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Synthesis of TCNQ Salts with Dithiocarbamato- and Dithiophosphatobis(aryl isocyanide)rhodium(I) and their Spectroscopic and Electrical Properties

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The title salts with formula $Rh(Me_2NCS_2)(RNC)_2(TCNQ)$ and $Rh((EtO)_2PS_2)(RNC)_2(TCNQ)$ (R = Ph, $4\text{-}MeC_6H_4$, and $4\text{-}MeOC_6H_4$) were prepared. The binding energies of Rh $3d_{3/2}$ and $3d_{5/2}$ electrons obtained from X-ray photoelectron spectra of these salts fall between those of $Rh^{I}L(RNC)_2$ and $Rh^{III}L(RNC)_2I_2$, and are almost the same as those of the TCNE salts, $RhL(RNC)_2(TCNE)$ (L = Me_2NCS_2 and $(EtO)_2PS_2$). These results, in addition to electronic absorption and ESR spectra, suggest that the TCNQ salts involve the Rh(II) species and the $TCNQ^{\cdot-}$ radical anion and that the Rh(II) species exist as dimers with the Rh(II)–Rh(II) bonding in the solid state. All the TCNQ salts behave as semi-conductors in the 20–90 °C range, although the electrical resistivities are large (10^7–10^{11} Ω cm at 298 K as compacted samples).

Introduction

In the previous paper [1], one of the authors reported the preparation and electrical resistivities of simple and complex salts of tetrakis(isocyanide)rhodium(I) cation with 7,7,8,8-tetracyano-*p*-quinodimethan (TCNQ) radical anion, $[Rh(RNC)_4]^+(TCNQ)_n^{\cdot-}$ (R = t-Bu, $c\text{-}C_6H_{11}$, $4\text{-}MeC_6H_4$, $4\text{-}MeOC_6H_4$, $2,6\text{-}Me_2C_6H_3$, and $2,4,6\text{-}Me_3C_6H_2$; n = 1, 2, or 3), all of which behave as semi-conductors. In particular, $[Rh(PhNC)_4]^+(TCNQ)_2^{\cdot-}$ exhibits a relatively small electrical resistivity (9.3 Ωcm) as compacted samples at 298 K. On the other hand, neutral dimethyldithiocarbamatorhodium(I) complexes are known to react with tetracyanoethylene (TCNE) forming an adduct of the charge-tranfer (CT) type [2]. Thus, the present work was undertaken to synthesize the CT type adducts between neutral rhodium(I) complexes and neutral TCNQ from analogy to the TCNQ–tetrathiafulvalene complex [3, 4].

This paper reports the preparation of the TCNQ salts with dimethyldithiocarbamato- and diethyldithiophosphatobis(aryl isocyanide)rhodium(I), $Rh(dtc)(RNC)_2$ and $Rh(dtp)(RNC)_2$ (dtc = Me_2NCS_2; dtp = $(EtO)_2PS_2$; R = Ph, $4\text{-}MeC_6H_4$, and $4\text{-}MeOC_6H_4$), and their electronic absorption, ESR, and X-ray photoelectron spectra, and electrical resistivities. The binding energies of Rh $3d_{3/2}$ and $3d_{5/2}$ electrons obtained from X-ray photoelectron spectra of the TCNQ salts are discussed in comparing with those of $Rh^{I}L(RNC)_2$, $Rh^{III}L(RNC)_2I_2$, and $RhL(RNC)_2(TCNE)$ (L = dtc and dtp).

Experimental

Materials

Dimethyldithiocarbamatobis(aryl isocyanide)rhodium(I), $Rh(dtc)(RNC)_2$ [2], their tetracyanoethylene adducts, $Rh(dtc)(RNC)_2(TCNE)$ [2], and dimethyldithiocarbamatobis(aryl isocyanide)diiodorhodium(III), $Rh(dtc)(RNC)_2I_2$ [5] (dtc = Me_2NCS_2; R = Ph, $4\text{-}MeC_6H_4$, and $4\text{-}MeOC_6H_4$), were prepared by literature methods.

Diethyldithiophosphatobis(phenylisocyanide)rhodium(I), $Rh(dtp)(PhNC)_2$ (dtp = $(EtO)_2PS_2$), was prepared as follows; to a petroleum ether (b.p. 40–60 °C, 40 cm^3) solution of Rh(dtp)(COD) (COD = 1,5-cyclooctadiene) (1.71 g, 4.3 mmol) was added dropwise to phenylisocyanide (0.89 g, 8.6 mmol) in the same solvent (40 cm^3) with stirring. The mixture was stirred for a further 5 h to give a yellow precipitate of $Rh(dtp)(PhNC)_2$, which was filtered and dried *in vacuo*, 63% yield, m.p. 105–108 °C. *Anal.* Found: C, 43.47. H, 4.11; N, 5.69%. Calcd for $C_{18}H_{20}N_2O_2S_2PRh$: C, 43.74; H, 4.08; N, 5.67%.

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TABLE I. Melting Points and Analytical Data of the Rh–TCNQ Salts.

Salt	M.p. (dec.) °C	Found (Calcd)		
		C	H	N
Rh(dtc)(RNC)$_2$(TCNQ)				
R = Ph	>300	55.02	3.18	15.07
		(54.98)	(3.18)	(15.48)
4-MeC$_6$H$_4$	>300	56.32	3.72	14.31
		(56.28)	(3.66)	(14.82)
4-MeOC$_6$H$_4$	>300	54.10	3.37	14.38
		(53.68)	(3.49)	(14.14)
Rh(dtp)(RNC)$_2$(TCNQ)				
R = Ph	>200	51.78	3.48	12.34
		(51.58)	(3.46)	(12.03)
4-MeC$_6$H$_4$	175–180	53.44	3.80	11.87
		(52.90)	(3.88)	(11.57)
4-MeOC$_6$H$_4$	>175	50.97	3.74	11.37
		(50.67)	(3.72)	(11.08)

The 4-methyl- and 4-methoxyphenylisocyanide analogs, Rh(dtp)(4-MeC$_6$H$_4$NC)$_2$ and Rh(dtp)(4-MeOC$_6$H$_4$NC)$_2$, were prepared similarly in 67 and 83% yields, respectively, by the reactions of Rh(dtp)(COD) with the corresponding isocyanides. Rh(dtp)(4-MeC$_6$H$_4$NC)$_2$, m.p. 108–112 °C. *Anal.* Found: C, 45.98; H, 4.63; N, 5.36%. Calcd for $C_{20}H_{24}N_2O_2S_2PRh$: C, 46.48; H, 4.75; N, 5.53%. Rh(dtp)(4-MeOC$_6$H$_4$NC)$_2$, m.p. 111–115 °C. *Anal.* Found: C, 43.33; H, 4.36; N, 5.05%. Calcd for $C_{20}H_{24}N_2O_4S_2PRh$: C, 43.62; H, 4.40; N, 5.19%.

Diethyldithiophosphatobis(phenylisocyanide)(tetracyanoethylene)rhodium(I), Rh(dtp)(PhNC)$_2$(TCNE), was obtained as follows; to a benzene solution (10 cm^3) of Rh(dtp)(PhNC)$_2$ (0.10 g, 0.20 mmol) was added TCNE (0.026 g, 0.20 mmol), and the mixture was stirred for 2 h. To the solution was added petroleum ether (b.p. 40–60 °C) to yield yellow microcrystals of Rh(dtp)(PhNC)$_2$(TCNE), which were filtered and dried *in vacuo*, 71% yield, m.p. 177–179 °C (decomp.). *Anal.* Found: C, 46.10; H, 3.30; N, 13.38%. Calcd for $C_{24}H_{20}N_6O_2S_2PRh$: C, 46.31; H, 3.24; N, 13.50%. The 4-methylphenylisocyanide analog Rh(dtp)(4-MeC$_6$H$_4$NC)$_2$(TCNE) was obtained similarly in 75% yield by the reaction of TCNE with the corresponding Rh(I) complex in dichloromethane, m.p. 170–172 °C (decomp.). *Anal.* Found: C, 46.66; H, 3.48; N, 14.77%. Calcd for $C_{26}H_{24}N_6O_2S_2PRh \cdot CH_2Cl_2$: C, 46.58; H, 3.31; N, 14.62%.

Diethyldithiophosphatobis(aryl isocyanide)diiodorhodium(III), Rh(dtp)(RNC)$_2$I$_2$ (R = Ph, 4-MeC$_6$H$_4$, and 4-MeOC$_6$H$_4$), was prepared by the same procedure as the case of Rh(dtc)(RNC)$_2$I$_2$.

Preparation of Dimethyldithiocarbamato- and Diethyldithiophosphatobis(aryl isocyanide)(7,7,8,8-tetracyanoquinodimethan)rhodium, RhL(RNC)$_2$(TCNQ) (L = dtc and dtp; R = Ph, 4-MeC$_6$H$_4$, and 4-MeOC$_6$H$_4$)

To a hot acetonitrile solution (110 cm^3) of Rh(dtc)(PhNC)$_2$ (0.44 g, 1.0 mmol) was added neutral TCNQ (0.21 g, 1.0 mmol) in hot acetonitrile (120 cm^3). The mixture was allowed to stand in a refrigerator overnight. The resulting dark brown precipitate of Rh(dtc)(PhNC)$_2$(TCNQ) was filtered and dried *in vacuo*, 49% yield. The 4-methyl- and 4-methoxyphenylisocyanide analogs, Rh(dtc)(4-MeC$_6$H$_4$NC)$_2$(TCNQ) and Rh(dtc)(4-MeOC$_6$H$_4$NC)$_2$(TCNQ), were obtained similarly in 37 and 43% yields respectively by the reactions of TCNQ with the corresponding Rh(I) complexes.

The Rh(dtp)(PhNC)$_2$(TCNQ) salt was prepared by the reaction of neutral TCNQ (0.12 g, 0.6 mmol) with Rh(dtp)(PhNC)$_2$ (0.30 g, 0.60 mmol) in hot tetrahydrofuran (35 cm^3); to the mixture was added petroleum ether (b.p. 40–60 °C, 35 cm^3), giving a dark brown precipitate, which was filtered and dried *in vacuo*, 36% yield. By the same procedure, Rh(dtp)(4-MeC$_6$H$_4$NC)$_2$(TCNQ) and Rh(dtp)(4-MeOC$_6$H$_4$NC)$_2$(TCNQ) were obtained in 54 and 67% yields respectively by the reactions of TCNQ with the corresponding Rh(I) complexes. All the synthetic procedures were carried out under dry nitrogen. Properties and analytical data of the TCNQ salts are listed in Table I.

Physical Measurements

Electrical resistivities, magnetic susceptibilities, and electronic absorption spectra were measured as

TABLE II. Anode Peak Potentials of the Rh(I) Complexes, V *vs.* SCE in Acetonitrile.

R	Rh(dtc)(RNC)$_2$	Rh(dtp)(RNC)$_2$
Ph	0.00	0.64
4-MeC$_6$H$_4$	−0.05	+0.60
4-MeOC$_6$H$_4$	−0.10	+0.56

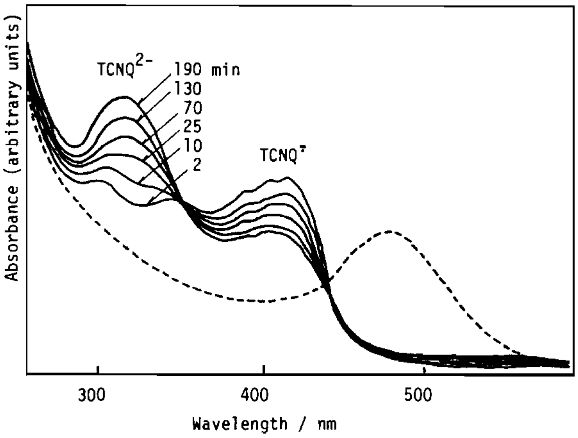

Fig. 1. The spectral change after mixing Rh(dtc)(PhNC)$_2$ and (Bu$^n_4$N)$^+$TCNQ$^{\cdot-}$ (mol ratio 1:1) in degassed acetonitrile at room temperature (——) and the spectrum on exposure of the solution to air in 190 min after mixing (-----).

described previously [6]. Electronic reflectance spectra were recorded on a Hitachi 340 spectrophotometer equipped with a Hitachi NIR (near IR) or R-10A (UV and visible) integrating sphere unit. Cyclic voltammetry measurements were performed in acetonitrile using (Bu$^n_4$N)$^+$ClO$_4^-$ as a supporting electrolyte, as described previously [7]. ESR spectra were measured with a JEOL JES-ME-3X spectrometer. X-Ray photoelectron spectra were obtained by irradiating the compounds with Mg Kα X-rays (250 W) at 223 ± 3 K using a Shimadzu ESCA 650B electron spectrometer, and were calibrated with the photoelectron peak of Au 4f$_{7/2}$ (83.8 eV). The peak shift caused by charge-up effect was corrected with the Si 2s$_{1/2}$ peak (149 eV) [8]. The error of the binding energy determination was estimated to be ±0.2 eV.

Results and Discussion

The cyclic voltammograms of Rh(dtc)(RNC)$_2$ and Rh(dtp)(RNC)$_2$ in acetonitrile at sweep rate 250 mV s^{-1} showed an irreversible anodic current wave with the peak potential in the ranges 0.00 to −0.10 V and 0.64 to 0.56 V *vs.* SCE, respectively (Table II). The irreversibility was evidenced by the fact that the anode peaks shifted to more positive potentials with increasing the sweep rate, with no cathodic wave observed on the reverse scan. On the other hand, the redox potential of TCNQ/TCNQ$^{\cdot}$ is 0.20 V *vs.* SCE in acetonitrile [9], which is close to the anode peak potentials of Rh(dtc)(RNC)$_2$ and Rh(dtp)(RNC)$_2$. This is compatible with the result that the Rh(I) complexes reacted with the neutral TCNQ to give adducts as precipitates in acetonitrile. Moreover, the reaction of the TCNQ$^{\cdot-}$ radical anion with Rh(dtc)(RNC)$_2$ afforded the TCNQ^{2-} dianion, as confirmed by the electronic absorption spectrum of a degassed acetonitrile solution containing equimolar Rh(dtc)(RNC)$_2$ and (Bu$^n_4$N)$^+$TCNQ$^{\cdot-}$, which shows an absorption band at 325 nm characteristic of the TCNQ^{2-} dianion [10] in 190 min after mixing the reactants, as shown in Fig. 1. This is consistent with the redox potential of TCNQ$^{\cdot-}$/TCNQ^{2-} (−0.33 V *vs.* SCE in acetonitrile [9]), rather close to the anode peak potentials of Rh(dtc)(RNC)$_2$. Exposure of the solution to air results in the formation of an absorption band at 480 nm (Fig. 1), assignable to α,α-dicyano-*p*-toluoylcyanide anions which can readily be formed by the reaction of the TCNQ^{2-} dianion and O$_2$ [11]. The formation of TCNQ^{2-} dianion, however, has not been detected in the mixture of Rh(dtp)(RNC)$_2$ and (Bu$^n_4$N)$^+$-TCNQ$^{\cdot-}$ in degassed acetonitrile, as expected from the anode peak potentials of Rh(dtp)(RNC)$_2$ which are positively away from the redox potential of TCNQ$^{\cdot-}$/TCNQ^{2-} (Table II).

Table III lists the binding energies of Rh 3d$_{3/2}$ and Rh 3d$_{5/2}$ electrons obtained from X-ray photoelectron spectra for several types of rhodium complexes. As expected from the oxidative addition of I$_2$ toward the Rh(I) complexes, the photoelectron peaks of Rh^{III}L(RNC)$_2$I$_2$ (L = dtc and dtp) occur in the higher energy regions (313.4–314.0 eV for Rh 3d$_{3/2}$ and 308.7–309.4 eV for Rh 3d$_{5/2}$) than those of Rh^{I}-L(RNC)$_2$ (311.3–312.0 eV for Rh 3d$_{3/2}$ and 306.6–307.3 eV for Rh 3d$_{5/2}$). On the other hand, the binding energies for Rh 3d$_{3/2}$ and 3d$_{5/2}$ electrons of the TCNE adducts (312.7–313.1 and 308.0–308.4 eV, respectively) lie between those of Rh^{I}L(RNC)$_2$ and of Rh^{III}L(RNC)$_2$I$_2$. This result indicates an important contribution of the CT from the Rh(I) moiety to TCNE. The TCNQ salts also show the peaks due to Rh 3d$_{3/2}$ and 3d$_{5/2}$ electrons in almost the same energies as those of the TCNE adducts. In the TCNQ adducts, therefore, TCNQ may be reduced by Rh(I) to exist essentially as a radical anion. This is compatible with the fact that the adducts exhibited electronic absorption bands assignable to the TCNQ$^{\cdot}$ radical anion in acetonitrile, as described later, and the ESR signal due to TCNQ$^{\cdot}$ in the solid state.

TABLE III. Binding Energies (eV) Observed in X-ray Photoelectron Spectra of the Rhodium Complexes.

R Complex	Ph		4-MeC$_6$H$_4$		4-MeOC$_6$H$_4$	
	Rh 3d$_{3/2}$	Rh 3d$_{5/2}$	Rh 3d$_{3/2}$	Rh 3d$_{5/2}$	Rh 3d$_{3/2}$	Rh 3d$_{5/2}$
Rh(dtc)(RNC)$_2$	311.6	306.9	311.3	306.6	311.7	306.9
Rh(dtc)(RNC)$_2$I$_2$	313.6	308.9	313.6	309.0	313.4	308.7
Rh(dtc)(RNC)$_2$(TCNE)	312.7	308.0	312.9	308.3		
Rh(dtc)(RNC)$_2$(TCNQ)	313.0	308.4	312.8	308.2	312.7	308.2
Rh(dtp)(RNC)$_2$	311.9	307.2	311.8	307.3	312.0	307.3
Rh(dtp)(RNC)$_2$I$_2$	313.7	309.0	314.0	309.4	313.6	308.9
Rh(dtp)(RNC)$_2$(TCNE)	312.9	308.3	313.1	308.4		
Rh(dtp)(RNC)$_2$(TCNQ)	313.2	308.7	313.1	308.6	313.1	308.5

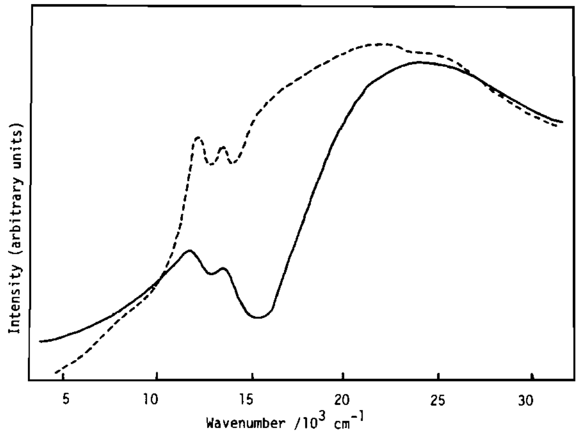

Fig. 2. Electronic reflectance spectra of Rh(dtc)(PhNC)$_2$(TCNQ) (———) and Rh(dtp)(PhNC)$_2$(TCNQ) (------).

TABLE IV. Magnetic Susceptibility (χ_M), Electrical Resistivity (ρ), and Activation Energy (E$_a$) of the Rh–TCNQ Salts.

Salt	χ_M^{a} emu mol^{-1}	ρ_{298K} Ω cm	E$_a$ eV
Rh(dtc)(RNC)$_2$(TCNQ)			
R = Ph	-2.2×10^{-4}	1.3×10^{11}	0.62
4-MeC$_6$H$_4$	-1.7×10^{-4}	2.0×10^{9}	0.42
4-MeOC$_6$H$_4$	-0.76×10^{-4}	4.7×10^{10}	0.69
Rh(dtp)(RNC)$_2$(TCNQ)			
R = Ph	-1.2×10^{-4}	4.8×10^{9}	0.39
4-MeC$_6$H$_4$	-0.21×10^{-4}	8.0×10^{9}	0.38
4-MeOC$_6$H$_4$	-3.0×10^{-4}	1.1×10^{10}	0.49

^{a}Measured at room temperature.

Thus, the rhodium moiety should be oxidized to the Rh(II) state. There has, however, been found no ESR signals due to the Rh(II) species. This is probably because the Rh(II) species exist as a dimer with Rh(II)–Rh(II) bonding, as reported for [(4-MeC$_6$H$_4$NC)$_8$Rh$_2^{II}$I$_2$][PF$_6$]$_2$ [11] and [Rh$_2^{II}$(1,3-diisocyanopropane)$_4$Cl$_2$]Cl$_2$·8H$_2$O [12].

Figure 2 illustrates the electronic reflectance spectra of Rh(dtc)(PhNC)$_2$(TCNQ) and Rh(dtp)(PhNC)$_2$(TCNQ), both of which display two bands around 12000 cm^{-1} assignable to transitions to the first locally-excited state of the TCNQ$^{\bar{\cdot}}$ radical anion (LE$_1$) [13]. Broad bands in the 20000–25000 cm^{-1} region may be contributed not only from the second locally-excited state of the TCNQ$^{\bar{\cdot}}$ radical anion (LE$_2$, usually observed in 20000–25000 cm^{-1}) [13], but also from a long tail of the metal-to-ligand CT band of Rh(dtc)(PhNC)$_2$ or Rh(dtp)(PhNC)$_2$ (around 25000 cm^{-1}). Similar spectra were observed in other TCNQ salts obtained here.

Table IV lists the magnetic susceptibilities (χ_M) and the specific resistivities of the TCNQ salts as compacted samples at 298 K (ρ_{298K}), together with the activation energies (E$_a$) calculated from the equation $\rho = \rho_0 \exp(E_a/kT)$. All the salts exhibit weak diamagnetisms. Thus, the TCNQ$^{\bar{\cdot}}$ radical anions may interact so weakly with each other that no CT band between TCNQ$^{\bar{\cdot}}$ radical anions with an appreciable intensity has been observed. The TCNQ salts obtained here behave as typical semi-conductors in the temperature range measured (293–373 K). The ρ_{298K} values, however, are very large (of the order of 10^9–10^{11} Ω cm), suggesting that the TCNQ moiety assumes no columnar structure.

An equimolar mixture of fine powdered neutral TCNQ and Rh(dtc)(PhNC)$_2$, prepared by grinding

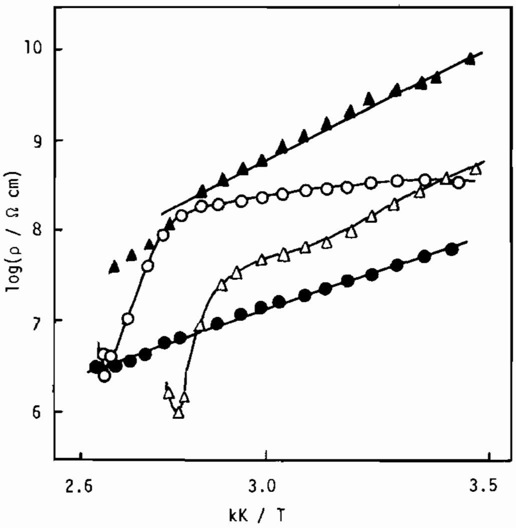

Fig. 3. Temperature dependences of the specific resistivities of an equimolar mixture of $Rh(dtc)(PhNC)_2$ and TCNQ (compacted samples) on the initial heating (○) and on heating after the solid phase reaction (●), and of an equimolar mixture of $Rh(dtp)(PhNC)_2$ and TCNQ (compacted samples) on the initial heating (△) and on heating after the solid phase reaction (▲).

in an agate mortar, exhibited the $\rho_{298 K}$ value of 3.8×10^8 Ω cm as compacted samples. Temperature dependence of the specific resisitivity of the mixture (compacted samples) is shown by open circles in Fig. 3, which indicates an abrupt decrease of the electrical resistivity around 355 K on elevating the temperature. After cooling down to room temperature, it behaves as a typical semi-conductor, as shown by closed circles in Fig. 3; $\rho_{298 K} = 6.5 \times 10^7$ Ω cm and $E_a = 0.32$ eV. The abrupt decrease of the resistivity on heating may, therefore, be due to the solid phase reaction between $Rh(dtc)(PhNC)_2$ and TCNQ. The resistivity of $Rh(dtc)(PhNC)_2(TCNQ)$ thus obtained in the solid phase reaction is smaller by four order of magnitude than that prepared by the reaction in solution. In addition, the electronic reflectance spectrum of this sample exhibited a weak broad band around 7000 cm^{-1}, characteristic of the coupled $TCNQ^{\cdot}$ radical anion [13], suggesting the presence of at least a partial columnar structure of the $TCNQ^{\cdot}$ radical anion. An analogous solid phase reaction is observed around 340 K between $Rh(dtp)(PhNC)_2$ and TCNQ, as shown in open triangles in Fig. 3. The resulting product, however, displays almost the same temperature dependence of the resistivity (see closed triangles) as $Rh(dtp)(PhNC)_2(TCNQ)$ obtained by the reaction in solution.

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