Organometallics **1996,** *15,* 4675−4677

From Order to Disorder and Return: Remarkable Molecular and Crystal Dynamics in Solid $[(C_5H_5)_2Co][PF_6]$

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Received March 28, 1996[⊗]

Summary: Crystalline $[(C_5H_5)_2Co][PF_6]$ has been shown, by variable-temperature X-ray diffraction experiments (at 293, 243, and 313 K) carried out on the same crystal specimen, to undergo two fully reversible phase changes. The room-temperature ordered monoclinic crystal (form I) transforms, below 252 K, into another ordered monoclinic crystal (form II) with different relative orientation of the two independent $[(C_5H_5)_2Co]^+$ cations and into a semiplastic cubic system (form III) containing ordered PF_6^- anions and orientationally disordered $[(C_5H_5)_2Co]^+$ cations above 314 K.

Organometallic systems showing phase transitional behavior and solid state dynamics[1] are attracting much attention because of the current interest in materials chemistry[2] and supramolecular interactions.[3] Indeed, the change in crystal structure associated with a phase transition, in which intermolecular bonds are broken and formed, is the *crystalline* equivalent of an isomerization at the molecular level. The chemical and physical properties of the crystalline material can change dramatically with the solid-state transformation.

Organometallic systems combine intramolecular structural flexibility (arising from delocalized bonding interactions) with the intermolecular flexibility of molecular crystals.[4] Many crystals of globular organometallic molecules have been shown to form plastic phases at high temperature. Examples are provided by the substituted ferrocene derivatives $[(C_5H_5)(C_5H_4CHO)Fe]$[5a] and $[(C_5H_5)(C_5H_4CMeO)Fe]$[5b] as well as by salts of the type $[(FC_6H_5)(C_5H_5)Fe][A]$ [A = AsF_6, PF_6, SbF_6, and BF_4].[5c] Plastic crystals are characterized by short-range orientational disorder and long-range order, the transition from the ordered phase to a disordered one usually being associated with the onset of reorientational motion of the molecules or ions.[6] This is also the case of crystalline $[(C_5H_5)_2Fe][PF_6]$,[7] which has been shown to undergo a phase transition from a monoclinic crystal to a plastic cubic phase at 347 K.[7b] Both phases have been characterized by single-crystal X-ray diffraction and investigated by ^{2}H NMR and ^{57}Fe Mössbauer techniques.

In this communication, we report our novel findings on the behavior with temperature of crystalline $[(C_5H_5)_2Co][PF_6]$,[8] which, although isomorphous with crystalline $[(C_5H_5)_2Fe][PF_6]$ at room temperature, shows remarkable differences in the phase transitional phenomena. We have discovered that $[(C_5H_5)_2Co][PF_6]$ possesses three crystalline phases within a very narrow temperature interval.[9a] The three crystal phases have been

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[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1996.

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[8] Preparation of crystalline $[(C_5H_5)_2Co][PF_6]$: 100 mg (0.03 mol) of commercial $[(C_5H_5)_2Co]$ (Aldrich) dissolved in acetonitrile was treated with HClaq. From the orange solution, yellow crystals of $[(C_5H_5)_2Co][PF_6]$ were precipitated by adding $[NH_4][PF_6]$. The yellow crystals are stable in the air and in the mother liquor.

[9] (a) Crystal Data. form I: monoclinic, space group $P2_1/c$, a = 13.355(3); b = 9.441(8); c = 9.427(6) Å; β = 92.87(4); V = 1187(1) Å^3; Z = 4, T = 293(2) K; d_c = 1.869 g cm^{-1}; μ = 1.634 mm^{-1}; 2215 reflections measured, refinement on F^2 (2073 independent reflections) for 166 parameters; $wR(F^2$ all) = 0.143, R_1 (1183 reflections with $I > 2\sigma(I)$) = 0.042, S = 1.014. form II: monoclinic, space group $P2_1/c$, a = 13.419(7), b = 9.286(5), c = 9.342(6) Å; β = 96.17(6); V = 1157(1) Å^3; Z = 4, T = 243(2) K; d_c = 1.917 g cm^{-1}; μ = 1.676 mm^{-1}; 2115 reflections measured, refinement on F^2 (2025 independent reflections) for 206 parameters; $wR(F^2$ all) = 0.116, R_1 (1276 reflections with $I > 2\sigma(I)$) = 0.037, S = 1.025. Form III: cubic, space group *Pm-3*; a = 6.72(1) Å; V = 304(1) Å^3; Z = 1, T = 323(2) K, d_c = 1.828 g cm^{-1}, μ = 1.598 mm^{-1}, 317 reflections measured, refinement on F^2 (116 independent reflections) for 15 parameters; $wR(F^2$ all) = 0.284, R_1 (107 reflections with $I > 2\sigma(I)$) = 0.073, S = 1.707. Common parameters: formula: $C_{10}H_{10}CoF_6P$; M = 334.08; crystal size 0.15 × 0.20 × 0.08 mm, $F(000)$ = 664; Mo Kα radiation, λ = 0.710 69 Å; monochromator graphite; θ-range 2.0−25.0°. The computer programs SHELX86 (Sheldrick, G. M. *Acta Crystallogr.*, **1990**, *A46*, 467) and SHELX93 (Sheldrick, G. M. *Program for Crystal Structure Determination*; University of Gottingen, Göttingen, Germany, 1993) were used for structure solution and refinement. All atoms except the hydrogen atoms were treated anisotropically. Hydrogen atoms were added in calculated position in form I and refined riding on their respective C atoms, while in form II they were found in difference Fourier maps and refined. In form III, 24 positions for the C atoms were generated by symmetry from the three found independent positions; therefore, the occupancy factors of the C atoms were set to the values giving the electron density corresponding to 10 C atoms. For all molecular representations, the graphic program SCHAKAL93 (Keller, E. *Graphical Representation of Molecular Models*, University of Freiburg, Germany, 1993) was used. (b) The reversibility of the two phase transitions was confirmed by collecting other data sets at 293 and 313 K on the same crystal specimen discussed herein as well as at 223, 293, and 313 K on another two crystal specimens taken from the same preparation batch. A detailed comparison of these results will be given in a future report. (c) F···H separations were evaluated on C−H bonds normalized to 1.08 Å; seven bonds shorter than 2.60 Å are present in both form I (three <2.45 Å), and form II (five <2.45 Å). F···H bonds were not evaluated in the disordered form III.

S0276-7333(96)00242-7 CCC: $12.00

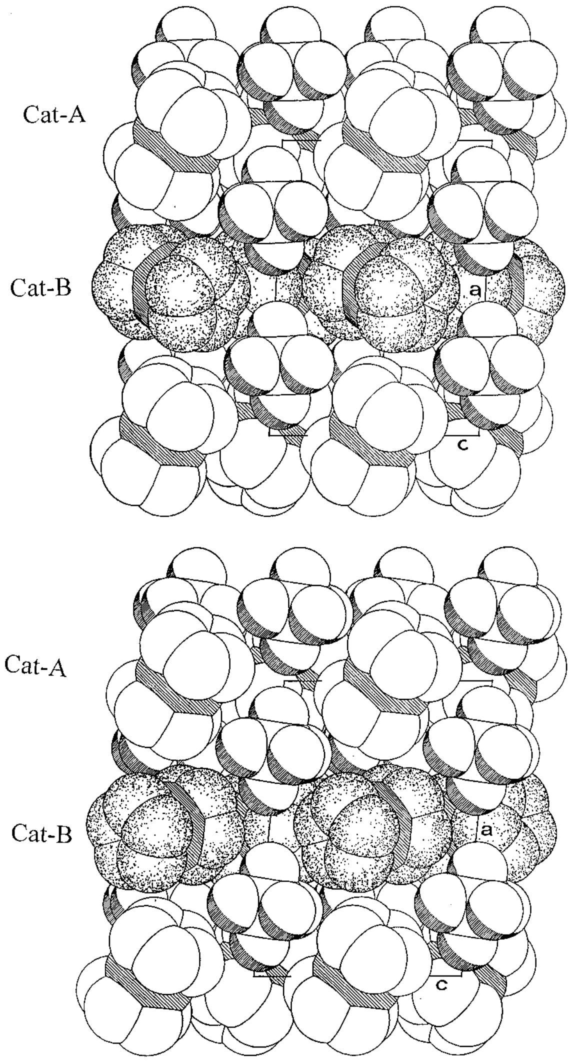

Figure 1. Molecular arrangement in the (a) room-temperature (form I) and in the (b) low-temperature (form II) phases: space-filling view in the *ac*-plane. H atoms are omitted for clarity.

fully characterized by single-crystal X-ray diffraction at variable temperature on the same crystal.[9b] Our results can be summarized as follows:

(i) The room-temperature crystal of $[(C_5H_5)_2Co][PF_6]$ (form I) is isomorphous with that of monoclinic $[(C_5H_5)_2Fe][PF_6]$.[7] The monoclinic $P2_1/c$ cell contains one PF_6^- anion in general position and two independent half-cations located on crystallographic centers of inversion.

(ii) Form I ⇔ form II transformation: when the crystal of $[(C_5H_5)_2Co][PF_6]$ is cooled at 243 K, a phase change occurs leading from the room-temperature $P2_1/c$ monoclinic cell (form I) to another $P2_1/c$ monoclinic cell (form II) with a different β-angle [92.87(3) and 96.17(1)° for form I and form II, respectively] and slightly different unit cell axes. On passing through the phase transition, the *b*- and *c*-axes shorten with respect to the room-temperature cell, while the *a*-axis lengthens. Comparative views of the two crystal structures are shown in Figures 1 and 2. The form I ⇔ form II transformation is accompanied by a change in cell volume from 1187 to 1157 Å^3 and by a change in packing coefficient from 0.67 to 0.69.[10]

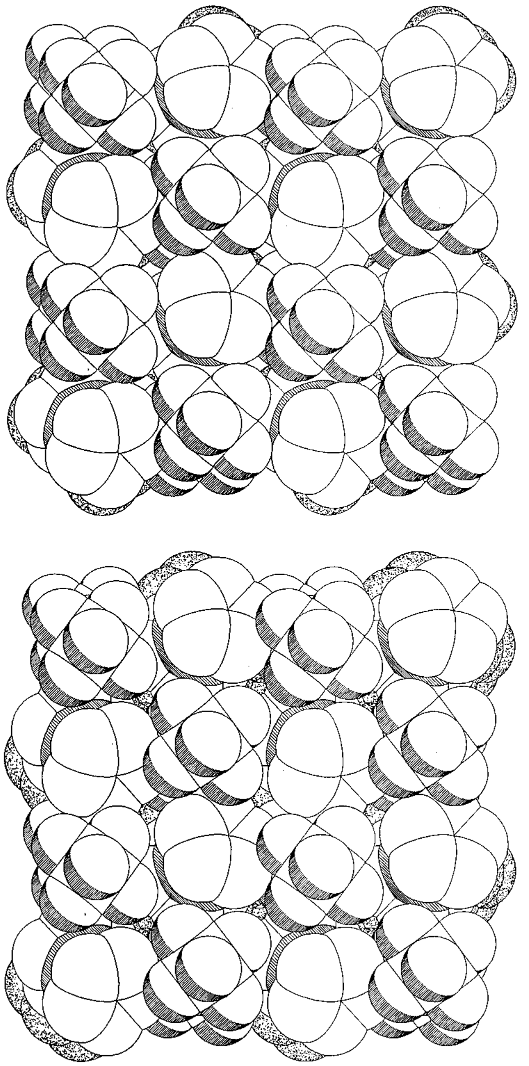

Figure 2. Space-filling view of (a) form I and (b) form II in the *bc*-plane.

(iii) The form I ⇔ form II phase transition is fully reversible, and the relationship between the two crystal structures is simple to depict. Let us first distinguish between those cations with the molecular axes almost parallel to the *a*-axis (cat-A) and those cations with the molecular axes almost perpendicular to the *a*-axis (cat-B) (see Figure 1). On passing (ideally) from form II to form I, cat-A and cat-B change from a staggered (in projection) to an eclipsed juxtaposition along the *a*-axis (see Figure 3). Whether this model bears any relationship with the actual phase transition mechanism is difficult to assess only from diffraction data. However, it is interesting to note that, since the centers of mass of the cations do not move, the transformation only requires the Cp ligands to slide to their new positions while the PF_6^- anions "give way".

(iv) Form II ⇔ form III transformation: the crystal undergoes a second phase transition to a *semi*disordered cubic crystal above 314 K. The high-temperature phase (form III) measured at 323 K shows *fully ordered anions* (Figure 4) and *orientationally disordered cations*, thus differing from the high-temperature plastic phase of the Fe complex with both anions and cations orientationally disordered. In this respect, form III can be defined as *semiplastic*, since only one component (the cation) appears to have lost short-range ordering. As in the

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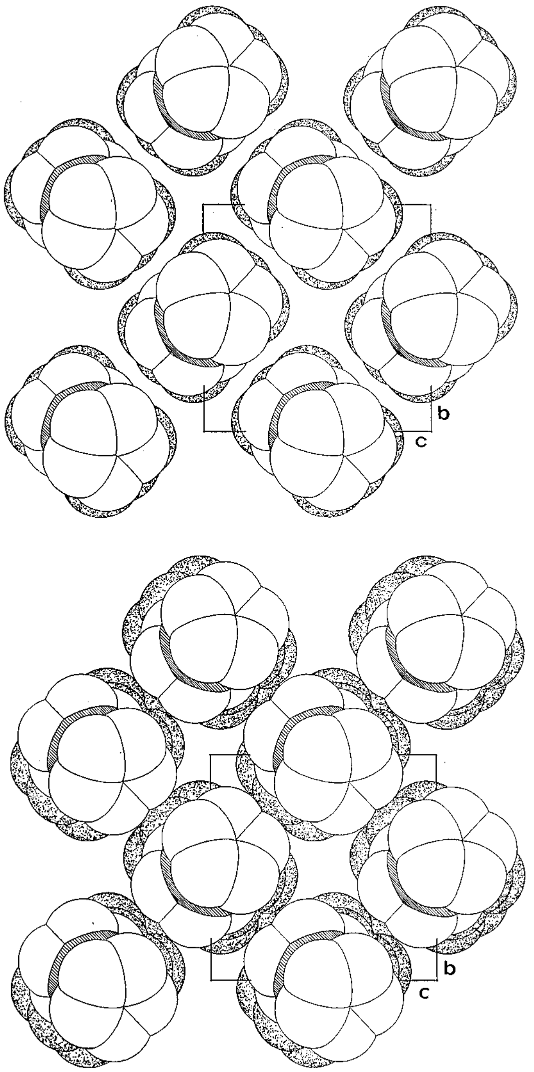

Figure 3. The same molecular representation as in Figure 2 after removing the PF_6^- anions: note the eclipsing of cat-A and cat-B in form I (a) and the staggering of cat-A and cat-B in form II (b).

case of the form I ⇔ form II transformation, the form I ⇔ form III transition is also fully reversible.

(v) In both form I and form II there is an intricate network of C−H···F hydrogen-bonding interactions between the C_5H_5 ligands and the PF_6^- anions, the shortest F···H separations falling in the range 2.41−2.45 Å.[9c]

(vi) Both transitions are clearly observed in DSC thermograms showing two endothermic peaks at 252 and at 314 K.[11] The enthalpy differences associated with the two transitions are 1.30 and 3.05 kJ mol^{-1} for the form II ⇔ form I and form I ⇔ form III phase transitions, respectively. These values fall within the range observed for most polymorphic organic crystals.[12]

In summary, crystalline $[(C_5H_5)_2Co][PF_6]$ behaves as a remarkable "crystal switch" between three phases. The crystalline material is particularly robust so that diffraction data could be collected across the three phase changes on the same crystal specimen. The low-temperature transformation is *between two ordered crystals* with similar unit cells but with very different ion arrangements, whereas the high-temperature transformation leads to a semiplastic phase in which the cation is orientationally disordered within an ordered anion cage. Most importantly, the two transformations are fully reversible.

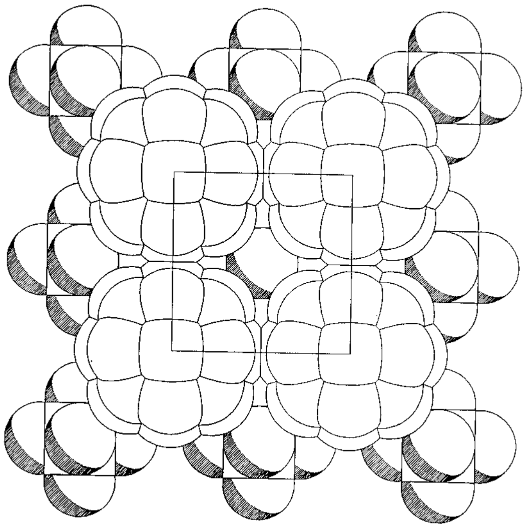

Figure 4. High-temperature cubic phase (form III) of crystalline $[(C_5H_5)_2Co][PF_6]$: space-filling representation along a cell axis. Note how the crystal is constituted of fully ordered anions and orientationally disordered cations.

In the near future we plan to fully characterize the dynamical processess in crystalline $[(C_5H_5)_2Co][PF_6]$ by means of solid-state NMR techniques. We will also investigate in detail the relationship between the crystals of the iron and cobalt salts in terms of C−H···F hydrogen-bonding interactions. These bonds, though weaker than the conventional O−H···O type hydrogen bonds, are of comparable length (hence, most likely, strength) with respect to the C−H···O interactions which have been demonstrated to play a crucial role in organometallic crystals[13] and have now begun to be used in crystal synthesis.[14]

Acknowledgment. D.B. and S.M.D. gratefully acknowledge Ciba-Geigy for an ACE fellowship and the ERASMUS exchange program "Crystallography" for financing L.S. Dr. G. Cojazzi is thanked for her invaluable help with the DSC measurements. Dr. E. Marseglia and Prof. A. Gavezzotti are thanked for helpful discussions. Financial support from the University of Bologna, Project "Intelligent Molecules and Molecular Aggregates (D.B. and F.G.), is acknowledged.

Supporting Information Available: Tables of anisotropic thermal parameters and fractional atomic coordinates, complete list of bond lengths and angles, and DSC thermograms for forms I and II (14 pages). Ordering information is given on any current masthead page.

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[11] DSC thermograms were measured on a Perkin-Elmer DSC-7 in sealed Al pans; 5.150 mg of crystals was taken from the same crystal batch used for the diffraction experiments. The repeated cycles of cooling and heating (scanning rate 5.0 deg/min) had histereses of 12.7 and 4.5 K, for the form I ⇔ form II and the form I ⇔ form III transitions, respectively.

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