

# Thermal Transformations and Stability of Organometallic Materials with Electrical and Optical Properties: The Case of Polycrystalline *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)]

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Received: May 20, 2004; In Final Form: October 29, 2004

In this paper the solid-state transformations under heating of *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)] are discussed. The complexity of the transformations was revealed by integrating infrared spectroscopy, conventional and bidimensional X-ray diffraction, thermal analysis, and hot stage optical microscopy. During heating anisotropic expansion of the lattice along the Ir–Ir stacking takes place. Then *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)] undergoes an irreversible solid–solid phase transition to a lattice of higher symmetry followed by a reversible transition into the amorphous phase. Under proper cooling a partial recrystallization takes place. Experiments in the presence of oxygen must be carried out in short time periods to avoid oxidation from Ir(I) to Ir(III).

## Introduction

Organometallic compounds are gaining increasing interest in material science because they may display interesting optoelectronic properties which make them candidates for the development of new nanomaterials for microelectronic and optoelectronic devices.<sup>1</sup> Square planar Ir(I) complexes have been particularly investigated. With the aim of designing organometallic molecules with significant second-order nonlinear optical properties, work has been recently devoted to determination of the role of the Ir(I) center in the increase of the quadratic hyperpolarizability of Ir(I)-coordinated organic “push–pull” ligands such as *para*-substituted pyridines and stilbazoles.<sup>2</sup> Moreover, square planar iridium(I) carbonyl complexes have been extensively investigated in the past as materials with anisotropic electrical properties originated by the stacking of strong Ir–Ir interactions in their crystalline structures.<sup>3–5</sup> Recently, we have initiated an investigation on the anisotropic electrical behavior of layers of microcrystalline pyridine iridium(I) carbonyl complexes, in particular of *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)]. X-ray microdiffraction investigations seem to indicate that thin layers of this compound, deposited in air at 80 °C from CH<sub>3</sub>CN solution, exhibit a crystalline structure quite different from that of the polycrystalline starting material.<sup>6</sup>

Compared with inorganic or even polymeric organic materials, the drawbacks of organometallic materials are their moderate chemical and thermal stability. Indeed, thin layer deposition is a common process, often performed at relatively high temperatures, and thus, the preliminary knowledge of the polycrystalline material chemical stability and thermal structural changes during the process of deposition is mandatory. However, even if there is a major demand for their processability, few papers in the literature report detailed studies on microstructural and

chemical behavior under heating of polycrystalline organometallic compounds.<sup>7</sup>

In this work we have shown that understanding the structural changes associated with the solid-state transformations of organometallic compounds can be successfully achieved by integrating different investigation techniques. In addition we have pointed out that care must be taken in the control of the experimental conditions since some chemical transformations can occur in parallel with structural changes.

We studied microstructural changes upon increasing temperature of polycrystalline *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)], whose X-ray structure is known,<sup>8</sup> by hot stage optical microscopy (HSM), thermal analysis (differential scanning calorimetry, DSC, and thermogravimetric analysis, TGA), temperature-resolved X-ray diffraction (XRD) and microdiffraction (XRD<sup>2</sup>), and, finally, infrared (IR) spectroscopy.

## Experimental Section

**Synthesis of *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)].** An acetonitrile solution of [Ir(CO)<sub>2</sub>Cl]<sub>2</sub>, obtained from [Ir(cyclooctene)<sub>2</sub>Cl]<sub>2</sub>, is a very convenient starting material for the synthesis of various iridium(I) carbonyl compounds.<sup>9</sup> Therefore, this methodology has been used to synthesize *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)]. Through a suspension of [Ir(cyclooctene)<sub>2</sub>Cl]<sub>2</sub> (150 mg, 0.168 mmol) in CH<sub>3</sub>CN (30 mL) under a nitrogen atmosphere, CO was bubbled till a yellow solution was obtained (2–3 min); then pyridine (0.5 mL) (molar ratio Ir:pyridine = 1:18) was added. After 5 min at room temperature, the reaction mixture was evacuated (10<sup>–2</sup> Torr) to remove the solvent and the excess pyridine, affording the black crystalline complex (99% yield). Anal. Calcd for *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)]: C, 23.16; H, 1.38; N, 3.86; O, 8.82. Found: C, 23.39; H, 1.45; N, 3.80; O, 8.11.

**Physicochemical and X-ray Diffraction Experiments.** HSM with polarized light was carried out on a few crystals of *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)] placed into an open quartz crucible and heated at a rate of 10 °C/min to a final temperature of 80 °C, working either in air or under a commercial nitrogen atmosphere.

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TGA was performed under a commercial nitrogen purge at a rate of 25 mL/min on a Perkin-Elmer Pyris 1. The samples were placed into aluminum pans, inserted into the TGA furnace, and heated at a rate of 10 °C/min from ambient temperature up to 150 °C.

DSC data were collected, under commercial nitrogen as above, using a Perkin-Elmer Pyris 1. The samples, aluminum pans containing about 3 mg of compound, were scanned at a rate of 10 °C/min to the final temperature of 90 °C. Cooling was carried out with the same rate, or with a rate of 1 °C/min.

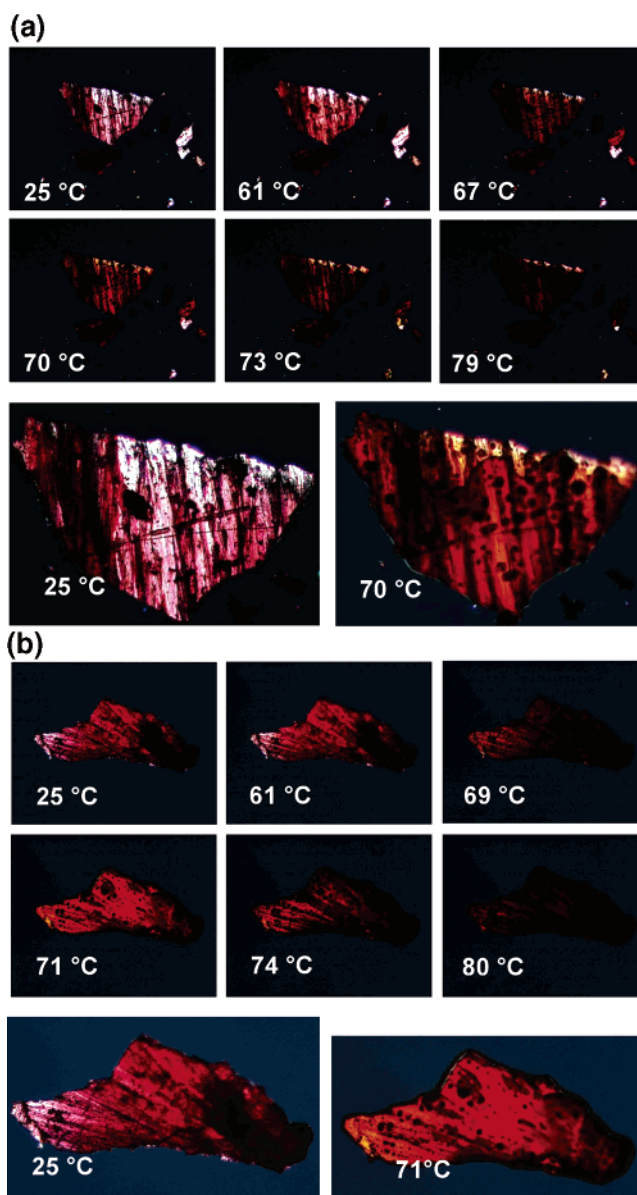
X-ray diffraction experiments were performed with a Rigaku D-Max rapid microdiffractometer and a  $\theta/\theta$  Bruker D8 Advance diffractometer. The microdiffractometer is equipped with a two-dimensional detector, allowing the instantaneous collection of the diffraction Debye rings (a technique generally referred to as XRD<sup>2</sup>). The temperature-resolved XRD diffraction patterns were collected in air with the  $\theta/\theta$  diffractometer, and the temperature, with an increase of 10 °C/min, was controlled with a Linkam furnace. Cell parameter refinements and XRD pattern simulations were performed by means of the Accelerlys software Materials Studio.<sup>10</sup>

Reflectance IR spectra were collected on pressed pellets working with a Biorad FTS6000 instrument on samples thermally treated under nitrogen totally purified from oxygen traces or in air.

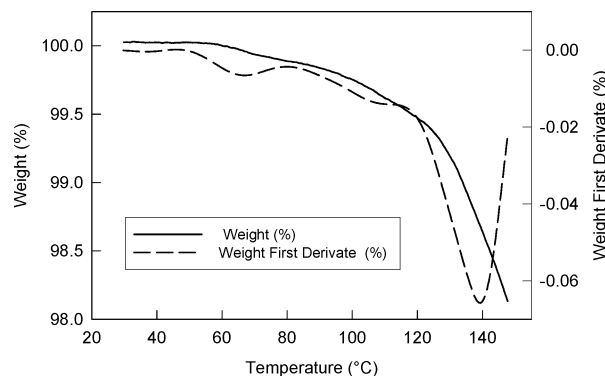
**Thermal Treatment of *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)].** Thermal treatment under ultrapure nitrogen of a sample of *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)] at 80 °C for 5 h did not produce any change in both elemental analysis and the IR spectrum as a pressed pellet, suggesting that the complex is stable under these conditions. On the contrary, when the thermal treatment was carried out in air at 80 °C for 5 h, both elemental analysis and the IR spectrum were quite different from those of the freshly prepared *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)]. Anal. Found: C, 20.20; H, 1.52; N, 3.66; O, 9.23. Compare Anal. Calcd for *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)]: C, 23.41; H, 1.42; N, 3.85; O, 8.23. Reflection IR spectrum as a pressed pellet:  $\nu_{\text{CO}}$  of the points of inflection, 2112, 2083, and 2056 cm<sup>-1</sup>, against 2066 and 2006 cm<sup>-1</sup> of *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)] (see the Results and Discussion).

## Results and Discussion

Several experiments were initially conducted with polarized-light HSM, providing preliminary data to gain some insight into the thermal behavior of polycrystalline *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)]. Transmission of polarized light by a material is closely related to its microstructure.<sup>11</sup> In Figure 1a the photographic sequences referring to polycrystalline *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)] grains heated from 25 to 80 °C in about 6–7 min working in open air are shown. Above 67 °C, the darkening of the crystals, which indicates that some structural or chemical transformation occurs, is accompanied by the appearance of black spots clustered along the fracture lines. These spots may be bubbles due to CO or CO<sub>2</sub> emission, or/and nucleation seeds of a new phase. The same HSM experiment, but under a flux of commercial nitrogen, was then performed (Figure 1b). Here the clear-cut color changes with temperature (darkening/lightening/darkening) evidence, better than in open air, three possible transformations. The first below 69 °C, the second between 69 and 71 °C, and the third between 71 and 80 °C. Also in this case some black spots appear. At the end of all the HSM experiments the grains retained the same shape that they had at the beginning, but they always look darker, thus suggesting a global solid–solid phase transition toward a microstructure characterized by lower crystallinity.

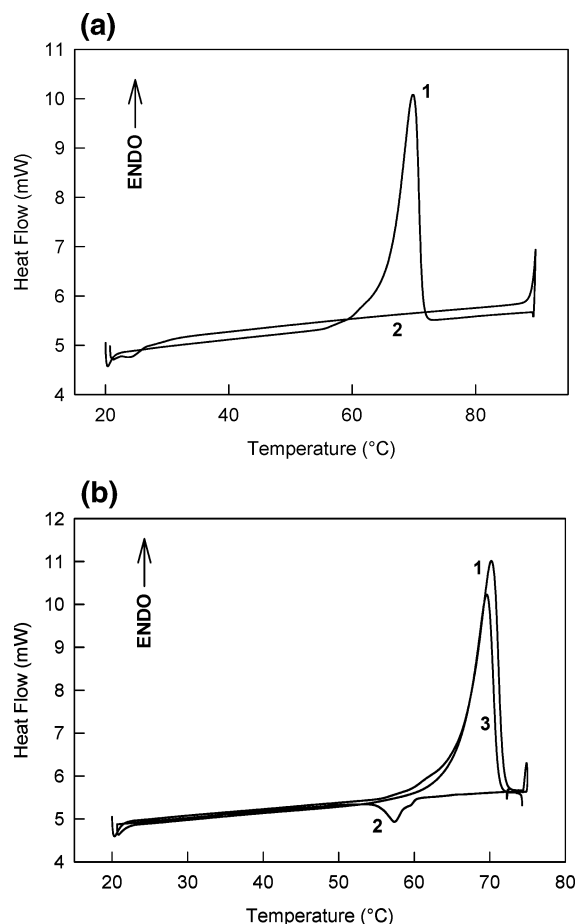


**Figure 1.** Polarized-light HSM in open air (a) and under commercial nitrogen flux (b) of polycrystalline grains of *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)]. The more significant images have also been magnified.



**Figure 2.** TGA profile (continuous line and left ordinate axis) and its first derivative (dashed line and right ordinate axis) of *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)].

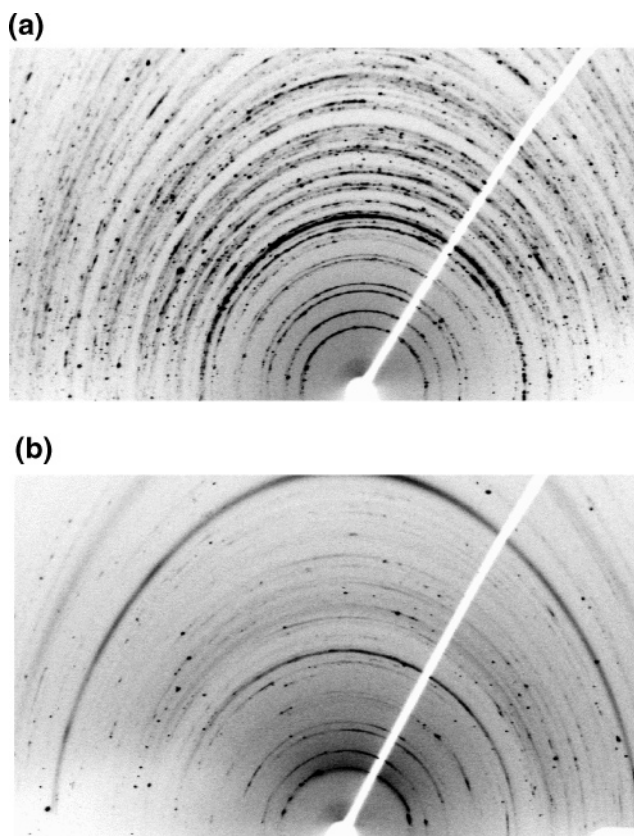
The TGA profile under commercial nitrogen of the polycrystalline material and its first derivative are shown in Figure 2 by the continuous and the dashed lines, respectively. They evidence a very small weight loss spread over temperatures



**Figure 3.** (a) DSC profile of *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)] performed at a rate of 10 °C/min: 1, heating run; 2, cooling run. (b) DSC profile of *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)], heating/cooling/heating cycle performed at different rates, 10 °C/min heating and 1 °C/min cooling: 1, first heating run; 2, cooling run; 3, second heating run.

spanning from 40 to 147 °C. In particular, the TGA differential profile shows the maximum loss (ca. 0.15%) between 47 and 80 °C, which however is not localized enough to be directly linked to one of the thermal transformations observed by HSM. This latter evidence suggests that the black spots, observed both in air and in commercial nitrogen HSM microphotographs, are not bubbles due to CO or CO<sub>2</sub> emission, but probably seeds of nucleation of a new phase.

In Figure 3a the DSC profile of a heating/cooling cycle performed in nitrogen at a rate of 10 °C/min is shown, while in Figure 3b is shown a heating/cooling/heating cycle performed in nitrogen at different rates: 10 °C/min heating and 1 °C/min cooling. The first information that can be drawn is that the upper threshold of the cooling rate that allows the material to recrystallize in the temperature range between ambient temperature and the temperature of the last endothermic transition is 10 °C/min. Actually, the cooling branch (2) of the DSC profile of Figure 3a is smooth until about 25 °C, indicating that no thermal transformation occurs. Below 25 °C a weak and incomplete exothermic signal appears. On the other hand, in the cooling branch (2) of Figure 3b a structured exothermic event at about 58 °C is present, producing certain evidence that a complete crystallization has occurred. In both parts a and b of Figure the branch of the first heating run (1) shows two distinct endothermic events, a smaller one around 62 °C and one at 70.17 °C. However, the profile of the second heating run (branch 3 in Figure 3b), performed after recrystallization, shows a single endothermic event at 69.57 °C. This suggests that the event at



**Figure 4.** XRD<sup>2</sup> images of an as-prepared sample of polycrystalline *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)] (a) and of the same sample which after 3 min of thermal treatment at 74 °C was allowed to freely cool in open air (b).

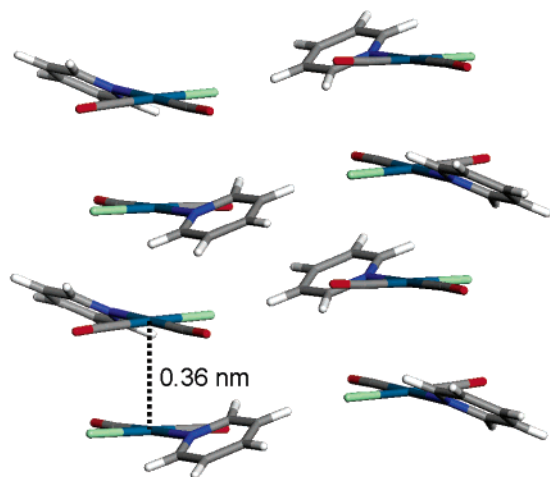
62 °C is an irreversible process, while the thermal event at 70.17 °C identifies a reversible transition. At the second heating run this latter transition occurs at a slightly lower temperature and with a remarkably lower enthalpy (36.647 J/g with respect to 49.223 J/g to the first heating run). This means that recrystallization yields a less ordered material.

XRD<sup>2</sup> transmission images are reported in Figure 4. The top image (Figure 4a) refers to a sample of polycrystalline *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)] as prepared, while the bottom image (Figure 4b) refers to the same sample which after 3 min of thermal treatment in air at 74 °C was allowed to freely cool. The radii of the Debye rings of the two images coincide, indicating the same crystallographic phase. In other words, after the thermal treatment the sample recrystallizes. However, as the recrystallized sample presents rare and faint spots, we can conclude that the sample partially recrystallizes and ends up with a less ordered microstructure, in agreement with DSC experiments.

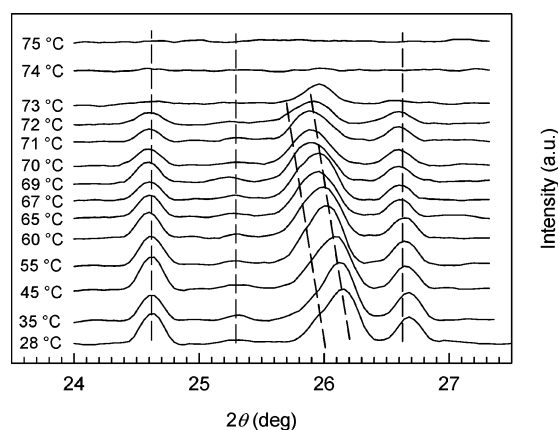
The XRD spectra correspond to the crystal structure of *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)] reported by Jeter et al.<sup>8</sup> and shown in Figure 5. The cell parameters are  $a = 17.58$  Å,  $b = 7.16$  Å,  $c = 11.65$  Å, and  $\beta = 142.9^\circ$ . In this structure, while maintaining a nearly stacked and linear arrangement of the Ir–Ir chain, the interlayering of the tilted pyridine rings determines a larger Ir–Ir distance (0.36 nm) with respect to other iridium(I) carbonyl compounds.<sup>4</sup>

The in situ temperature-resolved powder XRD experiments are given in Figure 6, where the XRD patterns collected from 24° to 28° ( $2\theta$  scale) are shown. The samples have been kept at each temperature for 2 min, a compromise time for allowing satisfactory data collection and following the structural transitions. The temperature evolution of the diffraction pattern is





**Figure 5.** Crystallographic molecular packing of *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)]. The Ir–Ir chain distance is evidenced.

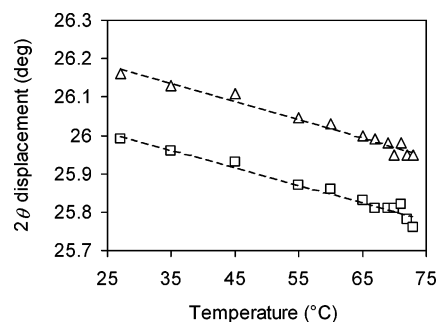


**Figure 6.** In situ XRD patterns collected from  $2\theta = 24^\circ$  to  $2\theta = 28^\circ$  at the temperatures indicated at the right side of the figure. The evolution of the diffraction peak positions with temperature is indicated by the dashed lines.

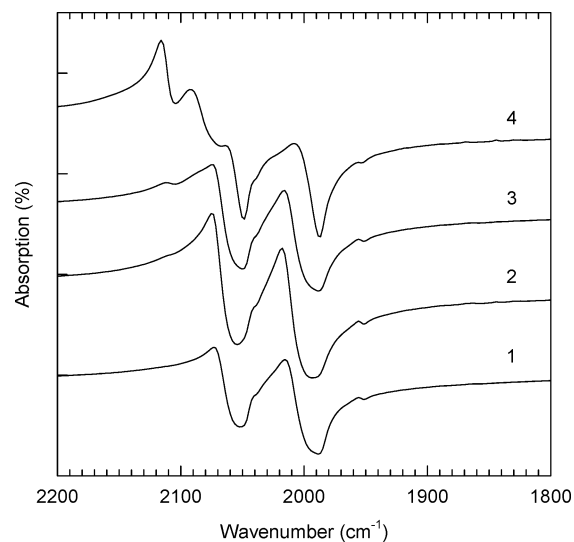
characterized by the gradual shifting of the peaks at  $25.99^\circ$  and at  $26.16^\circ$  toward lower angles (e.g., larger interplanar distances), while the positions of peaks at  $24.60^\circ$ ,  $25.28^\circ$ , and  $26.66^\circ$  do not change during the thermal treatment. At about  $73^\circ\text{C}$  the three fixed peaks disappear, and those at  $25.99^\circ$  and  $26.16^\circ$  converge to a single one at about  $26^\circ$ . Finally, at  $74^\circ\text{C}$  all peaks disappear, thus suggesting that the crystalline structure turns to amorphous.

Even if the refinement of the cell parameters is not possible because of the limited number of diffraction peaks, the XRD patterns shown in Figure 6 can be simulated from the crystal structure of *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)] by only changing the *b* axis. Thus, appreciable thermal expansion occurs only along *b*, and the thermal expansion coefficients (TECs) of the crystals are anisotropic along the different crystallographic axes. Figure 7 shows in detail the temperature variation of the peak positions related to the thermal expansion along this axis, which corresponds to the Ir–Ir chain direction. The plot evidences an almost linear temperature evolution. The linear TEC, evaluated from 20 to  $72^\circ\text{C}$ , is  $2.15 \times 10^{-4}^\circ\text{C}^{-1}$ , corresponding to an enlargement of the *b* axis from 7.16 to 7.24 Å. This result suggests that the interactions between Ir atoms along the chain are quite weak, consistently with the relatively large Ir–Ir distance.<sup>8</sup>

In view of the HSM observations, in particular those obtained from the darkening/lightening/darkening sequence of Figure 1b, the pattern at  $73^\circ\text{C}$  may be attributed to a new phase with a



**Figure 7.**  $2\theta$  displacement of peaks at  $25.99^\circ$  and at  $26.16^\circ$ . This corresponds to an enlargement of the *b* axis (i.e., along the Ir–Ir chain) from 7.16 to 7.24 Å.



**Figure 8.** Reflectance IR spectra of pressed pellets of *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)] collected under different conditions: 1, at ambient temperature in air; 2, after 15 min of thermal treatment at  $80^\circ\text{C}$  in air; 3, after 5 h of thermal treatment at  $80^\circ\text{C}$  under extrapure nitrogen; 4, after 5 h of thermal treatment at  $80^\circ\text{C}$  in air. The spectra have been shifted and scaled on the ordinate axes for clarity.

higher symmetry with respect to the original structure. Unfortunately, diffraction data are not sufficient to refine the cell parameters and define the structure of this phase.

To verify the chemical stability of *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)] upon heating conditions, IR spectroscopic experiments and elemental analysis were performed. In particular, we studied the reflectance IR spectra of pressed pellets of *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)] as a crystalline material and as powder samples of the original material maintained at  $80^\circ\text{C}$  both in air and under nitrogen. The IR spectrum at ambient temperature of a pressed pellet of crystalline *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)] (Figure 8, line 1) shows two bands typical for *cis*-dicarbonyl species, whose points of inflection are at 2066 and  $2006\text{ cm}^{-1}$ . The same spectrum of the pressed pellet was observed after the crystalline material was heated at  $80^\circ\text{C}$  under extrapure nitrogen for 5 h (Figure 8, line 3). The absence of a process of CO emission under these conditions, suggested by the above IR evidence, was confirmed by elemental analysis.

However, a very slow oxidation reaction takes place in air and even under commercial nitrogen (containing small amounts of oxygen). Significant changes appear in the IR spectra of pressed pellets of crystalline *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)] maintained at  $80^\circ\text{C}$  for 5 h (Figure 8, line 4). In particular, a new strong inflection peak at  $2112\text{ cm}^{-1}$  occurs, together with two minor inflection peaks at 2083 and  $2056\text{ cm}^{-1}$ . These changes in the IR spectrum would suggest an oxidation to an Ir(III) species

with gas evolution,<sup>12</sup> as confirmed by elemental analysis (see the Experimental Section).

If the heating at 80 °C is limited to 15 min, the reflectance IR spectrum of the pellet remains unchanged not only under commercial nitrogen but even in air (Figure 8, line 2). It follows thus that a very slow chemical transformation corresponding to an oxidation process occurs, but it seems to be irrelevant if experiments are carried out in a few minutes (in agreement with the very small weight loss evidenced by the TGA profile under commercial nitrogen).

Therefore, experiments carried out in air and under commercial nitrogen in about or less than 15 min can be compared and are related only to physical transformations.

With this in mind, temperature-resolved XRD measurements add structural insight into the thermal events that occur in crystalline *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)] during quick heating. The birefringence change due to anisotropic thermal expansion of the lattice (first darkening observed in HSM microphotographs) is followed by a fast rearrangement of the crystalline structure into a phase of higher symmetry (first, and irreversible, phase transformation corresponding to the lightening observed in HSM microphotographs) which subsequently undergoes a solid–solid phase transition and becomes amorphous (second, and reversible, phase transformation, definitive darkening observed in HSM microphotographs).

## Conclusions

The solid-state transformations upon heating of *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)] have been studied by combining complementary techniques which allowed some light to be shed on a complex solid-state process. It was found that during quick heating polycrystalline *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)] experiences an anisotropic thermal expansion of the lattice along the Ir–Ir chain, followed by a fast, irreversible rearrangement at about

73 °C into a phase of higher symmetry which subsequently undergoes at about 74 °C a reversible solid–solid phase transition and becomes amorphous. If the compound is immediately and properly cooled, a partial recrystallization takes place, accompanied by significant microstructural changes.

In addition, we have shown that, especially with organometallic crystalline materials, particular care must be taken of possible chemical transformations which can be switched by thermal treatments and therefore influence the chemical stability of the material during temperature-resolved experiments. In the particular case of *cis*-[Ir(CO)<sub>2</sub>Cl(C<sub>5</sub>H<sub>5</sub>N)] some oxidation occurs, which however is slow enough to allow physicochemical and spectroscopic experiments of 10–15 min to be carried out without introducing factors due to this chemical instability.

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