Tetragonal Co-ordination Polymers of Rhodium(I) with Stereochemically Rigid Aryl Di-isocyanide Linkages‡

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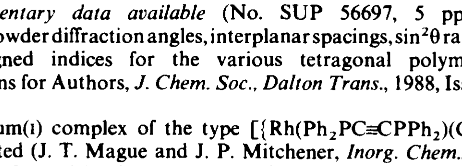
Tetragonal polymers of the type $\{[Rh(L)_2]Cl\}_n$ with stacked layer ($Rh^I \cdots Rh^I$ 3.31—3.41 Å) structures have been prepared by the reaction of $[\{Rh(CO)_2Cl\}_2]$ with the polymerizing ligands (L) 1,4-di-isocyanobenzene, 1,4-di-isocyanonaphthalene, 4,4'-di-isocyanobiphenyl, 2,4-di-isocyanotoluene, bis(4-isocyanophenyl)methane, or 1,5-di-isocyanonaphthalene. The new materials have been characterized by elemental analysis, thermal gravimetric analysis, i.r. and diffuse-reflectance spectra, as well as from their *X*-ray powder diffraction patterns.

Much attention has been focused during the past decade on the study of polymer-supported metal complexes.[1] Supported systems of such types are generally prepared by the chemical bonding or adsorption of metal complexes to the existing backbone of various polymers. In this regard, the anchored metal complex may be viewed as a substituent since it is not an integral part of the polymeric backbone. In contrast with polymer-supported metal complexes, co-ordination polymers represent an entirely different class of metal-containing polymers, where the metal constitutes an integral part of the polymeric network. The polymerization of mononuclear metal complexes through non-chelating bidentate bridging ligands provides a conceivable synthetic route to co-ordination polymers. These requirements of the bridging ligand, although essential, are by themselves insufficient to effect the polymerization of mononuclear complexes. For example, the co-ordination chemistry of bis(diphenylphosphino)acetylene, a typical non-chelating bidentate ligand, revealed the formation of a variety of mono- di-, tri-, and tetra-bridged dinuclear complexes[2] and the absence of any polymeric materials.§ These dinuclear complexes represent systems of low-energy surfaces whose preferred formation is most probably the result of the low-energy barrier of rotation around the P–C bonds in $Ph_2PC{\equiv}CPPh_2$. Ligands of the type bis(diphenylphosphino)acetylene may be termed as stereochemically non-rigid linkages, since the low-energy barrier of rotation around the P–C bonds would dictate an infinite number of relative orientations for M and M', see (I).



(I)

In order to force the formation of co-ordination polymers it was thought necessary to confine the degrees of freedom of the bridging ligand, and this led to the formulation of the stereochemical rigidity requirement which defines the fixed spatial relationship between the metal sites of the co-ordinated linkage. For example, the interaction of non-chelating stereochemically rigid bidentate ligands capable of forming collinear linkages with the co-ordination symmetries $D_{\infty h}$, D_{4h}, and T_d of metals provides a conceivable route to well defined one-, two-, and three-dimensional co-ordination polymers of the type $[\{M(bridge)_m\}_n]$, where $m = 1$, 2, or 3 (pentagonal dodecahedron), respectively. This approach to co-ordination polymers, which incorporates molecular design concepts, is of interest from the standpoint of the development of unconventional polymeric materials with 'tailor-made' properties. Parts of this investigation have been previously reported in preliminary communications.[3–5]

Results and Discussion

Neutral rhodium(I) complexes such as $[\{Rh(CO)_2Cl\}_2]$ and $[\{Rh(cod)Cl\}_2]$ (cod = cyclo-octa-1,5-diene) have been observed to undergo facile exchange reactions with monoisocyanides to afford cationic complexes of the type $[Rh(CNR)_4]^+$, which oligomerize through weak intermetallic interactions to form the polynuclear cations $[\{Rh(CNR)_4\}_n]^{n+}$.[6] For instance, the geometry of $[\{Rh(CNR)_4\}_2]^{2+}$ was shown to be staggered with R = Ph[7] and eclipsed with R = 4-nitrophenyl[8] or 4-fluorophenyl.[8] Another example of an eclipsed configuration was reported[9] in the 'windmill' shaped cationic complex $[Rh_2(CNCH_2CH_2CH_2CH_2NC)_4]^{2+}$. Therefore, anticipating similar co-ordination chemistry with aryl di-isocyanides, the preparation of some rhodium(I) polymers with stereochemically rigid linkages was carried out by reacting $[\{Rh(CO)_2Cl\}_2]$ with various di-isocyanides(L) (Table 1) in CH_2Cl_2 at 25 °C. The dark insoluble products formed were filtered off, washed extensively with CH_2Cl_2, and then vacuum dried (80—100 °C/0.1 Torr). The elemental analyses revealed a ligand-to-metal ratio in the range 2 ± 0.15 and these results appear to be consistent with the presence of extended polymeric networks. The approximation formula of the products will henceforth be considered as $\{[Rh(L)_2]Cl\}_n$. Evidence in support of this stoicheiometry was also obtained by measuring gas evolution during their formation. Carbon monoxide evolution was monitored with the aid of a gas burette. Accordingly, carbon monoxide evolution stops at a point where the molar amount of the added ligand is about equal to that of the released gas. These experiments also revealed a facile replacement process by which the polymers are quantitatively formed according to equation (1) (L = di-

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‡ *Supplementary data available* (No. SUP 56697, 5 pp.): table of *X*-ray powder diffraction angles, interplanar spacings, $\sin^2\theta$ ratio terms, and assigned indices for the various tetragonal polymers. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii–xx.

§ A rhodium(I) complex of the type $[\{Rh(Ph_2PC{\equiv}CPPh_2)(CO)Cl\}_n]$ was reported (J. T. Mague and J. P. Mitchener, *Inorg. Chem.*, 1969, **8**, 119) to be formed in the reaction of $[\{Rh(CO)_2Cl\}_2]$ with the $Ph_2PC{\equiv}CPPh_2$. On the basis of its limited solubility the value of n in this complex was suggested to be greater than 2. The possibility of $n \longrightarrow \infty$ in this system is rather unlikely. A more realistic structure in this system is that of a low (n = 3 or 4) cyclic oligomer.

Table 1. Idealized parameters of certain stereochemically rigid non-chelating di-isocyanide linkages co-ordinated to rhodium(I)

Linkage	Co-ordinated linkage parameters Geometry	s^a/Å	α^b/°	d^c/Å
1,4-Di-isocyanobenzene	Collinear	11.79	—	—
1,4-Di-isocyanonaphthalene	Collinear	11.79	—	—
4,4′-Di-isocyanobiphenyl	Collinear	16.07	—	—
1,3-Di-isocyanobenzene	Bent	10.21	120	—
2,4-Di-isocyanotoluene	Bent	10.21	120	—
Bis(4-isocyanophenyl)methane	Bent	14.35	109	—
1,5-Di-isocyanonaphthalene	*anti*-parallel	12.24	—	2.42
1,8-Di-isocyanonaphthalene	*syn*-parallel	2.42	—	2.42

[a] Bridge span. [b] Angle between vectors in bent linkages. [c] Separation between vectors in parallel linkages.

Table 2. Selected physical data of $\{[Rh(L)_2]Cl\}_n$[a]

L	T.g.a. Decomp. (°C)	I.r. ν(NC)/cm^{-1}	Diffuse-reflectance (nm)	
1,4-Di-isocyanobenzene	425	2 140	400	660
1,4-Di-isocyanonaphthalene[b]	~300	2 040		
4,4′-Di-isocyanobiphenyl	410	2 135	410	660
1,3-Di-isocyanobenzene	380	2 145	400	725
2,4-Di-isocyanotoluene[b]	372	2 143		
Bis(4-isocyanophenyl)methane	460	2 143	445	730
1,5-Di-isocyanonaphthalene	320	2 039	410	685

[a] Dark green materials, except in the instance of the bis(4-isocyanophenyl)methane polymer, which is brown. [b] The diffuse-reflectance spectrum of this polymer was not measured.

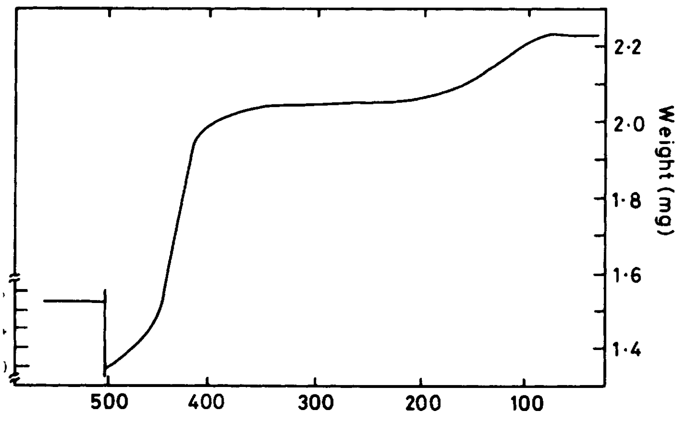

Figure 1. Thermal gravimetric analysis of a typical $\{[Rh(L)_2]Cl{\cdot}xH_2O\}_n$ polymer with 4,4′-di-isocyanobiphenyl linkages and x = 2.53; a change of scale is indicated on the left

isocyanide). The co-ordination polymers under review do not contain co-ordinated carbonyl groups, as evidenced by the absence of ν_{CO} in their i.r. spectra.

$$\frac{n}{2}[\{Rh(CO)_2Cl\}_2] + 2nL \longrightarrow \{[Rh(L)_2]Cl\}_n\downarrow + 2n\,CO\uparrow \quad (1)$$

A noteworthy feature of the polymers is connected with their ability to absorb water when exposed to air. Therefore, they are best formulated as $\{[Rh(L)_2]Cl{\cdot}xH_2O\}_n$ unless they are rigorously dried. The presence of water is evident from their elemental analyses, and the degree of hydration was established by thermal gravimetric analysis (t.g.a.) measurements. A typical t.g.a. measurement is shown for the 4,4′-di-isocyanobiphenyl polymer $\{[Rh\{(C_6H_4NC\text{-}p)_2\}_2]Cl{\cdot}2.53H_2O\}_n$ in Figure 1. Water release in this instance is encountered in the temperature range 100—200 °C, and its thermal decomposition starts above 400 °C. In addition, the percentage weight of the residue in this experiment (~28%) is the approximate sum of the rhodium and chloride contents (~26%) as obtained from elemental analysis (see Experimental section). Although the degree of hydration may vary from one sample to another, the maximum hydration (see Experimental section) may suggest some correlation between the porosity and the water content.*

The i.r. and diffuse-reflectance spectra of a typical rhodium(I) polymer, $\{[Rh\{(C_6H_4NC\text{-}p)_2\}_2]Cl\}_n$, are shown in Figure 2. The spectral data for the other polymers are given in Table 2. The presence of terminally co-ordinated di-isocyanide linkages is quite evident from the positions of the ν_{CN} stretching frequencies. Since the local symmetry of each metal centre is that of D_{4h}, this should give rise to just one strong ν_{CN} band, as indeed was observed [Figure 2(*a*)]. The diffuse-reflectance spectra consist of absorptions centred at 420 ± 25 and 700 ± 40 nm. The former absorption is relatively narrow whereas the latter consists of a rather broad envelope. The spectral features of the polymers, which are illustrated by comparison with the spectrum of TiO_2 in Figure 2(*b*), are noteworthy. The strong absorption in the visible range (~700 nm) could, perhaps, be accounted for by the presence of extensive columnar metal chains and highly porous geometries which would allow for light penetration beyond the external surfaces. The gross electronic spectral features of these polymers are similar to those reported[9] for oligomers of the type

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* The maximum water content in polymers with a long bridge span [*e.g.* 4,4′-di-isocyanobiphenyl or bis(4-isocyanophenyl)methane] was in general found to be greater than that of the shorter-span polymers (*e.g.* 1,4-di-isocyanobenzene, 1,3-di-isocyanobenzene, or 1,5-di-isocyanonaphthalene). The addition of substituents to the linkages in the polymers (*e.g.* 2,4-di-isocyanotoluene or 1,4-di-isocyanonaphthalene) further reduces their ability to absorb water.

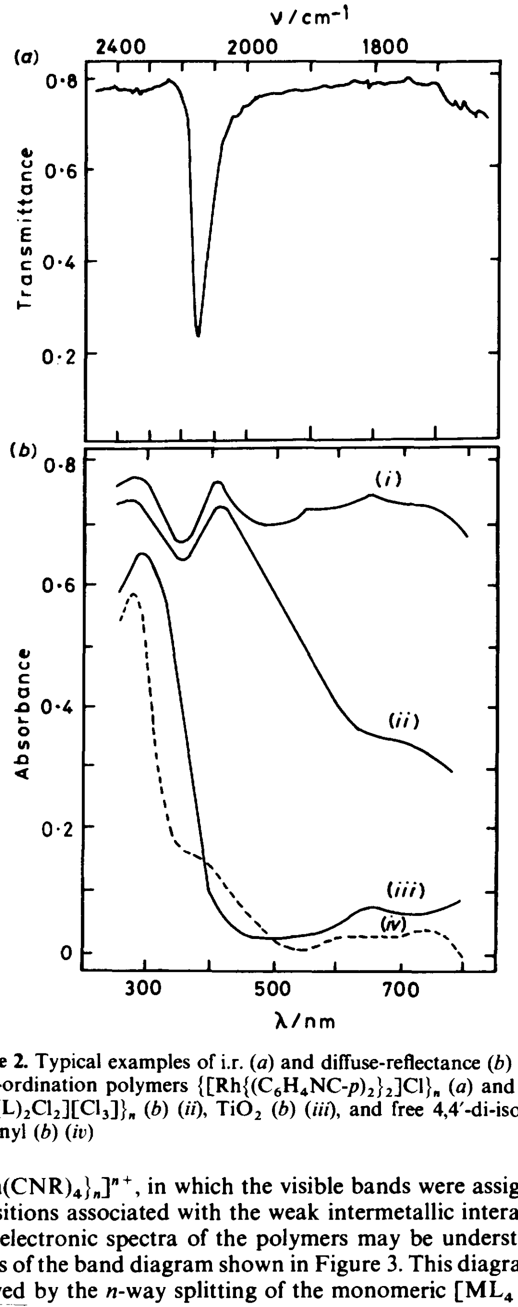

Figure 2. Typical examples of i.r. (*a*) and diffuse-reflectance (*b*) spectra of co-ordination polymers $\{[Rh\{(C_6H_4NC\text{-}p)_2\}_2]Cl\}_n$ (*a*) and (*b*) (*i*), $\{[Rh(L)_2Cl_2][Cl_3]\}_n$ (*b*) (*ii*), TiO_2 (*b*) (*iii*), and free 4,4′-di-isocyano-biphenyl (*b*) (*iv*)

$[\{Rh(CNR)_4\}_n]^{n+}$, in which the visible bands were assigned to transitions associated with the weak intermetallic interactions. The electronic spectra of the polymers may be understood in terms of the band diagram shown in Figure 3. This diagram was derived by the *n*-way splitting of the monomeric $[ML_4\ (D_{4h})]$ a_{1g}(h.o.m.o.) and a_{2u}(l.u.m.o.) levels (highest occupied and lowest unoccupied molecular orbitals, respectively) of a supposedly isolated columnar metal chain section $[(ML_4)_n$-eclipsed$]$ of the polymers. The bonding (d_{z^2}) and antibonding ($p_{z-\pi^*}$) bands are comprised of *n*-filled (2*n* electrons) and empty levels, respectively. These high-energy transitions appear to be of comparable energies to those assigned as $^1A_{1g} \longrightarrow {}^1A_{2u}$ in the spectra of the mononuclear complexes $[Rh(CNR)_4]^+$ ($\sim$410 nm).[7] It therefore would seem that the high-energy band at 420 nm in the spectra of the polymers may possibly be due to some terminal 'dangling' $[Rh(L)_4]^+$ moieties. The wide envelope of low-energy transitions are most probably due to transitions associated with the band-gap. This may be viewed as resulting from a multitude of transitions occurring between the upper region of the bonding and the lower region of the antibonding bands. According to this spectral interpretation, the breaking of intermetallic bonding interactions should only affect the low-energy transitions.

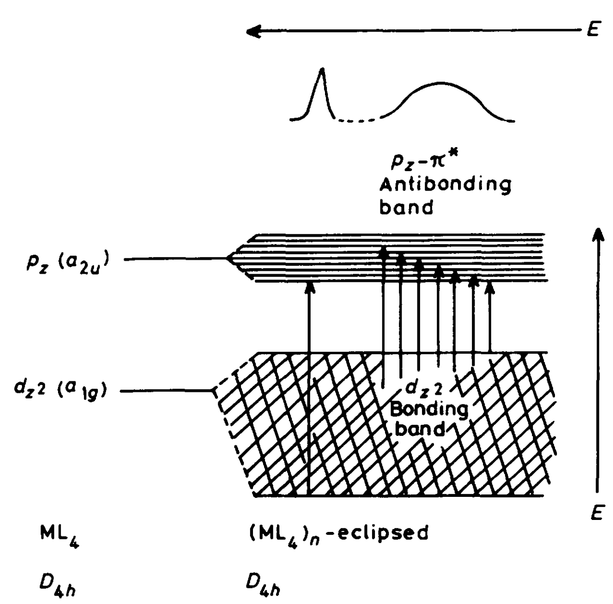

Figure 3. Proposed band diagram and its relationship to the electronic spectrum for tetragonal polymers of the type $\{[Rh(L)_2]Cl\}_n$

Metal–metal bond breaking processes in such a system may be accomplished with the aid of oxidative-addition reactions. The chlorination of the suspended $\{[Rh\{(C_6H_4NC\text{-}p)_2\}_2]Cl\}_n$ polymer in a CH_2Cl_2 solution gave, after isolation in air, a highly hydrated product of the approximate composition $\{[Rh(L)_2]Cl_3{\cdot}8.6H_2O\}_n$ whose i.r. spectrum shows a ν_{CN} band at 2 205 cm^{-1}.

It may be suggested that the extra chlorine atoms chlorinate the aromatic rings rather than form a Cl_3^- anion or ClI_2^- and $ClBr_2^-$ anions in the case of iodinations and brominations, respectively. However, in the case of the iodinated polymers, anion exchange with anions not containing iodine, *i.e.* PF_6^-, have shown significant decreases in the percentages of iodine in the exchanged polymers as indicated by elemental analyses. This should not have occurred if iodination of the aromatic rings had taken place. We therefore believe that the excess halogen forms part of the complex anion. However, even after anion exchange, elemental analyses have indicated slight excesses of iodine compared to that expected theoretically if only two iodine atoms per metal have been oxidatively added. This is undoubtedly due to incomplete anion exchange, a phenomenon already observed with the unoxidized polymers.[10] Most probably the chlorinated and brominated polymers behave similarly towards anion exchange. The formation of mixed-halogen anions of this type are known for large cations.[11]

The shift in ν_{CN} compared with that observed for the starting polymer (2 135 cm^{-1}) is consistent with the expected change for a complete oxidative-addition reaction in this system. The diffuse-reflectance spectrum of the chlorine oxidized polymer [Figure 2(*b*)] shows a significant drop in absorption in the visible region. However, the high-energy band is quite similar in position and width to that found in the starting polymer. Alternatively, this band, although at somewhat lower energy ($\sim$420 nm), may possibly be due to the $\sigma \longrightarrow \sigma^*$ transitions ($\sim$338 nm) of Rh^{II}–Rh^{II} units. These units have been known to form in binuclear complexes.[9] The bromination and iodination of $\{[Rh\{(C_6H_4NC)_2\}_2]Cl\}_n$ gave similar results. These findings appear to be consistent with the band diagram interpretation of the electronic spectra of the rhodium(I) polymers.

The solution spectra (u.v.) of the reaction used to prepare the polymers was also examined during the course of this study.

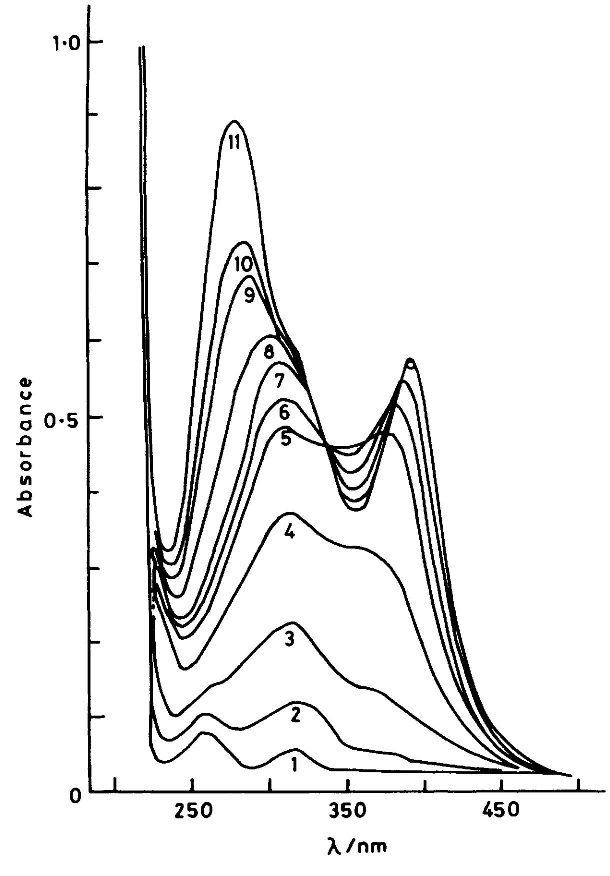

Figure 4. U.v. spectral changes during the titration of a CH_2Cl_2 solution (500 cm^3) of $[\{Rh(CO)_2Cl\}_2]$ (2.58×10^{-5} mol dm^{-3}) with a solution of 4,4′-di-isocyanobiphenyl (2.45×10^{-3} mol dm^{-3}) in the same solvent [titration points (cm^3 of ligand solution added, ligand-to-metal molar ratio): 1(0, 0); 2(2, 0.19); 3(6, 0.57); 4(10, 0.95); 5(15, 1.33); 6(18, 1.71); 7(20, 1.90); 8(24, 2.28); 9(28, 2.66); 10(30, 2.85); 11(35, 3.32)]

This was accomplished by monitoring the u.v. spectral changes during the titration of a dilute CH_2Cl_2 solution (2.58×10^{-5} mol dm^{-3}) of $[\{Rh(CO)_2Cl\}_2]$ with that of the di-isocyanide (2.45×10^{-3} mol dm^{-3}) in the same solvent. High dilution conditions were necessary in order to prevent the precipitation of polymers. The results of a typical experiment with the polymerizing ligand 4,4′-di-isocyanobiphenyl are shown in Figure 4. The new bands observed at ~300 and ~400 nm are found in similar positions to those assigned to $^1A_{1g} \longrightarrow {}^1E_u$ and $^1A_{1g} \longrightarrow {}^1A_{2u}$, respectively, in the spectra of the cationic $[Rh(CNR)_4]^+$ complexes.[7] The free polymerizing ligand band (~270 nm) starts to appear in this titration only beyond the equimolar amount required for the formation of $\{[Rh\{(C_6H_4NC)_2\}_2]Cl\}_n$. The results of this titration are consistent with the stoicheiometry of the reaction given by equation (1). In the absence of any bands in the visible region during the course of this titration, it may be concluded that sufficiently soluble oligomers are formed through the linking ligand rather than by intermetallic interactions. The spectral changes in the visible region were examined from a similar titration conducted with a higher initial concentration of $[\{Rh(CO)_2Cl\}_2]$ (2.58×10^{-3} mol dm^{-3}). The results shown in Figure 5 revealed low-intensity absorptions at ~600 and ~750 nm. The former absorption is observed at ligand-to-metal molar ratios of 1.4—1.8. The latter is the only visible band observed when the molar ratio reaches or exceeds the value of two. If considered in the context of the reported[7] spectral features of $[\{Rh(CNPh)_4\}_n]^{n+}$, the 600 and 750 nm absorptions appear in the regions assigned for di- and tri-nuclear oligomers, respectively. These results may suggest the beginning of metal $\cdots$ metal bond formation in solution at the concentration levels defined by the experimental details of this titration (Figure 5). Attempts further to follow this process by utilizing initial concentrations of $[\{Rh(CO)_2Cl\}_2]$ higher than those given in Figure 5 were unsuccessful due to the precipitation of the polymeric product.

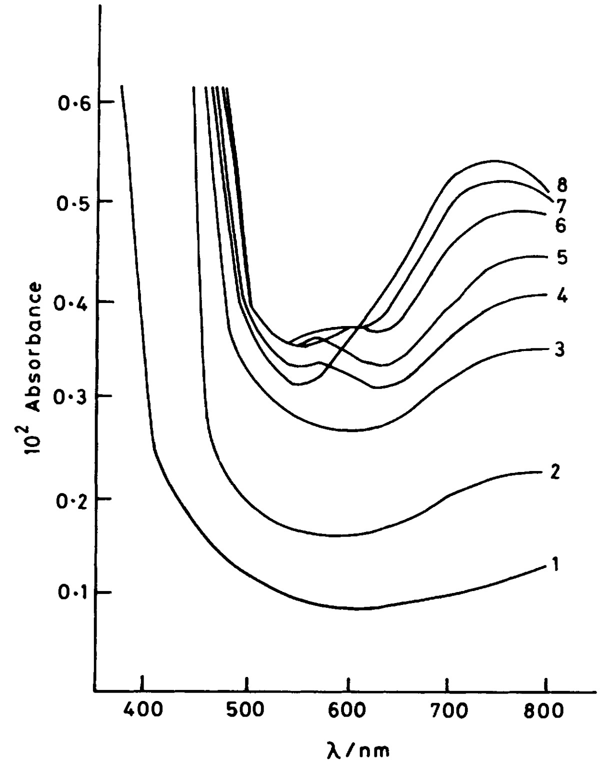

Figure 5. Visible spectral changes during the titration of a CH_2Cl_2 solution of $[\{Rh(CO)_2Cl\}_2]$ (2.58×10^{-3} mol dm^{-3}) with a solution of 4,4′-di-isocyanobiphenyl (2.45×10^{-3} mol dm^{-3}) in the same solvent [titration points (ligand-to-metal molar ratio): 1(0.2); 2(0.5); 3(1.0); 4(1.4); 5(1.6); 5(1.6); 6(1.8); 7(2.0); 8(2.5)]

These polymers are polycrystallinic substances which are insoluble in either polar or non-polar solvents. Attempts to grow single crystals have not been successful. While the symmetry properties of common organic and organometallic crystals are generally extended by intermolecular non-bonding packing forces, the situation in organized co-ordination polymers requires the attainment of order *via* intramolecular bonding forces. The dissolution of a common crystal constitutes a facile process by which the weak non-bonding contacts are being disrupted in favour of a disordered solution state. On the other hand, the dissolution of an organized co-ordination polymeric matrix would require the breaking of chemical bonds and this process may only take place at the expense of decomposition.

However, *X*-ray powder diffraction techniques were found to be particularly useful in the context of this study. The eclipsed stacking of two-dimensional co-ordination polymers of the types considered in Figures 6—8 should result in the formation of tetragonal P_4 rhodium-atom systems. An *X*-ray powder diffraction pattern originating from the heavy metal-atom tetragonal system should be easily detectable by a fast-scan diffractometric trace technique or with a Debye–Scherrer

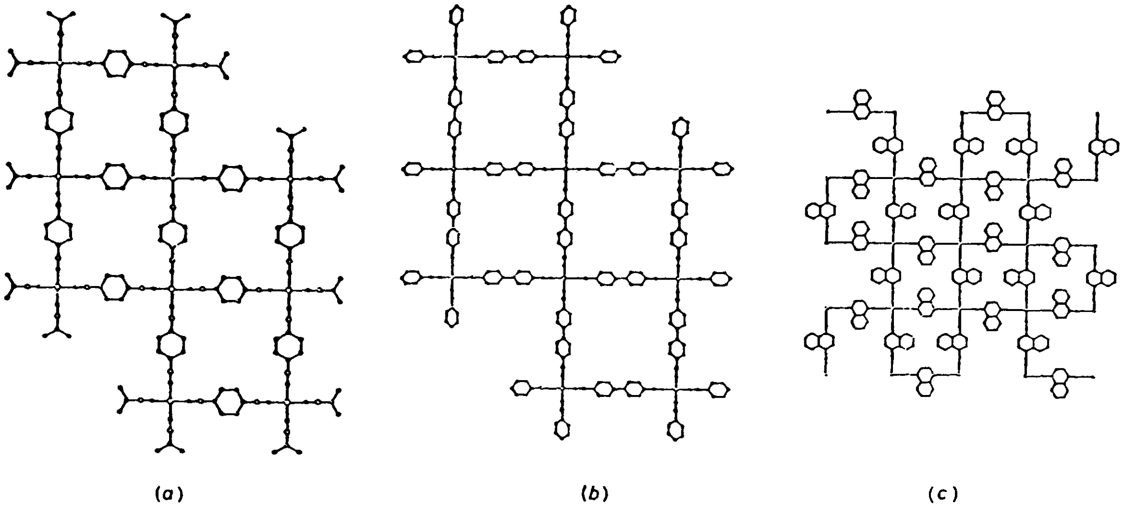
(*a*) (*b*) (*c*)

Figure 6. Idealized two-dimensional molecular models of the $\{[Rh(L)_2]\}_n$ networks in tetragonal rhodium(I) polymers with the collinear linkages 1,4-di-isocyanobenzene (*a*), 4,4′-di-isocyanobiphenyl (*b*), or 1,4-di-isocyanonaphthalene (*c*)

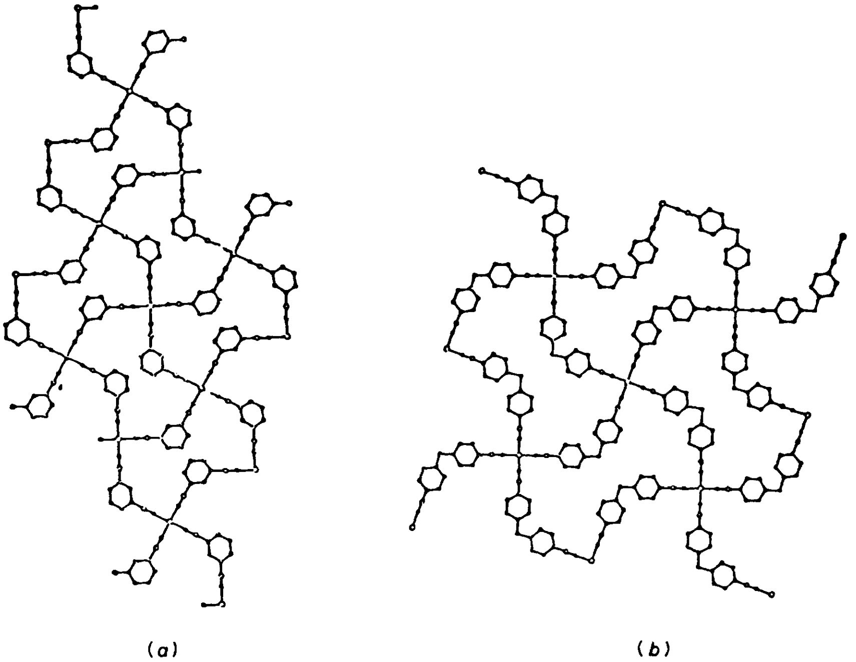
(*a*) (*b*)

Figure 7. Two-dimensional molecular models of the $\{[Rh(L)_2]\}_n$ networks in tetragonal rhodium(I) polymers with the bent linkages 1,3-di-isocyanobenzene (*a*) or bis(4-isocyanophenyl)methane (*b*)

camera. The gross structural features of such tetragonal matrices may be determined by locating the metal sites, in view of the stereochemical rigidity of the bridging linkages in the polymers. For instance, the distance between adjacent metals in the matrix should correspond to either the ligand bridge span or the weak $Rh^I \cdots Rh^I$ interactions for which good estimates are available.

The diffraction trace data of several co-ordination polymers of the type $\{[Rh(L)_2]Cl\}_n$ with the linkages 1,4-di-isocyanobenzene, 1,4-di-isocyanonaphthalene, 4,4′-di-isocyanobiphenyl, 1,5-di-isocyanonaphthalene, 2,4-di-isocyanotoluene, or bis(4-isocyanophenyl)methane are available in Supplementary Publication No. SUP 56697.* Interpretation[12] of the diffraction data is consistent with the presence of tetragonal co-ordination polymers. The diffractometric trace data of a similar polymer with 1,3-di-isocyanobenzene linkages, which has not yet been satisfactorily resolved, is detailed in the Experimental section. Noteworthy are the relationships between the bridge span of linkages and the cell dimensions in the well resolved polymers. The model-derived two-dimensional unit cells for the co-ordination polymers with 1,4-di-isocyanobenzene [Figure 6(*a*)], 4,4′-di-isocyanobiphenyl [Figure 6(*b*)] or 1,5-di-isocyanonaphthalene (Figure 8) may be obtained by presuming $a(= b) = d(100)$ = bridge span. On the other hand, the linkage geometries in the instances of 1,4-di-isocyanonaphthalene [Figure 6(*c*)], 1,3-di-isocyanobenzene [Figure 7(*a*)], or bis(4-isocyano-

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* The data presented in SUP No. 56697 are more complete and refined than those previously communicated (see refs. 3—5).

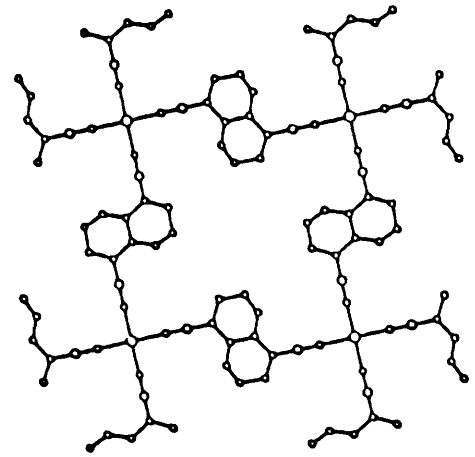

Figure 8. Two-dimensional molecular model of the $\{[Rh(L)_2]\}_n$ network in the tetragonal rhodium(I) polymer with the *anti* parallel linkage 1,5-di-isocyanonaphthalene

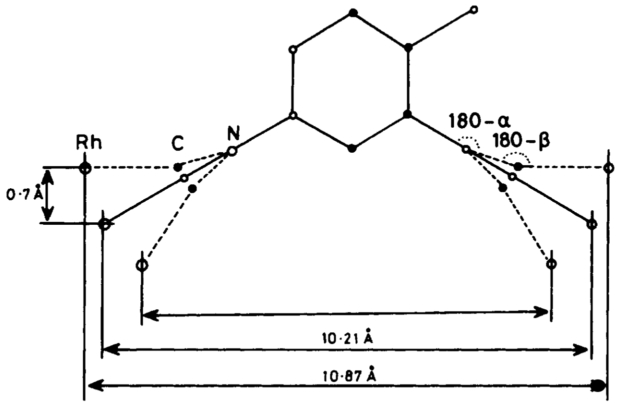

Figure 9. Bridge span in the terminally co-ordinated 2,4-di-isocyanotoluene polymers [theoretically calculated (10.21 Å) and experimentally determined (10.87 Å)]

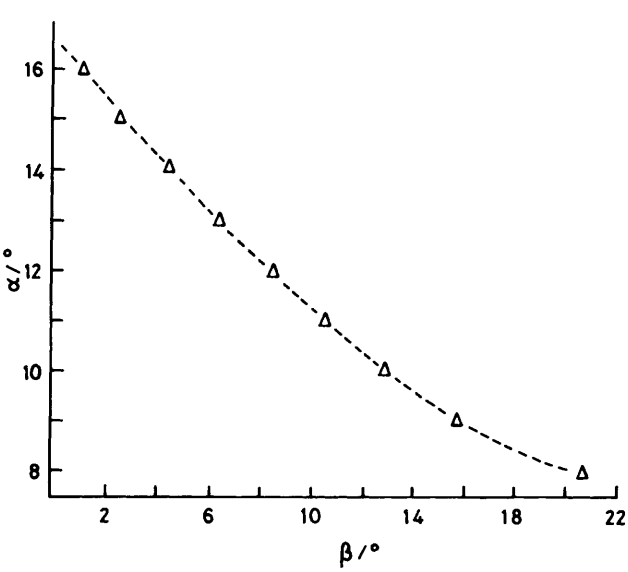

Figure 10. Complementary angles (α and β) calculated[15] for the terminally co-ordinated isocyanide groups of the 2,4-di-isocyanotoluene linkages in $\{[Rh\{MeC_6H_3(NC)_2\text{-}2,4\}_2]Cl\}_n$

phenyl)methane [Figure 7(*b*)], make it necessary to postulate unit cells where $a(= b) = d(110) \times [\sin\theta(110)/\sin\theta(100)]$ and $d(110)$ = bridge span. The experimentally determined cell dimensions (SUP No. 56697) reveal that these assignments are essentially correct with just one exception, that of the 1,4-di-isocyanonaphthalene polymer. The alternatively oriented benzo moieties in this polymer appear to produce a negligible symmetry effect on the two-dimensional unit cell which was found to be similar to that of the 1,4-di-isocyanobenzene polymer. The experimentally determined bridge spans in polymers where $a(= b) = d(100)$ are found to be some 4.1—6.6% shorter compared with the respective model-calculated terms (Table 1). By contrast, the experimentally-determined bridge spans of the polymers where $a(= b) = d(100) \times [\sin\theta(110)/\sin\theta(100)]$ are found to be some 8.7—11.3% longer than the respective model-derived terms. These effects imply the presence of non-idealized Rh–C–N–C bond angles in the real polymers. In general, this feature is well documented from the single-crystal *X*-ray structural data of many terminally co-ordinated monoisocyanide complexes.[7,8,*] In the context of the current study of polymers with terminally co-ordinated collinear di-isocyanide linkages, the development of such angles would account for the observed shortening of the bridge spans. This shortening may also be anticipated for polymers with anti-parallel linkages and this effect was indeed observed in the instance of the 1,5-di-isocyanonaphthalene polymer. A special situation with respect to the length of the bridge span exists for polymers with bent linkages, since the development of Rh–C–N–C bond angles may account for both its elongation or reduction, depending on the motion (Figure 9). Comparison between the respective model-calculated (Table 1) and experimentally determined (SUP No. 56697) terms may suggest the preferred elongation of the bridge span in polymers with bent linkages. Bridge-span elongation in the instances of the bent linkage polymers with 1,3-di-isocyanobenzene and 2,4-di-isocyanotoluene may account for a release of steric strain which exists according to the two-dimensional molecular model of the polymer with the former linkage [Figure 7(*a*)]. In comparison with the idealized model, the observed displacement (~0.7 Å) of the toluene unit towards the 110 plane in the real polymer effects interbridging separations [*e.g.* C(6) ··· C(6) *ca.* 3.6 Å and $CH_3 \cdots CH_3$ *ca.* 4.9 Å], which are significantly longer than the respective (*e.g. ca.* 1.5 and *ca.* 2.8 Å) model-derived distances. Consequently, the real polymer is not expected to be sterically constrained due to short non-bonding contacts as was implied from the appropriate model. Complementary Rh–C–N (180 − α) and C–N–C (180 − α) angles for the rhodium(I) polymer with 2,4-di-isocyanotoluene linkages, which correspond to a bridge span elongation of 0.66 Å, may be calculated from a simple trigonometric relationship.† Such angles are shown in Figure 10. The smallest identical angles which fit this relationship correspond to α = *ca.* 10.8°. Bond angles of 169° are quite characteristic in the structures of terminally co-ordinated isocyanide complexes.[7,8]

The *X*-ray powder diffraction data of the polymers show unique 001 diffractions. The *hkl* diffractions were identified by consideration of the $N_{expt.}$ and $N_{calc.}$ terms as well as from the

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* See review by F. Bonati and G. Minghetti, *Inorg. Chim. Acta*, 1974, **9**, 95, and pertinent references therein concerning the *X*-ray crystal structures of isocyanide complexes.

† $\sin(60 + \alpha + \beta) = [0.33 + 3.088\sin 60 - 1.143\sin(60 + \alpha)]/1.945$. The angles α and β are as shown in Figure 10. The values of 1.143 Å [*d*(NC)], 1.945 Å [*d*(RhC)], and 3.088 Å [*d*(NC) + *d*(RhC)] are the mean values reported in reference 7 for $[\{Rh(CNPh)_4\}_2]^{2+}$. The value of 0.33 Å represents the half-bridge span elongation [(10.87 − 10.21)/2 = 0.33 Å].

observed and calculated angles of diffraction. The 001 diffraction in these polymers does not overlap with the *hk*0 diffractions and this separation does allow the rigorous assignment of the intermetallic distances. Except in the instance of 001, the scrambling between certain *hkl* and *hkl* diffractions makes rigorous assignments difficult in some cases. Intrachain Rh$^{I}\cdots$Rh^{I} distances in the polymers under review are found in the range 3.30—3.40 Å. These are significantly longer than those reported for the dinuclear cations $[\{Rh(CNR)_4\}_2]^{2+}$ [R = phenyl (3.19 Å),[7] 4-fluorophenyl (3.21 Å),[8] or 4-nitrophenyl (3.26 Å)[8]] and $[Rh_2(CNCH_2CH_2CH_2NC)_4]^{2+}$ (3.26 Å).[9] Interactions between adjacent rhodium(I) atoms in the columnar metal chains of these polymers may be expected to be somewhat weaker than those found in discrete dinuclear complexes, since in the former case both axial positions of each metal are engaged in bonding. This feature manifests itself by the presence of somewhat shorter bond distances in the dinuclear cations. On the other hand, the longest Rh$^{I}\cdots$Rh^{I} bond distance thus far reported, which was characterized in the hexagonal structural modification of $\{[Rh\{(C_6H_4NC\text{-}p)_2\}_2]Cl\}_n$ (3.5 Å),[13] most probably signifies weaker intrachain metal$\cdots$metal interactions than those found in the related tetragonal polymers. By comparison with the isocyanide-containing cationic complexes and polymers, shorter intermetallic distances were characterized in certain chloro-bridged carbonyl complexes such as $[\{Rh(CO)_2Cl\}_2]$ (3.12 Å)[14] or $[\{Rh(CO)(PMe_2Ph)Cl\}_2]$ (3.17 Å).[15]

Chemical and Physical Properties of $\{[Rh(L)_2]Cl\}_n$.—The stacked-layer three-dimensional structures of these polymers with direct interlayer Rh$^{I}\cdots$Rh^{I} interactions suggests the existence of various physical and chemical properties of interest. Specifically, the presence of extensive networks of columnar metal chains may suggest electrical conductivity properties. In addition, the combination of external surfaces (*e.g.* 001 faces) capable of undergoing oxidative-addition reactions and terminating surface ligands which could be labilized suggests the application of these polymers as heterogeneous catalysts. Both electrical[16,17] and catalytic[18] features of these systems have been studied and are currently being reported elsewhere. Therefore only a short summary of these investigations will be mentioned here.

The $\{[Rh(L)_2]Cl\}_n$ polymers have shown[16] specific conductivities on compressed pellets in the range 10^{-4}—10^{-6} ohm^{-1} cm^{-1}. The conductivity appears to demonstrate dependence on the Rh$^{I}\cdots$Rh^{I} interlayer distances present. Temperature-dependent (25–150 °C) conductivity studies of the Rh^{I} polymers having the collinear linkages 1,4-di-isocyanobenzene or 4,4′-di-isocyanobiphenyl show these materials to have semiconductive behaviour as well. A plot of ln resistivity as a function of $10^3/T$ is linear, whose slope gives values of 0.47 and 0.25 eV for the band-gap energies of the two $\{[Rh(L)_2]Cl\}_n$ polymers, respectively.[16] Recent photoconductivity measurements[17] performed on $\{[Rh(L)_2]Cl\}_n$ pellets as well as on thin films of $\{[Rh(L)_2]Cl\}_n$ oligomers have shown these materials to demonstrate photoelectric properties as well with normalized photoconductive responses in the range 2—140 nA W^{-1}. Photoconductive spectral selectivity has been noted for the latter materials.

The $\{[Rh(L)_2]Cl\}_n$ polymers show catalytic activity in the hydrogenation and isomerization of hex-1-ene in methanolic solutions.[18] The percentage of rhodium surface sites in the $\{[Rh\{(C_6H_4NC\text{-}p)_2\}_2]Cl\}_n$ polymer decreases as *n* increases. We have reported the preparation and characterization of similar co-ordination polymers, $[\{RhCl(CO)[C_6H_4(NC)_2\text{-}1,4]_2\}_n]$.[19] The carbonyl ligands have been shown to be both chemically and photochemically labile, supplying an additional vacant catalytic site in the hydrogenations and isomerizations of a hex-1-ene substrate.

Experimental

Di-isocyanides[20,21] and $[\{Rh(CO)_2Cl\}_2]$[22] were prepared according to published procedures. Reactions were routinely carried out under an argon atmosphere. Solvents used during the course of this investigation were dried, deoxygenated, and freshly distilled before use. Microanalyses were performed by Dornis and Kolbe Mikroanalytisches Laboratorium, Mulheim, West Germany, as well as by the Microanalytical Laboratories at the Hebrew University (Jerusalem) and the Weizmann Institute of Science (Rehovot).

Infrared spectra, taken in KBr pellets of Nujol mull, were recorded on a Perkin-Elmer 467 grating i.r. spectrometer and calibrated with the aid of a polystyrene film. Ultraviolet and diffuse-reflectance spectra were measured on a Cary-15 spectrometer. Trace metal analyses were performed using a Varian Techtron model 1000 atomic absorption spectrophotometer. Thermal gravimetric analyses were obtained using a Perkin-Elmer TGS-1 DSC-18 instrument. *X*-Ray powder diffractometric traces were obtained on a Phillips diffractometer using filtered Ni radiation and a scan speed of 1° (2θ) min^{-1} or 0.5° (2θ) min^{-1}.

Preparation of $\{[Rh(L)_2]Cl\}_n$ *Polymers*.—A general procedure for the preparation of these polymers involves the dropwise addition of a CH_2Cl_2 solution (100 cm^3) of the di-isocyanide (*ca.* 0.08 mol dm^{-3}) into a magnetically stirred solution (50 cm^3) of $[\{Rh(CO)_2Cl\}_2]$ (*ca.* 0.02 mol dm^{-3}) in the same solvent at ambient temperature (*ca.* 25 °C). The ultimate di-isocyanide-to-rhodium molar ratio reached in these reactions was 4, which represents a two-fold molar excess of the polymerizing ligand. The dark (Table 2) precipitates of the products were filtered off, extensively washed with CH_2Cl_2, and then vacuum dried at 80—100 °C (0.1 Torr). The polymeric products, which were characterized as $[\{[Rh(L)_2]Cl\cdot xH_2O\}_n]$ (x = 0—10), were formed in quantitative yield with respect to the starting rhodium complex.

The elemental analytical data of the water-free, as well as selected hydrated polymers, are as follows [Found: values (%) are given in parentheses]. 1,4-Di-isocyanobenzene polymer $C_{16}H_8ClN_4Rh\cdot xH_2O$ x = 0: C, 48.70(48.35); H, 2.05(2.40); Cl, 9.00(9.45); N, 14.20(14.40); Rh, 26.10(25.70). x = 2.03: C, 44.55(45.00); H, 2.80(3.20); Cl, 8.20(8.60); N, 13.00(13.35): 4,4′-Di-isocyanobiphenyl polymer $C_{28}H_{16}ClN_4Rh\cdot xH_2O$. x = 0: C, 61.50(62.05); H, 2.95(2.95); Cl, 6.50(6.80); N, 10.25(9.55); Rh, 18.85(19.35). x = 2.53: C, 56.75(57.10); H, 3.55(4.25); Cl, 6.00(5.65); N, 9.45(9.00). x = 6.14: C, 51.20(52.0); H, 4.3(4.65); Cl, 5.4(5.00); N, 8.50(7.85). 1,4-Di-isocyanonaphthalene polymer $C_{24}H_{12}ClN_4Rh$: C, 58.25(57.90); H, 2.45(2.50); Cl, 7.15(7.30); N, 11.35(11.05); Rh, 20.80 (21.10). 1,3-Di-isocyanobenzene polymer $C_{16}H_8ClN_4Rh\cdot xH_2O$. x = 0: C, 48.5(48.55); H, 2.00(2.30); Cl, 9.00(8.65); N, 14.2(13.45); Rh, 26.10(26.65). x = 0.40: C, 47.80(47.75); H, 2.20(2.65); Cl, 8.85(8.5); N, 13.9(13.15). 2,4-Di-isocyanotoluene polymer $C_{18}H_{12}ClN_4Rh$: C, 51.30(51.15); H, 2.85(3.05); Cl, 8.40(7.80); N, 13.25(11.90); Rh, 24.35(25.50). Bis(4-isocyanophenyl)methane polymer $C_{30}H_{20}ClN_4Rh\cdot xH_2O$. x = 0: C, 62.65(61.6); H, 3.50(2.8); Cl, 6.20(6.80); N, 9.75(9.35); Rh, 17.95(18.15). x = 1.74: C, 59.45(58.60); H. 3.85(4.10); Cl, 5.85(5.45); N, 9.25(9.40). x = 7.77: C, 50.4(51.05); H, 5.00(5.25); Cl, 4.95(5.00); N, 7.85(7.75). 1,5-Di-isocyanonaphthalene polymer $C_{24}H_{12}ClN_4Rh\cdot xH_2O$. x = 0: C, 58.25(60.1); H, 2.45(2.55); Cl, 7.15(7.35); N, 11.35(10.60); Rh, 20.85(19.35). x = 1.5: C, 55.35(57.0); H, 2.90(2.80); Cl, 6.80 (6.80); N, 10.75(9.80).

The *X*-ray powder diffraction angles of the tetragonal rhodium(I) polymers are given in SUP No. 56697. The diffractometric trace of the 1,3-di-isocyanobenzene polymer, which does not conform with the presence of a tetragonal system, consists of diffraction angles at 4.05, 5.50, 6.20, 6.85, 8.35, 8.90, 9.80, 12.8, 13.95, 14.32, 17.00, 18.15, and 20.20°.

Oxidative Addition of Halogens to $\{[Rh(L)_2]Cl\}_n$.—A general procedure for this reaction involves the dropwise addition of the halogen dissolved in CH_2Cl_2 into a suspension of the polymer in the same solvent at room temperature. This reaction was normally carried out with a three-fold molar excess of the halogen. After a reaction period of *ca.* 60 min, the insoluble product was filtered off, extensively washed with CH_2Cl_2, and then vacuum dried at 80 °C (0.1 Torr).

Chlorine addition. For $C_{28}H_{16}Cl_5N_4Rh{\cdot}xH_2O$ [Found (%) values in parentheses]. $x = 0$: C, 48.80(46.30); H, 2.30(3.05); Cl, 25.75(25.00); N, 8.15(8.20). $x = 8.6$: C, 39.90(38.25); H, 3.95 (3.75); Cl, 21.05(21.00); N, 6.65(6.95). I.r. (KBr pellet): ν_{CN} at 2 205 cm^{-1}. For diffuse-reflectance spectrum see Figure 2(*b*).

Bromine addition. The total amount of halogen in the bromine oxidized polymers was found to be in the range 4.1—4.8 µmol halogen per µmol Rh. These results are consistent with the formulation of the products as $[Rh(C_{14}H_8N_2)_2Br_2]^+$ with a mixture of the counter ions Cl^- (calc. halogen total, 3 µmol halogen per µmol Rh) and $[ClBr_2]^-$ (calc. halogen total, 5 µmol halogen per µmol Rh). I.r. (KBr pellet): ν_{CN} at 2 175 cm^{-1}. Diffuse-reflectance spectrum: *ca.* 420 nm.

Iodine addition. The total amount of halogen in the iodine oxidized polymers was found to be in the range 4.2—4.9 µmol halogen per µmol Rh. These results are consistent with the formulation of the products as $[Rh(C_{14}H_8N_2)_2I_2]^+$ with a mixture of the counter ions Cl^-(calc. halogen total, 3 µmol halogen per µmol Rh) and $[ClI_2]^-$ (calc. halogen total, 5 µmol halogen per µmol Rh). I.r. (KBr pellet): ν_{CN} at 2 190 cm^{-1}. Diffuse reflectance spectrum: *ca.* 415 nm.

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