, as in the case of **3** the base interacts with four surrounding anions through $^{(-)}$O···H–N$^{(+)}$ hydrogen bonds, with the addition of two O···H–N$^{(+)}$ interactions involving the water molecules (Figure 7). These last bonds act as bridges between the dianions to form four-membered rings. The comparison

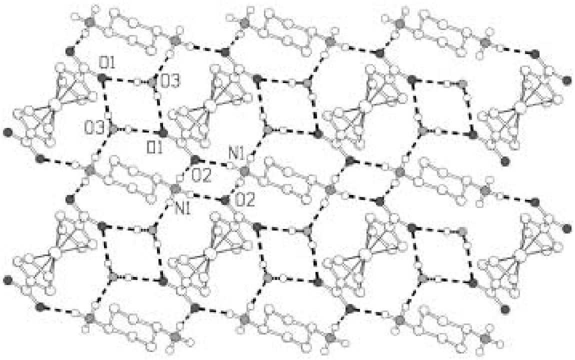

Figure 7. Crystalline **4**·2H_2O contains a dianion [Fe(η^5-C_5H_4COO)$_2$]$^{2-}$, two water molecules, and a fully protonated cyclohexanediamine molecule, with each nitrogen atom capable of donating three hydrogen bonds. The cyclohexanediamine interacts with four surrounding anions through $^{(-)}$O···H–N$^{(+)}$ hydrogen bonds, with the addition of two O···H–N$^{(+)}$ interactions involving the water molecules (H_{CH} atoms not shown for clarity).

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between the X-ray powder diffractogram measured on the ground polycrystalline product **4** and that calculated on the basis of the structure determined by single-crystal X-ray diffraction, **4**$\cdot$2H_2O, is shown in Figure 8.

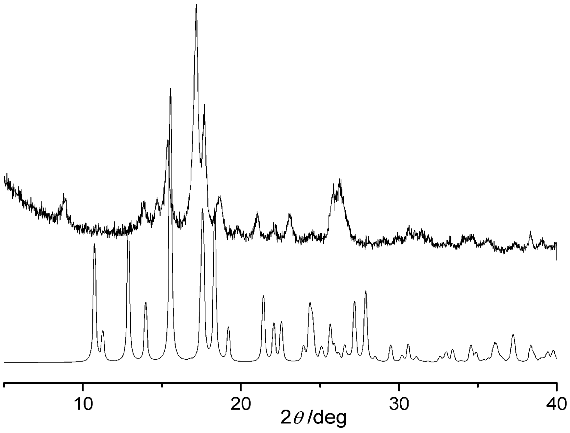

Figure 8. Comparison between (top) the X-ray powder diffractogram measured on a sample of anhydrous **4** obtained by grinding and (bottom) that calculated on the basis of the structure determined by single-crystal X-ray diffraction on **4**$\cdot$2H_2O.

In contrast to the cases discussed thus far, the calculated and observed diffractograms are different, reflecting the fact that the solid–solid grinding process leads to formation of a different product from solution crystallization. As mentioned above, even *seeding* of a solution of **4** in methanol failed to yield the desired single crystals of the anhydrous form **4**; crystallization from solution invariably yielded compound **4**$\cdot$2H_2O, which contains water of crystallization. In fact, a TGA experiment on the grinding product shows that water is not absorbed in the course of the solid–solid reaction upon grinding, but only when **4** is re-crystallized from methanol. It should be noted that, in our experiments, no precaution was taken to avoid hydration of the methanol solution (methanol 99.8%) during the slow evaporation in the air needed to grow single crystals. On the other hand, thermal treatment of **4**$\cdot$2H_2O in a TGA experiment shows that the two water molecules can be removed quantitatively from the lattice: the loss of weight corresponds precisely to two water molecules per formula unit. The powder diffraction pattern after water removal coincides with that of the compound obtained by grinding, that is, compound **4**.

Structure and mechanochemical preparation of $[C(NH_2)_3]_2[Fe(\eta^5\text{-}C_5H_4COO)_2]\cdot 2H_2O$ (5$\cdot$2H_2O): Reaction with solid guanidinium carbonate leads to formation of the hydrated salt $[C(NH_2)_3]_2[Fe(\eta^5\text{-}C_5H_4COO)_2]\cdot 2H_2O$ (**5**$\cdot$2H_2O). Because of the presence of two guanidinium cations the number of hydrogen bonding donor sites is very large (12 potential N–H donors). For this reason and because of the involvement of water, the hydrogen-bonding patterns in crystalline **5** are fairly complicated (see Figure 9). Charge-assisted $^{(-)}O\cdots H{-}N^{(+)}$ hydrogen bonds range between 2.850(5) and 2.972(5) Å. In spite of the complex structure, the same compound is unequivocally formed upon grinding (see Figure 10), as shown by the comparison of the calculated and measured X-ray powder diffractograms.

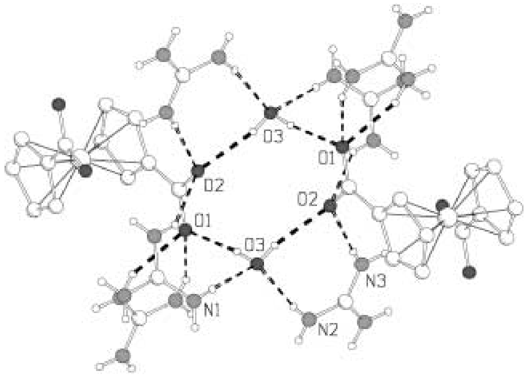

Figure 9. The dianion $[Fe(\eta^5\text{-}C_5H_4COO)_2]^{2-}$, the two water molecules, and two guanidinium cations in crystalline **5**$\cdot$2H_2O form a complex hydrogen-bonding pattern, dominated by charge-assisted $^{(-)}O\cdots H{-}N^{(+)}$ interactions (H_{CH} atoms not shown for clarity).

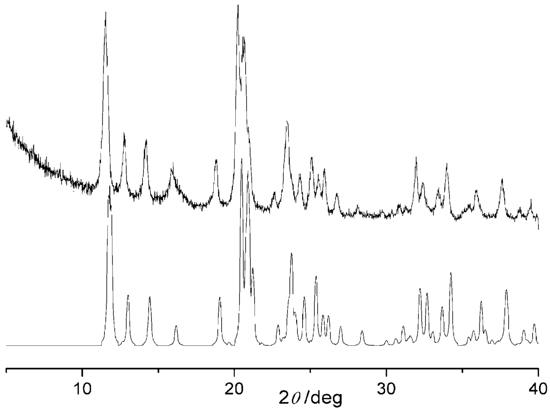

Figure 10. Comparison between (top) the X-ray powder diffractogram measured on a sample of **5**$\cdot$2H_2O obtained by grinding and (bottom) that calculated on the basis of the structure determined by single-crystal X-ray diffraction.

Conclusion

In this study we have shown that new hybrid organic–organometallic materials can be prepared quantitatively in solvent-free mechanochemical reactions. We have explored solid–solid acid–base reactions between a variety of solid bases and the dicarboxylic sandwich compound $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$.

The main outcomes of this study can be summarized as follows:

1) In the cases of the five bases studied herein, the solid-state reaction is quantitative and leads to complete conversion of the starting solid reactants into the products as shown by X-ray powder diffraction.
2) Recrystallization from a solution of the products, obtained via grinding, in methanol assisted by *seeding* with a small amount of the powder material, obtained mechanochemically, leads to single crystals suitable for X-ray diffraction.

3) In the cases of compounds **1**, **2**, **3**, and **5**$\cdot 2H_2O$ there is exact correspondence between the calculated and measured powder diffractograms; hence, the mechanochemical products possess the same structural features as those determined by single-crystal X-ray diffraction.
4) Compound **4** is exceptional since the phases obtained from grinding and from solution are different, the latter containing water molecules of crystallization, **4**$\cdot 2H_2O$, which can be removed quantitatively in a TGA experiment generating the anhydrous phase **4**.
5) The bases 1,4-diazabicyclo[2.2.2]octane and 1,4-phenylenediamine appear to be able to deprotonate the acid only once, thus forming compounds containing the organometallic moiety as a monoanion, namely $[HC_6H_{12}N_2][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ (**1**) and $[HC_6H_8N_2][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ (**2**), whereas the bases piperazine, *trans*-1,4-cyclohexanediamine, and guanidinium carbonate salt fully deprotonate the dicarboxylic acid, leading to compounds containing the organometallic dianion, namely $[H_2C_4H_{10}N_2][Fe(\eta^5\text{-}C_5H_4COO)_2]$ (**3**), $[H_2C_6H_{14}N_2][Fe(\eta^5\text{-}C_5H_4COO)_2]\cdot 2H_2O$ (**4**$\cdot 2H_2O$), and $[C(NH_2)_3]_2[Fe(\eta^5\text{-}C_5H_4COO)_2]\cdot 2H_2O$ (**5**$\cdot 2H_2O$).
6) In terms of supramolecular bonding the difference between **2** and the other compounds is not marginal: in the first two cases interanionic $^{(-)}O{-}H\cdots O^{(-)}$ hydrogen bonding interactions are established, while in the cases of **3**, **4**$\cdot 2H_2O$, and **5**$\cdot 2H_2O$ the organometallic dianion can only interact with the surrounding bases through $^{(-)}O\cdots H{-}N^{(+)}$ hydrogen bonds. In considering these differences, one should keep in mind that the adducts are prepared in the absence of solvent, whilst the p*K* concept and relative acidity scale are based of the extent of proton transfer to solvents; hence, common concepts such as Brønsted acidity cannot be applied *tout court* to acid–base reactions between solids.[20]

The processes discussed herein all require profound molecular rearrangements and take advantage of the conformational freedom of the organometallic building block.

While heterophase gas–solid reactions between acids and bases have been extensively investigated,[21] homophase solid–solid reactions with molecular systems are less popular and, to the best of the authors knowledge, never exploited before in organometallic chemistry. On the other hand, important results have been obtained with heterogeneous solid–gas reactions in the case of coordination complexes.[22]

In the course of a parallel exploratory work of solid–solid processes we have also discovered that the organometallic zwitterion $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ reacts mechanochemically in the solid state with a number of salts, such as KBr, NH_4PF_6, and KPF_6 to yield, through a complex supramolecular rearrangement the supramolecular complexes $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2\cdot C^+A^-$ [$C = K^+, Rb^+, Cs^+, NH_4^+$, $A^- = Cl^-, Br^-, PF_6^-$].[23] These findings, together with those reported in this paper, suggest that organometallic compounds are very versatile reactants for solvent-free mechanochemical reactions. With this awareness, we are now applying mechanochemical methods to obtain heterobimetallic solid systems.

In conclusion, we have shown that acid–base mechanochemistry is a viable alternative to reaction in solution to assemble hydrogen-bonded hybrid materials. The number of applications that can be envisaged in the organometallic and coordination chemistry fields, as well as across all traditional subdivisions of chemistry, is considerable. A useful aspect to consider is that, with respect to crystallization from solution, in mechanochemical reactions crystal formation does not depend on the kinetics of crystal nuclei formation in solution and on solubility. Furthermore, solid–solid processes reduce the formation of solvate species. These are both useful notions in the field of crystal engineering in which the kinetic–thermodynamic dualism always constitutes an intriguing aspect of the processes under investigation or exploitation, and whereby solvate formation is often an uncontrollable and sometimes an undesired consequence of crystallization.

Experimental Section

All the starting materials were purchased from Aldrich and used without further purification. Reagent grade solvents and doubly distilled water were used.

Mechanochemical and solution syntheses of $[HC_6H_{12}N_2][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ (1): $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ (20 mg, 0.073 mmol) and 1,4-diazabicyclo[2.2.2]octane (8.2 mg, 0.073 mmol) were manually ground in an agate mortar for 5 min. Single crystals of **1** suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a solution obtained by dissolving $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ (23 mg, 0.084 mmol) and 1,4-diazabicyclo[2.2.2]octane (9.4 mg, 0.084 mmol) in methanol (99.8 %;3 mL) seeded with the ground sample (5 mg).

Heterophase synthesis of 1: $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ (20 mg) was exposed at room temperature to vapours of 1,4-diazabicyclo[2.2.2]octane, obtained by producing a mild vacuum (water pump, ca. 30–40 mmHg) in the reaction apparatus; after 30 days the diffraction pattern showed peaks of the **1** together with residual peaks of the starting diacid.

Mechanochemical and solution syntheses of $[HC_6H_8N_2][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ (2): $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ (20 mg, 0.073 mmol) and 1,4-phenylenediamine (7.9 mg, 0.073 mmol) were manually ground in an agate mortar for 5 min. Single crystals of **2** suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a solution obtained by dissolving **2** (35 mg) in methanol (99.8 %, 3 mL) seeded with the ground sample (5 mg). The same product was obtained by dissolving $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ (25 mg, 0.091 mmol) and 1,4-phenylenediamine (9.9 mg, 0.091 mmol) in methanol (99.8 %, 3 mL) seeded with the ground sample (5 mg).

Mechanochemical and solution syntheses of $[H_2C_4H_{10}N_2][Fe(\eta^5\text{-}C_5H_4COO)_2]$ (3): $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ (20 mg, 0.073 mmol) and piperazine (6.3 mg, 0.073 mmol) were manually ground in an agata mortar for 5 min. Single crystals of **3** suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution obtained by dissolving **3** in methanol (99.8 %, 3 mL) seeded with the ground sample (5 mg). The same result was obtained by dissolving $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ (25 mg, 0.091mmol) and piperazine (8.7 mg, 0.091 mmol) in methanol (99.8 %, 3 mL) seeded with the ground sample (5 mg).

Mechanochemical synthesis of $[H_2C_6H_{14}N_2][Fe(\eta^5\text{-}C_5H_4COO)_2]$ (4) and solution synthesis of the hydrated form $[H_2C_6H_{14}N_2][Fe(\eta^5\text{-}C_5H_4COO)_2]\cdot 2H_2O$ (4$\cdot$2H$_2$O): $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ (20 mg, 0.073 mmol) and of *trans*-1,4-cyclohexanediamine (8.3 mg, 0.072 mmol) were manually ground in an agata mortar for 5 min, to yield the anhydrous form of compound **4**. Single crystals of **4**$\cdot 2H_2O$ suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution obtained dissolving $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ (20 mg, 0.073 mmol) and *trans*-1,4-cyclohexanediamine (8.3 mg, 0.073 mmol) in methanol (99.8 %,3 mL) seeded with the ground sample (5 mg). Seeding of a solution of **4** also yielded the hydrated form **4**$\cdot 2H_2O$.

No attempt to carry out the crystallization in the absence of humidity was made.

Mechanochemical and solution syntheses of $[C(NH_2)_3]_2[Fe(\eta^5\text{-}C_5H_4COO)_2]\cdot 2H_2O$ ($5\cdot 2H_2O$): $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ (20 mg, 0.073 mmol) and guanidinium carbonate (8.8 mg, 0.072 mmol) were manually ground in an agata mortar for 5 min. Single crystals of **5**$\cdot 2H_2O$ suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution obtained by dissolving $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ (25 mg, 0.091 mmol) and guanidinium carbonate (10.9 mg, 0.091 mmol) in methanol (99.8%, 3 mL) seeded with the ground sample (2 mg). The same result was obtained by recrystallization of **5**$\cdot 2H_2O$ from methanol.

Crystal structure determination: Crystal data of all compounds were collected on a Nonius CAD4 diffractometer. Crystal data and details of measurements are summarized in Table 2. Common to all compounds: $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, monochromator graphite. SHELX97[24a] was used for structure solution and refinement based on F^2. All non-hydrogen atoms were refined anisotropically, except for carbon atoms in **1**. Hydrogen atoms bound to carbon atoms were added in calculated positions. Data were corrected for absorption by azimuthal scanning of high χ reflections. The H_{COOH} and H_{NH} atoms in **1** were found but not refined; in **2**, **3**, **4**$\cdot 2H_2O$ and **5**$\cdot 2H_2O$ all the H_{COOH}, H_{NH}, and H_{water} atoms were found and refined. SCHAKAL99[24b] was used for the graphical representation of the results. The program PLATON[24c] was used to calculate the hydrogen-bonding interactions reported in Table 2. CCDC-191507, CCDC-191508 (**1** and **2**), CCDC-207630–207632 (**3**, **4**$\cdot 2H_2O$, and **5**$\cdot 2H_2O$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

Table 2. Crystal data and details of measurements for compounds **3**, **4**$\cdot 2H_2O$, and **5**$\cdot 2H_2O$.

	3	**4**$\cdot 2H_2O$	**5**$\cdot 2H_2O$
formula	$C_{16}H_{20}FeN_2O_4$	$C_{18}H_{28}FeN_2O_6$	$C_{14}H_{24}FeN_6O_6$
M_r	360.19	424.27	428.24
system	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
a [Å]	5.9833(2)	7.2436(7)	15.948(2)
b [Å]	6.907(19)	7.868(1)	8.550(6)
c [Å]	9.298(3)	8.672(3)	14.404(9)
α [°]	85.05(3)	88.90(2)	90
β [°]	87.09(3)	71.860(15)	109.28(9)
γ [°]	79.58(3)	87.47(1)	90
V [Å^3]	376.3(2)	469.2(2)	1854(3)
Z	1	1	4
$F(000)$	376	224	896
$\mu(Mo_{K\alpha})$ [mm^{-1}]	2.049	0.842	0.858
$2\theta_{max}$ [°]	50	50	60
measured reflns	1385	1771	2795
unique reflns	1300	1652	2696
refined parameters	105	135	146
GOF on F^2	1.113	1.022	0.990
$R1$ [on F, $I > 2\sigma(I)$]	0.0586	0.0321	0.0446
$wR2$(onF^2, all data)	0.1458	0.0882	0.1201

Powder diffraction measurements: Powder diffraction for all samples was measured on a Philips PW-1710 automated diffractometer, $Cu_{K\alpha}$, monochromator graphite, by using quartz sample holders; for the pure reagents 25 mg of substance were employed. The program PowderCell 2.2[23d] was used for calculation of X-ray powder patterns on the basis of the single-crystal structure determinations. Prolonged grinding of the compounds did not alter the diffraction patterns significantly. Grinding of the acid and base in stoichiometric amounts different from 1:1, for example, 2:1 and 1:2, invariably yielded a mixture of phase, whereby the presence of the excess unreacted base or acid could be easily recognized.

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