Ab Initio XRPD Structure Determination of Organometallic Compounds: The Case of Pd(Phen)(C(O)N(Me)OC(O)), a Model Intermediate in the Palladium−Phenanthroline-Catalyzed Reductive Carbonylation of Aromatic Nitro Compounds

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Received September 26, 1997

In the absence of suitable single crystals, the problem of determining the connectivity pattern of the title compound (and of its phenyl analogue), i.e. that of discriminating between two markedly different stereoisomers, has been solved by the powder diffraction technique. The structure of Pd(Phen)(C(O)N(Me)OC(O)) was solved by *ab initio* XRPD methods and refined by the Rietveld technique down to $R_{wp} = 0.123$, $R_p = 0.087$, and $R_F = 0.061$ for 5000 data points (847 reflections) collected in the $8 < 2\theta < 108°$ range. The diffraction results have been cross-validated by steric energy computations within the field of the given crystal lattice.

Introduction

In the last 25 years, the catalytic reductive carbonylation of organic nitro compounds has become a very intense field of research.[1] This is due to the fact that a series of industrially important compounds can be obtained from nitro compounds and carbon monoxide in a single step. Among the most important products that can be obtained by this route, ureas and carbamates are final products and intermediates in the synthesis of fertilizers and pesticides. On the other hand, mono- and diisocyanates are very important intermediates in the manufacture of pesticides, polyurethane foam plastics, synthetic leather, adhesives, and coating.

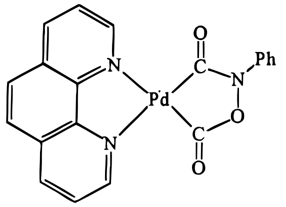
The classical method for carrying out the synthesis of isocyanates includes the intermediate catalytic hydrogenation of the nitro compounds, and subsequent reaction of the product aniline with phosgene. However, phosgene is an energy-intensive material, very poisonous and corrosive, and much effort has been devoted to find more environmentally friendly alternatives. One such process involves reductive carbonylation of the nitro compounds by reaction with carbon monoxide (eq 1).

The reaction can also be performed in the presence of an alcohol, affording directly a carbamate (eq 2).

$$RNO_2 + 3CO \rightarrow RNCO + 2CO_2 \qquad (1)$$

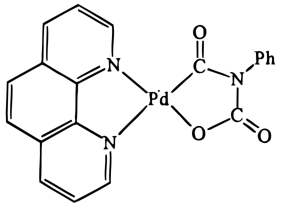
$$RNO_2 + R'OH + 3CO \rightarrow RNHCOOR' + 2CO_2 \qquad (2)$$

Among the catalytic systems able to catalyze reactions 1 and 2, the one which appears to be most promising from the point of view of the possible industrial application is based on the use of palladium−phenanthroline complexes, possibly in the presence of acidic promoters.[2,3] Despite much recent effort in studying this catalytic system, its mechanism is still poorly understood. A significant advancement in this respect is represented by the isolation of a plausible reaction intermediate (**1**).[3] On the basis of analytical and spectroscopic data, the following structure was proposed for the isolated complex:



(A)

Although the general characteristics of this structure seems to be indisputable, another structure in which the orientation of the "CO_2" fragment of the metallacycle is reversed



(B)

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(1) Cenini, S.; Ragaini, F. *Catalytic Reductive Carbonylation of Organic Nitro Compounds*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1997.

S0276-7333(97)00843-1 CCC: $15.00

is also consistent with the reported spectroscopic data. Structure **B** appears a priori as more plausible based on the fact that all the structurally characterized complexes containing a metallacycle composed at least in part by the $-N(R)(CO_2)-$ fragment have the CO_2 carbon atom bound to nitrogen, whereas the oxygen atom binds to the metal.[4,5] A ruthenium complex containing a metallacycle composed by the “PhNCO” and “CO_2” fragments has also been more recently characterized by X-ray crystallography and shown to have a structure corresponding to **B**.[6] To solve this ambiguity, we attempted growing crystals of the metallacyclic compound, but even after many different attempts, the complex failed to afford crystals suitable for single-crystal X-ray diffraction. Thus, to solve its structure, we resorted to the use of X-ray powder diffraction (XRPD), which, in the recent years, has been shown to be a valuable structural tool in chemists' hands, not only allowing validation or rejection of prefigured structural hypotheses but also acting as a fruitful tool for unearthing new structures.[7] In particular, *ab initio* XRPD studies of highly insoluble materials, not affording single crystals of decent quality, have lead to the unexpected structural model of a number of coordination and organometallic compounds, such as metal organo−phosphates,[8] alkali metal cyclopentadienyls and phenolates,[9] oligomeric ($[Ag(pz)]_3$, $[Ag(dmpz)]_3$, $[Cu(dmnpz)]_3$, $[Ag(pymo)]_6$, $[Pd(Hdmpz)_2(dmpz)_2]_2$) and polymeric ($[Ag(pz)]_n$, α-$[Cu(pz)]_n$, β-$[Cu(pz)]_n$, $[Ag(imz)]_n$) diazolates,[10] and metal carbonyls ($[(CO)_2RhCl_2Rh(cod)]$, $[HgRu(CO)_4]_4$, and polymeric $[Ru(CO)_4]_n$).[11] As the phenyl-substituted complex **1** was probably too large to be analyzed by XRPD *on conventional laboratory equipment*, we synthesized the methyl-substituted analogue (**2**) and the results of our study are here reported.

Results and Discussion

Reaction of $Pd(OAc)_2$, phenanthroline, and nitromethane in ethanol under CO pressure, under the same conditions under which **1** is formed from nitrobenzene, afforded a dark precipitate also containing some palladium metal. Extraction of this residue with CH_2Cl_2 afforded an orange microcrystalline compound, **2**, which was shown to be homologue to **1** by IR, ^1H NMR, and elemental analysis.[12] Complex **2** is more soluble than **1**, but it also failed to afford crystals suitable for X-ray diffraction. However, its higher simplicity allowed its full structural characterization by powder diffraction methods, which, *in primis*, revealed the molecular nature of **2**.

Crystals of **2** are based on flat molecules with normal intermolecular interactions but slightly short Pd···Pd contacts (3.569(1) Å), arranged in a chain running along the [100] direction, with neighboring (stacked) molecules showing a staggered conformation of the d^8-ML_4 fragments, as suggested by ligand···ligand repulsion and by the structural trends reported for “2D” species containing square planar Pd and Pt atoms.[13] In agreement with previous observations, also the Pd···Pd···Pd chain angle (θ in ref 13) is significantly less that 180° (168.3(2)°). The palladium atom is surrounded by a chelating Phen ligand and participates in a five-membered metallacycle which, given the observed substitution pattern ($=O$ and $-CH_3$ locations), corresponds to structure **A**. Consequently, the palladium coordination sphere contains two carbon atoms *trans* to the phenanthroline N atoms. Why structure **A** is obtained in this case instead of structure **B** is not obvious at this stage. As one of the two oxygen atoms of the “CO_2” moiety must be originally bound to nitrogen, structure

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(2) (a) Alessio, E.; Mestroni, G. *J. Mol. Catal.* **1984**, *26*, 337. Alessio, E.; Mestroni, G. *J. Organomet. Chem.* **1985**, *291*, 117. (b) Bontempi, A.; Alessio, E.; Chanos, G.; Mestroni, G. *J. Mol. Catal.* **1987**, *42*, 67. (c) Cenini, S.; Ragaini, F.; Pizzotti, M.; Porta, F.; Mestroni, G.; Alessio, E. *J. Mol. Catal.* **1991**, *64*, 179. (d) Ragaini, F.; Cenini, S. *J. Mol. Catal. A* **1996**, *109*, 1. (e) Montedison S.p.A. Jpn. Kokay Tokkyo Koho JP 61 07, 246 [86 07, 246], 1986; *Chem. Abstr.* **1986**, *105*, 114759w. (f) Drent, E. Eur. Pat. Appl. EP 224, 292, 1987; *Chem. Abstr.* **1987**, *107*, 199074h. (g) Drent, E. *Pure Appl. Chem.* **1990**, *62*, 661. (h) Drent, E.; Van Leeuwen, P. W. N. M. Eur. Pat. Appl. EP 86, 281, 1983 (or U.S. US 4,474,978); *Chem. Abstr.* **1983**, *100*, 6109x. (i) Drent, E. Eur. Pat. Appl. EP 231, 045, 1987; *Chem. Abstr.* **1987**, *109*, 128605n. (j) Drent, E. Eur. Pat. Appl. EP 250, 037, 1987; *Chem. Abstr.* **1987**, 109, 6236x. (k) Drent, E.; Prillwitz, P. E. Eur. Pat. Appl. EP 225, 673, 1987; *Chem. Abstr.* **1987**, *108*, 55671y. (l) Stapersma, J.; Steernberg, K. Eur. Pat. Appl. EP 296, 686, 1988; *Chem. Abstr.* **1988**, *111*, 133802v. (m) Goodall, B. L.; Terlouw, W. Eur. Pat. Appl. EP 319, 111, 1989; *Chem. Abstr.* **1989**, *111*, 214245t. (n) Wehman, P.; Dol, G. C.; Moorman, E. R.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Fraanje, J.; Goubitz, K. *Organometallics* **1994**, *13*, 4856. (o) Wehman, P.; Kaasjager, V. E.; de Lange, W. G. J.; Hartl, F.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Fraanje, J.; Goubitz, K. *Organometallics* **1995**, *14*, 3751. (p) Wehman, P.; Borst, L.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *J. Mol. Catal. A* **1996**, *112*, 23. (q) Wehman, P.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Chem. Commun.* **1996**, 217. (r) Wehman, P.; Borst, L.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Chem. Ber./Recueil* **1997**, *130*, 13. (s) Wehman, P.; Donge, H. M. A.; Hagos, A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *J. Organomet. Chem.* **1997**, *535*, 183. (t) Leconte, P.; Metz, P. Eur. Pat. Appl. EP 330.591, 1989; *Chem. Abstr.* **1989**, *112*, 78160c.

(3) Leconte, P.; Metz, F.; Mortreux, A.; Osborn, J. A.; Paul, F.; Petit, F.; Pillot, A. *J. Chem. Soc., Chem. Commun.* **1990**, 1616.

(4) Ragaini, F.; Cenini, S.; Demartin, F. *Organometallics* **1994**, *13*, 1178.

(5) (a) Jernakoff, P.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1610. (b) Küsthardt, U.; Hermann, W. A.; Ziegler, M. L.; Zahn, T.; Nuber, B. *J. Organomet. Chem.* **1986**, *311*, 163. (c) Glück, D. S.; Wu, J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 2041. (d) Cenini, S.; Porta, F.; Pizzotti, M.; Crotti, C. *J. Chem. Soc., Dalton Trans.* **1985**, 163. (e) Bellon, P. L.; Cenini, S.; Demartin, F.; Pizzotti, M.; Porta, F. *J. Chem. Soc., Chem. Commun.* **1982**, 265. (f) Demartin, F.; Pizzotti, M.; Porta, F.; Cenini, S. *J. Chem. Soc., Dalton Trans.* **1987**, 605.

(6) Breedlove, B. K.; Gargulak, J. D.; Gladfelter, W. L. Presented at the National Meeting of the American Chemical Society, Chicago, 1993; Division of Inorganic Chemistry, paper 372.

(7) Harris, K. D. M.; Tremayne, M. *Chem. Mater.*, **1996**, *8*, 2554. Poojary, D. M.; Clearfield, A. *Acc. Chem. Res.* **1997**, *30*, 414. Masciocchi, N.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1997**, 4643.

(8) For a review paper see: Poojary, D. M.; Clearfield, A. *J. Organomet. Chem.* **1996**, *512*, 237.

(9) Dinnebier, R E.; Olbrich, F.; Stephens, P. W. *Acta Crystallogr.* **1997**, *B53*, 153. Dinnebier, R E.; Behrens, U.; Olbrich, F. *Organometallics* **1997**, *16*, 3855. Dinnebier, R. E.; Pink, M.; Stephens, P. W. *Inorg. Chem.* **1997**, *36*, 398.

(10) Definitions: Hpz = pyrazole; Hdmpz = 3,5-dimethylpyrazole; Hdmnpz = 3,5-dimethyl-4-nitropyrazole; Hpymo = 2-hydroxypyrimidine; Himz = imidazole. (a) Masciocchi, N.; Moret, M.; Cairati, P.; Sironi, A.; Ardizzoia, G. A.; La Monica, G. *J. Am. Chem. Soc.* **1994**, *116*, 7668. (b) Masciocchi, N.; Moret, M.; Cairati, P.; Sironi, A.; Ardizzoia, G. A.; La Monica, G. *J. Chem. Soc., Dalton Trans.* **1995**, 1671. (c) Masciocchi, N.; Moret, M.; Sironi, A.; Ardizzoia, G. A.; Cenini, S.; La Monica, G. *J. Chem. Soc., Chem. Commun.* **1995**, 1955. (d) Masciocchi, N.; Ardizzoia, G. A.; La Monica, G.; Moret, M.; Sironi, A. *Inorg. Chem.* **1997**, *36*, 449. (e) Masciocchi, N.; Corradi, E.; Moret, M.; Ardizzoia, G. A.; Maspero, A.; La Monica, G.; Sironi, A. *Inorg. Chem.* **1997**, *36*, 5648. (f) Ardizzoia, G. A.; Cenini, S.; La Monica, G.; Masciocchi, N.; Maspero, A.; Moret, M. Submitted for publication.

(11) cod = 1,4-cyclooctadiene. (a) Masciocchi, N.; Moret, M.; Cairati, P.; Ragaini, F.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1993**, 471. (b) Masciocchi, N.; Cairati, P.; Ragaini, F.; Sironi, A. *Organometallics* **1993**, *12*, 4499. (c) Corradi, E.; Masciocchi, N.; Pályi, G.; Ugo, R.; Vizi-Orosz, A.; Zucchi, C.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1997**, 4651.

(12) Not all of the experimental conditions originally employed have been reported in ref 3. However, we have tested that, under the conditions used in this work, nitrobenzene affords **1** in almost quantitative yield.

A clearly corresponds to the first, “kinetic”, product formed during the reduction of nitrobenzene. However, the same situation also occurs in the case of the rhodium metallacycle $[PPN][(CO)_2\overline{RhON(Ph)C(O)O}]$,[4] in which the orientation of CO_2 is reversed. Clearly, isomerization is possible, and favored, in this last case. In the case of **1** and **2**, it is possible that isomerization to a more stable isomer of type **B** is a high(er)-energy process not occurring under the reaction condition, so that the kinetic isomer is isolated; however, we cannot completely exclude at this stage that the observed isomer is indeed more stable in this case but not in the other known metallacycles of the same class.[4−6] Theoretical calculations are in progress to ascertain this point.

Methodologically speaking, a number of comments are required in order to assess the reliability of the abovementioned *ab initio* XRPD structure determination process. Owing to the reduced numbers of accessible data (in terms of individual reflections) and to the accidental overlap of most peaks (for moderately complex molecules such as the present one, with 22 nonhydrogen atoms in the asymmetric unit), the independent atom refinement, requiring too many structural parameters (at least 4 × 22 in the present case), is likely to fail in the XRPD case. Nevertheless, it has been shown in a number of cases that, when chemically sound restraints can be sagaciously introduced as (*a priori*) external obervations, the stoichiometry, conformation, and, for metal-containing species, the M···M interactions can be reasonably well determined.[7] The low quality of the diffraction data, if compared to the single-crystal ones, is sometimes also evidenced in noisy Fourier maps, in unreliable thermal factors, and by similar, i.e. *noninformative*, profile agreement factors for a slightly different structural model, which, however, may bear very different chemical significance.[14]

To increase the confidence in commonly attainable XRPD results, we have recently proposed to couple experimental diffraction data with steric energy computations in the crystal lattice,[11c] hoping that discrimination between a few competitive models could be attained through the combination of packing energy evaluation dictated by the experimental, *i.e. accessible*, knowledge of lattice metrics, space group symmetry, and “heavy” atom locations derived from XRPD data. Given that the computed difference Fourier map reported in Figure 1 was highly informative, casting no doubt on the connectivity pattern about the metallacycle, we decided to validate the above approach by computing the different packing energies of different stereoisomers using a locally modified version of Allinger’s MM3 program,[15] capable to optimize the conformation of a given fragment within the field of its crystal lattice.[16] Since the experimentally determined lattice metrics and symmetry operations impose rather stiff constraints on the shape of interlocking molecules of **2**, our molecular mechanics computations revealed that, of the four structures depicted in Chart 1 (consisting of two different stereoisomers, each with two meaningful orientations in the cell), **2a**, i.e. that obtained by XRPD analysis, was, on steric grounds only, the most suitable (see Table 1). That is, the other models, even if chemically sound and plausible, happen to be *not* (or less, for **2b**) compatible with the observed cell, space group, and Pd coordinates (obtained from XRPD without a priori information), resulting in unfavorable contacts. Note that the force field parameters of Pd, which were chosen to favor a flat conformation of the whole molecule and to allow moderate distortions from the idealized PdL_4 square-planar geometry (see footnote in Table 1), are only roughly defined and the *intra*molecular steric energies of heavily distorted conformations have little value. Indeed, high-energy packing modes (**2c**,**d**) are accompanied by large molecular distortions and can be discarded as very unfavored cases. On the contrary, the two low(er)-energy packing modes, **2a**,**b**, share the same *intra*molecular energy and their *relative total* steric energy depends *only* from their different packing environments. Generally speaking, the roughness of the force field affects mainly the high-energy packing modes

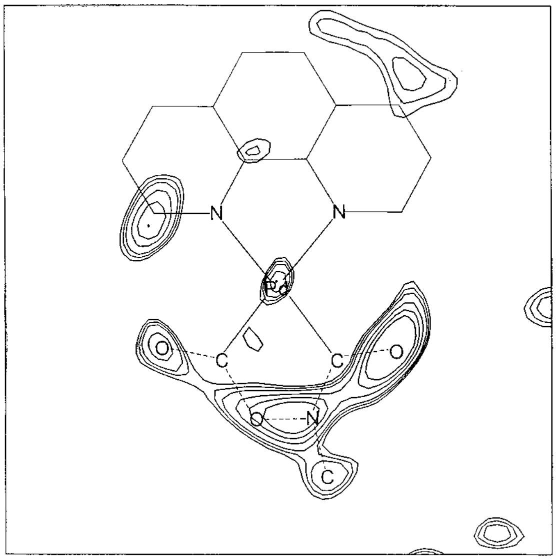
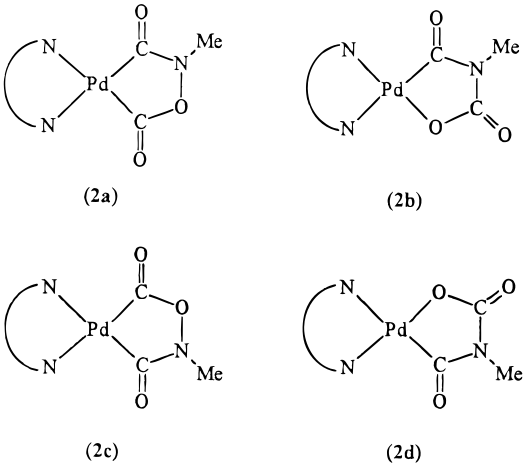


Figure 1. Difference Fourier map obtained after refinement of a rigid (Phen)PdC_2 fragment (R_{wp} = 0.214; R_p = 0.159; R_F = 0.089). The difference electron density map clearly peaks close to the missing atom locations (1 C, 1 N, and 3 O atoms), corresponding to the model **2a** of Chart 1.

Chart 1



(2a) (2b) (2c) (2d)

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(13) Aullón, G.; Alvarez, S. *Chem. Eur. J.* **1997**, *3*, 655.

(14) Masciocchi, N.; Corradi, E.; Sironi, A.; Moretti, G.; Minelli, G.; Porta, P. *J. Solid State Chem.* **1997**, *131*, 252.

(15) Allinger, N. L.; Yuh, Y. H.; Lii, J. H. *J. Am. Chem. Soc.* **1989**, *111*, 8551.

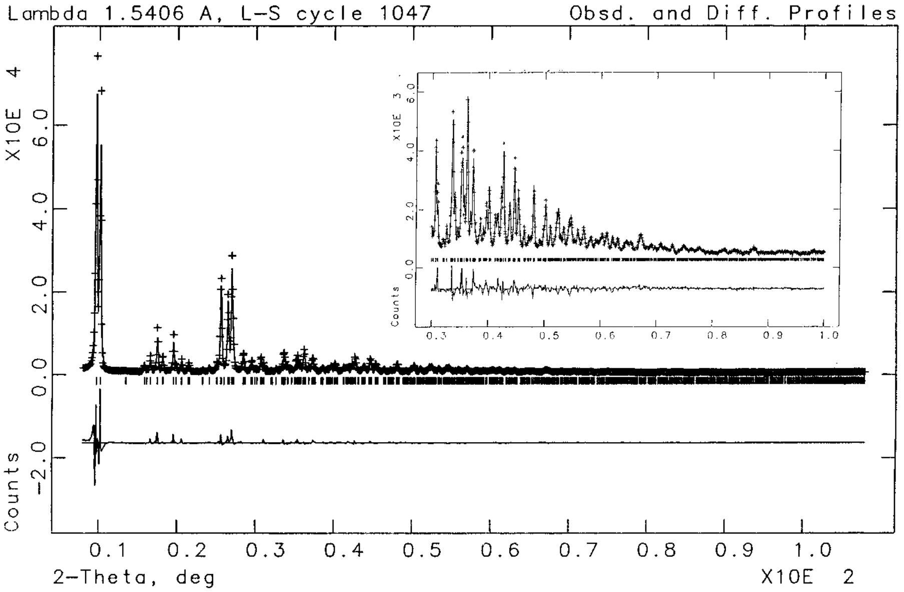

Figure 2. Final Rietveld refinement plot for **2**, with peak markers and difference plot at the bottom. The unperfect match in the low-angle region can be attributed mostly to the presence of optical aberrations (such as axial divergence), making any analytical modeling of the peak shape difficult. The insert shows the high-angle region in an expanded scale.

Table 1. Results of the Steric Energy Computations (kcal mol^{-1}) for Molecules 2a–d (Chart 1), Performed by Molecular Mechanics[16] in the Periodically Updated Crystal Lattice[a]

	fragment			
	2a	**2b**	**2c**	**2d**
tot steric energy, SE$_i$	−24.0	−17.4	+26.6	+7.1
intramolecular energy, IE$_i$	+25.2	+25.4	+38.5	+35.0
packing energy, PE$_i$	−49.2	−42.8	−11.9	−27.9
SE$_i$ − SE$_{2a}$	0.0	+6.6	+50.6	+31.1

[a] The force field about the Pd atom was chosen with the following reference values: Pd−N = 2.12 Å; Pd−X = 1.99 Å (X = C, O); k_S = 1.0 mdyne Å^{-1}; cis Y−Pd−Y = 90° (Y = N, C, O), k_B = 0.5 mdyne Å rad^{-2} ; trans Y−Pd−Y, k_B = 0.0 mdyne Å rad^{-2} ; all torsional angles involving Pd had V_1 = 0.0, V_2 = 2.0, and V_3 = 0.0 kcal mol^{-1}; on increasing nonzero force constants by as much as 4 times, the relative energy values are only slightly modified, thus making our *semiquantitative* results unsensitive to the chosen force field.

and only marginally the low-energy ones; thus, even small differences in *packing* energies allow a safe discrimination between different alternatives, favoring, in our case, **2a** *vs* **2b** by 6.6 kcal mol^{-1}.

Interestingly, if the Pd atom coordinates are left free to float in the crystal lattice, our molecular mechanics computations reveal two important features: (i) The two low-energy packing modes lie in a minimum of the potential energy hypersurface, and the molecule is not significantly shifted from its original position. (ii) Differently, **2c**,**d** experience rather large center-of-mass shifts and molecular reorientations, ending up in energetically more favorable packings (8.8 and 11.7 kcal mol^{-1} higher than **2a**, respectively), which are however *not consistent* with the observed diffraction pattern.

Conclusions

In this paper we have shown that the information that can be gained by XRPD is not limited to that of interest to polymer and materials science chemists but can also be relevant to solve problems in a much different field such as homogeneous catalysis. As a matter of fact, a similar task (the determination of the molecular structure of [(CO)$_2$RhCl$_2$Rh(cod)]^{11c}) has been recently tackled, and solved, with the very same approach, demonstrating that elusive catalysis intermediates can be structurally characterized even if such *soluble* species fail to afford crystals of suitable size and quality, provided that their structural complexity is moderate or can be lowered by simple substitution of bulky fragments (Me *vs* Ph in **2**, μ-Cl *vs* μ-OSiPh$_3$ in ref 11c).

Furthermore, the new methodological step in the *ab initio* XRPD structure determination process, i.e. the evaluation of steric energy in the crystal lattice of different structural models, once even a rough force field is available, is thought to increase the resolution inherent in the powder diffraction method and, therefore, to act as a lens capable to rescue subtle structural details which XRPD data may not afford. Indeed, we foresee that the use of a complex cost function, integrating a simultaneous refinement of the structural model *vs* diffraction and energetic data, may successfully lead, soon, to a significant increase of the complexity of the problems which can be tackled by XRPD from conventional sources, opening this methodology to a much wider audience.

Experimental Section

General Procedures. Absolute ethanol and nitromethane were degassed, but not dried, before use, CH$_2$Cl$_2$ was distilled from CaH$_2$ under dinitrogen, and Pd(OAc)$_2$ and anhydrous phenanthroline were commercial products and were used as received. IR spectra were recorded on a Bio-Rad FTS-7 spectrophotometer; NMR spectra were recorded on a Bruker AC 200 FT (200 MHz) spectrometer at room temperature. Elemental analyses were performed in the analytical laboratories of Milano University.

Synthesis of Pd(Phen)(C(O)N(Me)OC(O)] (2). Pd(OAc)$_2$ (100 mg, 0.45 mmol) and phenanthroline (241 mg, 1.34 mmol) were weighed inside a glass liner, and the liner was placed into a Schlenk tube with a wide mouth. The tube was evacuated and filled with dinitrogen, after which nitromethane (1.1 g, 0.970 mL, 18 mmol) and ethanol (6.5 mL) were added.

Table 2. Summary of Crystal Data and Refinement Parameters

compd	Pd(Phen)(C(O)N(Me)OC(O)), **2**
formula	$C_{15}H_{11}N_3O_3Pd$
fw	373.69
cryst system	orthorhombic
space group	$Pn2_1a$
a, Å	7.1021(3)
b, Å	10.6721(7)
c, Å	17.286(1)
V, Å^3	1310.2(1)
Z	4
F(000)	744
D_{calc}, g cm^{-3}	1.894
T, K	298(2)
diffractometer	Rigaku D-III/Max
λ, Å	Cu Kα, 1.5418
scan range, deg	$8 \leq 2\theta \leq 108$
scan mode	θ:2θ, $\Delta(2\theta) = 0.02°$, $t = 45$ s step^{-1}
slits used, deg	DS 0.5, AS 0.5, RS 0.15
no. of points	5000
no. of reflcns	847
no. of params	78
no. of restraints	54
R_{wp}[a]	0.123
R_p[a]	0.087
R_{exp}[a]	0.025
R_F[a]	0.061

[a] $R_p = \Sigma_i|y_{i,o} - y_{i,c}|/\Sigma_i|y_{i,o}|$; $R_{wp} = \Sigma_i w_i|y_{i,o} - y_{i,c}|^2/\Sigma_i w_i|y_{i,o}|;^2$ $R_{exp} = (N - P)/\Sigma_i w_i|y_{i,o}|;^2$ $R_F = \Sigma_k|F_{k,o} - F_{k,c}|/\Sigma_k|F_{k,o}|$ where $y_{i,o}$ and $y_{i,c}$ are the observed and calculated step intensities, respectively, w_i is a statistical weighting factor (taken as $1/y_{i,o}$), and $F_{k,o}$ and $F_{k,c}$ are the observed and calculated structure factors; i runs over all data points and k runs over the space-group permitted reflections. Note that the low value of R_{exp} in Rietveld refinements only reflects the good counting statistics obtained by long counting times, i.e. the *precision* of the measurement but *not* its accuracy, see: Hill, R.J.; Madsen, I. C. *Powder Diffr.* **1987**, *2*, 146. Indeed any shorter counting times than ours will provide higher R_{exp} values and, conversely, arbitrarily low χ^2 values!

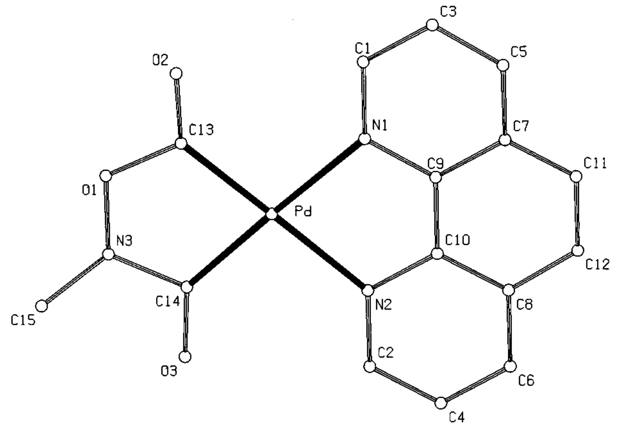

Figure 3. Molecular plot of the Pd(Phen)(C(O)N(Me)OC(O)) species, with labeling scheme. Relevant bond distances and angles: Pd···Pd 3.569(1) Å, N1−Pd−N2 81.0(2)°, C13−Pd−C14 81.7(4)°. Pd−N, Pd−C, and Phen(C−N, C−C) bonds have been restrained to known values (2.12, 1.98, and 1.38 Å).

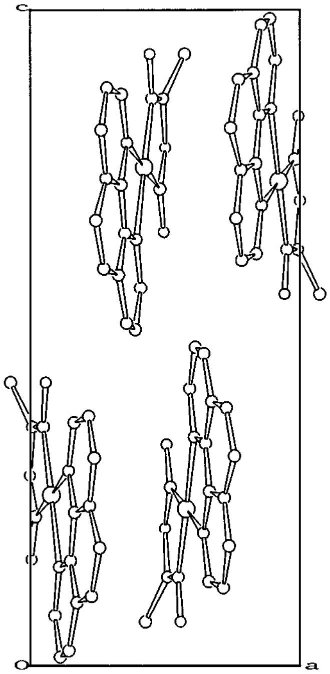

Figure 4. Packing diagram of the unit cell content of **2**, viewed down the 2_1 axis (b). The horizontal axis is a, and the vertical axis is c.

The liner was frozen with dry ice/acetone and quickly transferred to a 200 mL stainless steel autoclave equipped with magnetic stirring. The autoclave was evacuated and filled with dinitrogen three times, after which it was allowed to reach room temperature and charged with CO (30 bar). The autoclave was heated at 80 °C for 1 h and then was cooled with ice and vented. An orange solution was obtained, together with a dark residue, also containing some palladium metal. The residue was filtered off, washed with ethanol (2 × 7 mL), and finally extracted with CH_2Cl_2 (3 × 7 mL) to afford yellow-orange **2** (54 mg, 0.14 mmol, 31% yield). IR (Nujol): 1688, 1595 cm^{-1}. ^1H NMR (DMSO-d_6): δ 2.50 ppm, s (signals attributable to coordinated Phen are observable between 8 and 10 ppm). Anal. Calcd for $C_{15}H_{11}N_3O_3Pd$: C, 46.5; H, 2.9; N, 10.8. Found: C, 46.7, H, 3.2; N, 11.0. Use of nitrobenzene in place of nitromethane under the same conditions afforded complex **1** in almost quantitative yield, only a very small amount of metallic palladium being formed in this case.

Crystallography. A "standard" *ab initio* XRPD structure determination of **2** was undertaken and is briefly described by the following steps: (i) Peak search and indexing (by TREOR[17]) of data collected on a conventional powder diffractometer with graphite-monochromatized Cu Kα radiation (step scan of $\Delta(2\theta) = 0.02°$ and $t = 45$ s step^{-1} to ensure adequate statistics and detection of small peaks which are of utmost importance in the indexing process) afforded an orthorhombic unit cell of approximate dimension $a = 7.10$, $b = 10.68$, and $c = 17.30$ Å, $Z = 4$, $M(17)$[18] $= 33$, and $F(17)$[19] $= 56$ (0.009, 35). (ii) From systematic absences and successful solution (vide infra), space group $Pn2_1a$ (nonstandard setting of $Pna2_1$, No. 33) was determined. (iii) After integrated intensity extraction (by EXTRA[20]), interpretation of the Patterson map allowed location of a unique Pd atom. (iv) Since a noisy and not easily interpretable difference Fourier map was computed, orientation of a planar $(Phen)PdC_2$ fragment was performed by a rotational grid search about the (refinable) Pd atom position, using P-RISCON,[21] which succeeded in determining the true solution with $R = 0.20$ (on 47 reflections with $2\theta < 30°$); this initial orientation was optimized by a rigid-body Rietveld refinement, using a Z-matrix formalism implemented by us[22] into a local version of the program PREFIN,[23] which is now

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(16) Mercandelli, P..; Moret, M.; Sironi, A. Submitted for publication.

(17) Werner, P. E.; Eriksson, L.; Westdahl, M. *J. Appl. Crystallogr.* **1985**, *18*, 367.

(18) DeWolff, P. M. *J. Appl. Crystallogr.* **1968**, *1*, 267.

(19) Smith, G. S.; Snyder, R. L. *J. Appl. Crystallogr.* **1979**, *12*, 60.

(20) Altomare, A.; Cascarano.; G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Burla, M. C.; Polidori, G. *J. Appl. Crystallogr.* **1995**, *28*, 738.

(21) Masciocchi, N.; Bianchi, R.; Cairati, P.; Mezza, G.; Pilati, T.; Sironi, A. *J. Appl. Crystallogr.* **1994**, *27*, 426.

(22) Masciocchi, N.; Sironi, A. Unpublished results.

(23) Immirzi, A. *Acta Crystallogr.* **1978**, *A34*, S348; **1980**, *B36*, 2378.

incorporated into DEBVIN.[24] (v) A difference Fourier (GSAS;[25] see Figure 1) allowed to locate the few missing light atoms, leading to the final model for **2**. (vi) This model was then refined[26] by the Rietveld method ($R_{wp} = 0.123$; $R_p = 0.087$; $R_F = 0.061$; overall $U_{iso} = 0.071(1)$ Å;[2] see Figure 2) including the proper geometrical restraints (supplied in the Supporting Information) which have been taken from the structure of a compound with a similar Pd coordination, Pd(bipy)[C(O)-OCH_3)]$_2$.[27] (vii) A further validation step was performed by showing that, within the constraints imposed by lattice metrics, space group, and Pd location, the four possible structural models (two isomers with two orientations each; see Chart 1) had markedly different packing energy and that the best packing was that of the model derived by XRPD (**2a**). A trial refinement of the texture parameter, in March–Dollase formulation, showed insignificant deviations from the theoretical value of 1.00 and was therefore abandoned. A detailed description of the methodology used in our laboratory is reported in ref 28. Crystal data and refinement results are collected in Table 2. The Supporting Information contains the fractional atomic coordinates of **2**; a molecular plot and the packing diagram of **2** are drawn in Figures 3 and 4, respectively.

Note Added in Proof: After submission of this paper, Mestzoni and co-workers succeeded in growing single crystals of **1**·$C_6H_5NO_2$, containing clathrated nitrobenzene molecules (Sessanta o Santi, A.; Milani, B.; Mestzoni, G.; Zangrando, E.; Randaccio, L. *J. Organomet. Chem.* **1997**, *545-546*, 89). The basic features of the structure reported therein are in complete agreement with our results.

Acknowledgment. We thank the Italian MURST (40%) and CNR (Progetto Strategico Tecnologie Chimiche Innovative) for funding. The technical support of Mr. G. Mezza is also acknowledged.

Supporting Information Available: Listings of crystal data, positional and thermal parameters, geometrical restraints, and complete bond lengths and angles (11 pages). Ordering information is given on any current masthead page.

OM9708438

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[24] Brückner, S.; Immirzi, A. *J. Appl. Crystallogr.* **1997**, *30*, 207.

[25] Larson, A. C.; Von Dreele, R. B. LANSCE, MS-H805, Los Alamos National Laboratory, Los Alamos, NM 87545, 1994.

[26] Refinement of a (disordered) crystal phase in *Pnma* led to much higher residual and agreement factors and, what is worse, superposition of neighboring molecules. Indeed, *Pnma* requires a significant reorientation of the whole molecule from its actual location, ca. 80° about the *c* axis (see the packing diagram in Figure 4), with a mirror plane (normal to *b*) bisecting the N–Pd–N and C–Pd–C angles.

[27] Smith, G. D.; Hanson, B. E.; Merola, J. S.; Waller, F. J. *Organometallics* **1993**, *12*, 568.

[28] Masciocchi, N.; Cairati, P.; Sironi, A. *Powder Diffr.*, in press.