

Acid-Induced Transformation of Palladium(0)-Benzoquinone Complexes to Palladium(II) and Hydroquinone

Helena Grennberg, Adolf Gogoll, and Jan-E. Bäckvall*

Department of Organic Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

Received January 27, 1993

Electron transfer from palladium to coordinated quinone in [(1,5-cyclooctadiene)-Pd(0)-(1,4-quinone)] complexes was studied in different solvents. Addition of acid to these complexes initiates a redox reaction which yields a Pd(II)-di- π -olefin complex and hydroquinone. In some cases, the complexes underwent further reactions to give oxypalladation adducts.

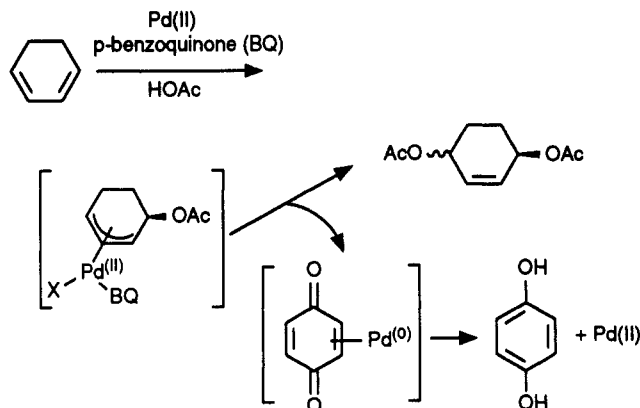
Introduction

Palladium(II)-catalyzed oxidations of unsaturated hydrocarbons are of great importance in organic synthesis and homogeneous catalysis.¹ In these reactions, it has been generally assumed that a short-lived Pd(0) species is formed, which would be recycled to Pd(II) by the oxidant. The nature of this process, however, has in most cases remained unclear.²

In our laboratory, a number of palladium(II)-catalyzed oxidations involving the Pd(II)/Pd(0)-benzoquinone/hydroquinone redox couples have been developed.^{1c,d,3} Of these reactions, the palladium(II)-catalyzed 1,4-oxidation of conjugated dienes,^{3a,b} exemplified by the 1,4-diacetoxylation in Scheme I, have been studied in some detail.^{3a,4,5} A coordination of benzoquinone (BQ) to palladium in the (π -allyl)palladium intermediate has been demonstrated.⁵ It has been suggested that the product-forming nucleophilic attack on this π -allyl species produces a Pd(0)-benzoquinone complex, which would undergo a redox reaction to give Pd(II) and hydroquinone.

The electron transfer in (π -allyl)-Pd(II)-quinone complexes is very rapid, making a direct mechanistic investigation under diacetoxylation conditions difficult. Therefore, direct proof of either the existence of the suggested Pd(0)-benzoquinone intermediate or its disproportionation into Pd(II) and hydroquinone is lacking. However, Pd(0)-quinone complexes,⁶ as well as quinone complexes of Ni(0)⁷ and Pt(0)⁸ are known. The present paper describes a study of the electron transfer in Pd(0)-benzoquinone complexes and, in particular, the finding

Scheme I

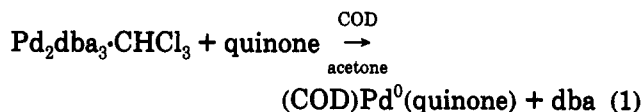


that the addition of acid induces a redox reaction between quinone and metal to give Pd(II) and hydroquinone.

Results

A. Preparation of Pd(0)-Benzoquinone Complexes.

The readily available Pd(0)-quinone complexes of 1,5-cyclooctadiene (COD) (eq 1)⁶ were chosen for the present



COD = 1,5-cyclooctadiene; dba =

dibenzylideneacetone

investigation of the electron transfer in the Pd(0)-benzoquinone system. The quinone complexes 1a-d were prepared according to eq 1. 2,5-Dichlorobenzoquinone and anthraquinone did not form isolable complexes with palladium.^{7a}

B. Characterization of Pd(0)-Quinone Complexes.

Complexation of quinone to COD-Pd(0) is indicated by the upfield shifts of the quinone and COD double bond protons (¹H NMR) and, in addition, by decrease of the T₁ relaxation time of the quinone protons. No exchange between complexed and free quinone is occurring according to ¹H NMR saturation transfer experiments of mixtures. For complexes 1a and 1b, which are of C_{2v} symmetry, only

(8) (a) Cenini, S.; Ugo, R.; La Monica, G. *J. Chem. Soc., Dalton Trans.* 1971, 416. (b) Chetcuti, M. J.; Howard, J. A. K.; Pfeffer, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1981, 276.

(1) (a) Henry, P. M. *Palladium-Catalyzed Oxidation of Hydrocarbons*; D. Reidel Publishing Co.: Dordrecht, 1980. (b) Bäckvall, J. E. *Acc. Chem. Res.* 1983, 16, 335. (c) Bäckvall, J. E.; Hopkins, R. B.; Grennberg, H.; Mader, M. M.; Awasthi, A. K. *J. Am. Chem. Soc.* 1990, 112, 5160. (d) Bäckvall, J. E. *Pure Appl. Chem.* 1992, 64, 429.

(2) (a) In the Pd(II)-catalyzed oxidation of ethylene by O₂, a process cocatalyzed by CuCl₂ (the Wacker Process), several different pathways for the reoxidation of Pd(0) have been proposed.^{1a,2b} (b) Hosokawa, T.; Miyagi, S.; Murahashi, S. I.; Sonoda, A. *J. Chem. Soc., Chem. Commun.* 1978, 687.

(3) (a) Bäckvall, J. E.; Byström, S. E.; Nordberg, R. E. *J. Org. Chem.* 1984, 49, 4619. (b) Bäckvall, J. E.; Vågberg, J. O. *J. Org. Chem.* 1988, 53, 5695. (c) Bäckvall, J. E.; Hopkins, R. B. *Tetrahedron Lett.* 1988, 29, 2885. (d) Bäckvall, J. E.; Gogoll, A. *J. Chem. Soc., Chem. Commun.* 1987, 1236.

(4) (a) Bäckvall, J. E.; Nordberg, R. E.; Wilhelm, D. *J. Am. Chem. Soc.* 1985, 107, 6892. (b) Grennberg, H.; Langer, V.; Bäckvall, J. E. *J. Chem. Soc., Chem. Commun.* 1991, 1190.

(5) Bäckvall, J. E.; Gogoll, A. *Tetrahedron Lett.* 1988, 29, 2243.

(6) Hiramatsu, M.; Shiozaki, K.; Fujinami, T.; Sakai, S. *J. Organomet. Chem.* 1983, 246, 203.

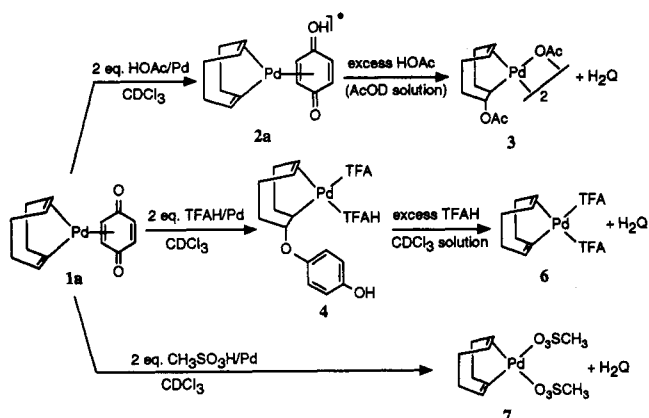
(7) (a) Uhlig, E.; Fischer, R.; Kirmse, R. *J. Organomet. Chem.* 1982, 239, 385. (b) Glick, M. D.; Dahl, L. F. *Ibid.* 1965, 3, 200.

Table I. COD-Pd(0)-Quinone Complexes

complex	quinone	$E^{\circ}_{ox}(\text{quinone}), \text{mV}$
1a	<i>p</i> -benzoquinone (BQ)	700 ^a 622 ^d
1b	duroquinone (DQ) ^b	463 ^a
1c	1,4-naphthoquinone (NQ)	484 ^a
1d	1,4-triptycenoquinone (TQ) ^c	567 ^d

^a Becker, H. D. In *The Chemistry of the Quinonoid Compounds*; Patai, S., Ed.; Interscience: New York, 1974. ^b Tetramethylbenzoquinone. ^c 9,10-Dihydro-9,10-*o*-benzoanthracene-1,4-dione (11) (this work). ^d In glacial acetic acid (this work).

Scheme II



one signal was observed for the COD double bond protons.⁹ Complexes 1c and 1d lack this symmetry, and for these complexes two broad signals for the two pairs of olefin protons of COD are observed.¹⁰ These signals collapse at higher temperatures, and from the coalescence temperatures, rotational barriers of 60 kJ/mol (1c) and 64 kJ/mol (1d) were determined.¹¹

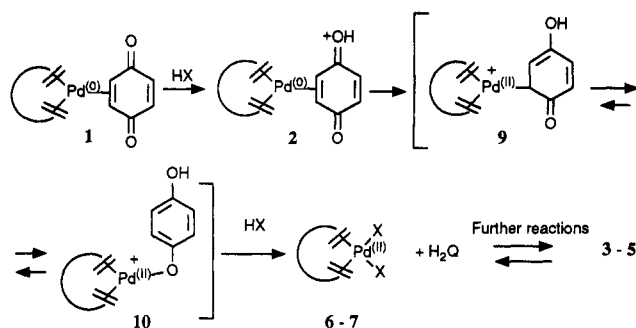
C. Reactivity of Pd(0)-Quinone Complexes. Upon treatment with acid, rapid transformations of 1a-d into different types of complexes were observed by ¹H NMR spectroscopy. The product formed depends upon the strength and nucleophilicity of the acid employed, as well as upon the redox potential of the quinone. Owing to the lability of some of the complexes obtained, all characterizations were performed directly in the reaction medium using ¹H and ¹³C NMR spectroscopy. Those products formed from reactions of the benzoquinone complex 1a, which are sufficiently stable in solution to allow a characterization by NMR spectroscopy, are summarized in Scheme II. When equimolar amounts of acetic acid were added to a chloroform solution of 1a (vide infra), protonation of the quinone ligand took place and 2a was observed.¹² An excess of acetic acid converts this complex to hydroquinone (H₂Q) and a σ - π -complex 3, a reaction involving oxidation of the metal by the quinone and a

(9) The ¹³C NMR spectrum of complex 1a presented only one set of signals both in the solid state and in solution (see Experimental Section). This indicates an η^4 -coordination of the quinone^{7b} since only two signals for the ring carbons are observed.

(10) The quinone in these complexes has two nonequivalent double bonds and is probably η^2 -coordinated to palladium.^{8b} Only one signal is observed in samples contaminated with traces of acid, as, e.g., present in chloroform.⁶

(11) Abrahams, R. J.; Fisher, J.; Loftus, P. *Introduction to NMR Spectroscopy*; John Wiley & Sons: New York, 1990.

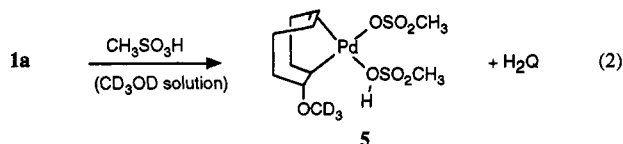
Scheme III



nucleophilic attack of the acetate ion from the solvent on one of the double bonds of COD in the short-lived intermediate COD-Pd(II) formed (cf. Scheme III). Complex 3 was characterized by comparison with reference material, prepared from COD-PdCl₂ (8).¹³ With the stronger acid but weaker nucleophile CH₃SO₃H, 1a gave the di- π -olefin complex 7 together with hydroquinone. In the presence of this strong acid, the hydroquinone underwent further reaction, yielding polymerized quinone derivatives. Trifluoroacetic acid (TFAH) is more nucleophilic and less acidic than CH₃SO₃H and shows an intermediate behavior. Addition of 2 equiv of this acid converted 1a to 4, where hydroquinone, formed in the oxidation of the metal, has acted as a nucleophile. For steric reasons it is likely that the hydroquinone has to be released from the metal prior to acting as a nucleophile. The addition of an excess of TFAH to 4 initiated a retroxypalladation to give the di- π -olefin complex 6^{13b} and free hydroquinone.

Complexes 1b-d, containing quinones with a lower redox potential and larger steric bulk, were less reactive. Only protonation was observed when the complexes were treated with equimolar amounts of strong acids (TFAH, CH₃SO₃H, HClO₄)¹⁴ or when the complexes were dissolved in acetic acid, generating a new solution species 2 (cf. Scheme II).

When the acidity of an acetic acid solution of the duro- or naphthoquinone complex was increased by the addition of CH₃SO₃H, an oxidation of the metal of 2b and 2c took place. The product observed was in both cases 3. A similar observation was made for 1a in methanol (eq 2), a solvent in which electron transfer from palladium to quinone does not take place unless CH₃SO₃H is added.^{3b} The product (5) is analogous to 4.¹⁵



Discussion

In the Pd(II)-catalyzed 1,4-diacetoxylation (Scheme I), electrons are transferred from a π -allyl ligand via palladium

(12) (a) The formation of complexes 2 was evident from downfield shifts of the quinone and COD protons and carbons as compared to the nonprotonated parent complexes 1. Addition of acid to the corresponding free quinones resulted in similar but considerably smaller shift changes. (b) The palladium-quinone bonding arrangement in complexes 1 remains unchanged after protonation, as was evident from ¹³C NMR spectroscopy.

(13) (a) Andersson, C. B.; Bureson, B. J. *J. Organomet. Chem.* 1967, 7, 181. (b) Treatment of 8 with AgTFA in CHCl₃ yielded 6.

(14) In some cases, parts of the complex polymerized.

(15) (a) The relative stereochemistry of the substituents in the σ - π -complexes 3-5, determined from NOE measurements, was found to be *trans*. The complete NMR spectroscopical characterization of these compounds will be published elsewhere.^{15b} (b) Grennberg, H.; Gogoll, A. manuscript.

to *p*-benzoquinone, which upon coordination to the metal induces the nucleophilic attack. In this process, the formation of a Pd(0)-benzoquinone intermediate has been suggested.³ This complex would, after electron transfer from the metal to the quinone, give Pd(II) and hydroquinone.¹⁶ From the above results it is evident that the presence of an acid is required in order to induce the electron transfer.¹⁷ A general mechanism for the transformation of Pd(0)-quinone complexes **1** to the Pd(II) complexes and hydroquinone described in this paper is proposed in Scheme III. An initial protonation of the quinone oxygen produces a Pd(0)-BQ complex of type **2**, which upon rearrangement would give the cationic palladium(II) complexes **9** and **10**.^{12b} Further addition of acid would release hydroquinone and a Pd(II)-di- π -olefin complex **6** or **7**, which under some of the reaction conditions undergoes further reaction.

In palladium-catalyzed 1,4-oxidations, it has been observed that acidic conditions are necessary for a successful catalytic reaction according to Scheme I, a requirement met either by using an organic acid as the solvent or by the addition of a catalytic amount of a strong acid.^{3b,c} Furthermore, the amount of acid can affect the product distribution,¹⁸ and an increased acidity, e.g. addition of a catalytic amount of a stronger acid to the acetic acid-containing solvent can increase the reaction rate.¹⁹ All these observations are consistent with an acid-induced recycling of Pd(0)-benzoquinone to Pd(II) and hydroquinone (cf. Scheme III).

Conclusion

In the presence of acid, palladium(0)-benzoquinone complexes undergo an electron transfer from Pd(0) to coordinated quinone, to give palladium(II) and free hydroquinone, a reaction which is initiated by protonation of the quinone.

Experimental Section

NMR spectra were recorded as follows: ¹H at 300 or 400 MHz and ¹³C at 75.4 or 100.6 MHz. Spectra were recorded for acid-free CDCl₃, CD₃OD, or CD₃COOD solutions. Chemical shifts are referenced indirectly to TMS via the solvent signal (¹H CDCl₃ at δ 7.26, CD₃COOD at δ 2.03, and CD₃OD at δ 3.35 ppm; ¹³C at δ 77.0, 20.0, and 49.0 ppm, respectively). Chemical shifts are for CDCl₃ solutions at 25 °C unless stated otherwise. The solid-state spectrum of **1a** was recorded with CP-MAS at 75.4 MHz using TMS as the chemical shift reference. ¹³C NMR spectrum assignments were done by means of HMQC^{20a} and selective INEPT.^{20b} Trace amounts of acid present in the commercial CDCl₃ were removed by filtration through basic Al₂O₃ prior to use. Solvents and chemicals were, unless otherwise noted, from commercial sources and were used as received.

Pd₂(dba)₃CHCl₃²¹ and (η^4 -1,5-cyclooctadiene)palladium dichloride **8**²² were prepared according to literature procedures. The spectral data for complexes **3**–**5** will be published elsewhere.^{15b}

(16) (a) Recent ESCA investigations of Pd complexes indicated that the Pd in complexes with ligands of different donor/acceptor capability has a rather constant electron density and merely transmits electrons between its ligands.^{16b} (b) Bökman, F.; Gogoll, A.; Petterson, L. G. M.; Bohman, O.; Siegbahn, H. O. G. *Organometallics* 1992, 11, 1784.

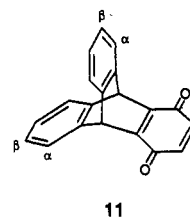
(17) Analogous results have been reported for a Ni(0)-benzoquinone complex.⁷

(18) Andersson, P. G. *Comprehensive Summaries from the Faculty of Science*, 343. Doctoral Dissertation, Uppsala, 1991.

(19) Akermarck, B.; Hansson, S.; Rein, T.; Vågberg, J. O.; Heumann, A.; Bäckvall, J. E. *J. Organomet. Chem.* 1989, 369, 433.

(20) (a) Summers, M. E.; Marzilli, I. G.; Bax, A. *J. Am. Chem. Soc.* 1986, 108, 4285. (b) Uhrin, D.; Liptaj, T. *J. Magn. Res.* 1989, 81, 82.

9,10-Dihydro-9,10-*o*-benzenoanthracene-1,4-dione (11). This quinone was prepared from [4 + 2] cycloaddition of *p*-benzoquinone to anthracene and subsequent oxidation according to Bartlett et al.²³



11

Determination of the Redox Potential for 11. A mixture of triptycenoquinone and triptycenoquinone (1:1) was dissolved in glacial acetic acid at room temperature. The potential of the solution was determined using a saturated calomel electrode (242 mV vs NHE). In this system, the potential of the TQ/TH₂Q redox couple was found to be 567 mV vs NHE and for the reference redox couple *p*-benzoquinone/hydroquinone, 622 mV vs NHE.

Preparation of Pd(0)-Quinone Complexes. Complexes **1a**–**c** were prepared according to ref 6. The complexes were obtained as brown solids.

COD-Pd(0)-BQ, 1a:⁶ ¹H NMR δ 5.84 (br s, 4H, BQ), 5.42 (br m, 4H, CH=CH, COD), 2.48 (br s, 4H, CH₂, COD); ¹³C NMR (25 °C) δ 177.9 (quinone C=O), 106.6 (COD CH), 105.9 (br, quinone CH), 29.5 (COD CH₂); ¹³C NMR (–55 °C) δ 171.3 (quinone C=O), 107.0 (quinone CH), 104.3 (COD CH), 29.5 (COD CH₂); ¹³C solid-state NMR δ 165.2 (quinone C=O), 108.3 (quinone CH), 100.5 (COD CH), 31.1 (COD CH₂).

COD-Pd(0)-DQ, 1b:⁶ ¹H NMR δ 4.53 (br s, 4H, CH=CH), 2.38 (br m, 4H, CH₂), 2.31 (br m, 4H, CH₂), 2.12 (s, 12H, CH₃); ¹³C NMR δ 160.5 (quinone C=O), 118.5 (quinone C=C), 103.4 (COD CH), 30.2 (COD CH₂), 12.6 (quinone CH₃).

COD-Pd(0)-NQ, 1c:⁶ ¹H NMR δ 8.08 (m, 2H, H-5,8), 7.69 (m, 2H, H-6,7), 5.55 and 5.08 (br, 2H each, CH=CH, COD), 4.87 (br s, 2H, CH=CH, NQ), 2.28 (br m 6H, CH₂), 1.5 (br m, 2H, CH₂). From the coalescence behavior of the signals at δ 5.55 and 5.08, an activation barrier for rotation of the quinone ligand of 60 kJ/mol was calculated.¹¹

COD-Pd(0)-TQ, 1d. Quinone **11**²³ (0.30 g, 1.06 mmol) and Pd₂(dba)₃CHCl₃ (0.31 g, 0.32 mmol) were mixed in dry acetone (5 mL) under argon. COD (170 μ L, 1.39 mmol) was added, and stirring was continued for 2 h. The solids were filtered off, washed with cold acetone and diethyl ether, and dried in air to yield **1d** (0.24 g, 75%) as a red powder. ¹H NMR: δ 7.47 and 7.42 (m, 2H each, H- α anthracenyl), 7.08 and 6.97 (m, 2H each, H- β anthracenyl), 5.95 (s, 2H, H-9,10 bridgehead), 5.48 (s, 2H, CH=CH quinone), 5.21 and 4.62 (br, 2H each, CH=CH COD), 2.24 (br 4H, CH₂), 1.9 (br, 2H, CH₂), 1.1 (br, 2H, CH₂). From the coalescence behavior of the signals at δ 5.21 and 4.62, an activation barrier of 64 kJ/mol for the rotation of the quinone ligand was calculated.¹¹

Acid-Induced Transformations of Complexes 1. The complex was dissolved in the appropriate deuterated solvent. After the recording of the ¹H NMR spectrum, 2 or more equiv of acid (relative to palladium) was added and the tube was recapped and vigorously shaken. The NMR characterization of the products formed was conducted without prior isolation.

Protonation of 1a to 2a. The addition of HOAc (10 equiv/Pd) to a CDCl₃ solution of **1a** caused a 0.05 ppm downfield shift of the signal at 5.84 ppm (quinone CH=CH).

Protonation of 1b to 2b. The addition of TFAH to a CDCl₃ solution of **1b** resulted in a successive downfield shift of the signal at 4.43 ppm (COD CH=CH) of 0.29, 0.45, and 0.55 ppm (2, 4,

(21) Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* 1974, 65, 253.

(22) Chatt, J.; Vallarino, L. M.; Venanzi, L. M. *J. Chem. Soc.* 1957, 3413.

(23) Bartlett, P. D.; Ryan, M. J.; Cohen, S. G., *J. Am. Chem. Soc.* 1942, 64, 2649.

and 10 equiv of TFAH/Pd). The signal at 2.12 ppm (quinone CH₃) was also shifted downfield (0.09, 0.15, 0.20 ppm for 2, 4, 10 equiv of TFAH/Pd). If instead CH₃SO₃H (2 equiv/Pd) was added, downfield shifts of 0.54 (signal at 4.43 ppm) and 0.17 ppm (signal at 2.12 ppm) were observed. The ¹³C NMR signals were shifted downfield as well. ¹³C NMR (1b + 2 equiv of CH₃SO₃H/Pd): 122.7 (quinone C=C), 109.3 (COD CH), 39.4 (CH₃SO₃H), 30.2 (COD CH₂), 13.3 (quinone CH₃). The carbonyl carbon signals are too broad to be detected.

Protonation of 1c to 2c. The treatment of a CDCl₃ solution of 1c with TFAH (2, 4, and 6 equiv/Pd) caused a downfield shift of the signal at 4.87 ppm (quinone CH=CH) of 0.37, 0.65, and 0.92 ppm. At 4 equiv, some product 6 was observed. Addition of CH₃SO₃H shifted the signal 0.33 (2 equiv/Pd) and 0.44 ppm (4 equiv/Pd) downfield.

Protonation of 1d to 2d. The addition of TFAH (2 equiv/Pd) to a CDCl₃ solution of 1d resulted in a downfield shift of all olefin and bridgehead signals, yielding a complicated pattern due to the loss of quinone symmetry.

COD-Pd^{II}(TFA)₂, 6:¹³ ¹H NMR δ 6.39 (br s, 4H, CH=CH), 3.14 and 2.55 (br d, 4H each, CH₂).

COD-Pd^{II}(SO₃CH₃)₂, 7, was obtained when 1a in CDCl₃ was treated with CH₃SO₃H (2 equiv/Pd): ¹H NMR δ 6.61 (br s, 4H, CH=CH), 2.95 and 2.34 (br m, 4H each, CH₂), 2.8 (br s, 6H, SO₃CH₃).

COD-Pd^{II}Cl₂, 8:²² ¹H NMR δ 6.32 (br s, 4H, CH=CH), 2.91 and 2.57 (br m, 4H each, CH₂); ¹³C NMR δ 116.7, 31.0.

Acknowledgment. Financial support from the Swedish Natural Science Research Council is gratefully acknowledged. We thank Dr. Jörgen Tegenfeldt, Department of Inorganic Chemistry, University of Uppsala, for performing the solid-state NMR experiment.

OM930045R