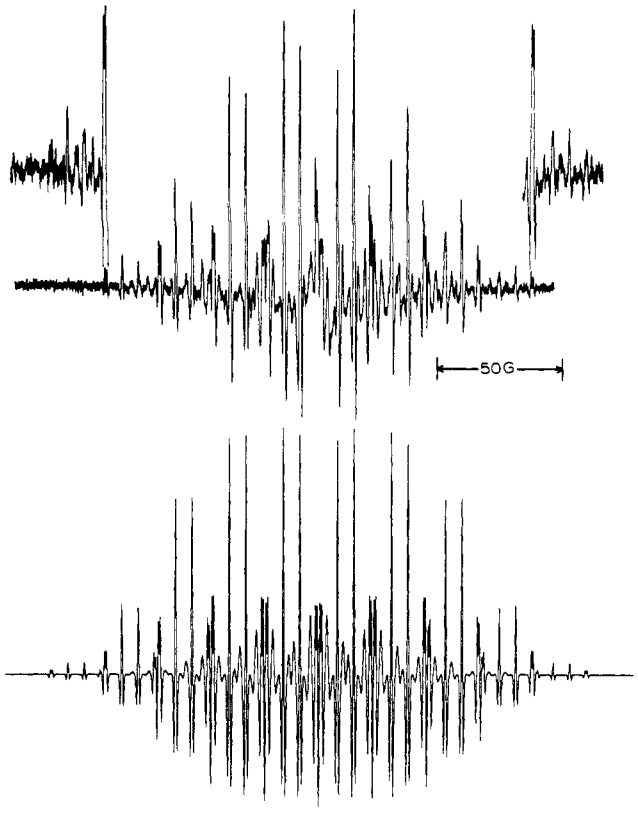

Figure 2. At the fast exchange limit the methylene protons of the β-bromo-*tert*-butyl radical should give a 1:2:1 pattern. At an intermediate rate of exchange the "two" intensity lines are broadened relative to the "one" intensity lines. The sum of the computed "one" intensiy lines and the broadened "two" intensity lines are shown together with the experimental second-derivative epr spectrum of the radical in adamantane-d_{16} at −71°: line widths = 0.70 G (narrow) and 1.40 G (broadened), relative abundances of ^{79}B:^{81}Br = 1:1.

With use of the relation $a = A + B\cos^2\theta$ for β-protons, we calculate the dihedral angles, θ, for the two methylene protons to be 45 and 15°, thus leading to the two equivalent conformations **2** and **3** with the bromine atom nearly in the nodal plane of the unpaired electron orbital. This explains the low hfs of bromine. Interconversion between **2** and **3** leads to the line width alternation as shown in Figure 2. The β-fluoro-*tert*-butyl radical is not yet reported[4] but the β-fluoroethyl radical in solution has been shown to prefer a staggered conformation[2a] similar to the one we have found for II, and indeed the limiting β-proton hfs of 28 G found for the former is quite close to the average value of 32 G in II.

Upon being cooled to −150° the spectrum of II became noticeably anisotropic but the bromine hfs increased to only ~8 G. In view of this it seems unlikely that the parameters reported by Symons[5] for a radical in γ-irradiated *tert*-butyl bromide (Br hfs ~280 G and β-H hfs ~12.5 G) correspond to radical II. Radical I was stable almost to room temperature at which point it decomposed to give the 2-methylallyl radical[6] (eq 1), while the bromo radical disappeared above −70° by reaction with the matrix to form the deuterio-*tert*-butyl radical (eq 2) or the *tert*-butyl radical

$$\mathrm{ClCH_2\dot{C}(CH_3)_2} \xrightarrow{\mathrm{C_{10}D_{16}}} \mathrm{CH_2{-}C(CH_3){-}CH_2} \quad (1)$$

$$\mathrm{BrCH_2\dot{C}(CH_3)_2} \xrightarrow[-70^\circ]{\mathrm{C_{10}D_{16}}} \mathrm{DCH_2\dot{C}(CH_3)_2} \quad (2)$$

in ordinary adamantane. Hydrogen atom exchange with the adamantane matrix has been observed previously with other radicals.[7,8] The high reactivity of radical II may explain the previous failure to observe it.[2a]

Further work in the conformation and reactions of β-haloalkyl radicals is in progress.

Acknowledgment. We wish to acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This work was also supported in part through a contract with the Atomic Energy Commission and this is AEC Document No. 000-1385-60.

(4) Since the submission of this communication the β-fluoro-*tert*-butyl radical has been prepared at University of Connecticut and it is found to prefer conformation 1. Details of the epr spectra and theoretical studies will be reported at a later date.

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Received April 17, 1974

Conductivity Measurements on One-Dimensional Systems

Sir:

In recent years the anisotropic electrical properties of one-dimensional inorganic and organic systems have received considerable attention.[1–5] The conductivity, σ, has been frequently used to monitor the electrical transport properties of these systems. There are important differences between the conductivity of one- and three-dimensional systems. Calculation of the conductivity, σ, of a three-dimensional substance, *e.g.*, copper wire, is made in a straightforward manner, eq 1,

$$\sigma = \frac{l}{RA} \quad (1)$$

where R is the observed resistance (ohm), l the length (cm), and A the cross-sectional area (cm^2) through which the measurement is made. For three-dimensional metals, *e.g.*, copper wire, the intrinsic resistivity arises from phonon coupling and electron scattering at the surface. For a typical piece of wire the former term predominates. The contribution of the electron scattering at the surface to the resistivity is directly propor-

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(3) H. R. Zeller, *Advan. Solid State Phys.*, **13**, 31 (1973).

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tional to the surface area. Therefore, as the cross-sectional area becomes small, the contribution of electron surface scattering to the resistivity becomes significant. This effect is most pronounced when the thickness of a wire is on the order of the mean free path of a free electron in the metal, *e.g.*, 450 Å for copper. This function of surface area for resistivity arises from the isotropic nature of the mean free path of a free electron in the metal, allowing scattering at the surface of the metal. For a one-dimensional metal the mean free path is anisotropic with a large component along the metal chain and a small component normal to the chain. Therefore, there is effectively no surface scattering component of the intrinsic resistivity for a one-dimensional metal. By virtue of its dimensionality, the conductivity of one-dimensional metals should approach the bulk conductivity of the metal.

One-dimensional inorganic systems exhibit collinear chains of metal atoms with short equivalent spacings (less than van der Waal radius) in the solid state and anisotropic physical properties. This is typified by a needle crystal of $K_2Pt(CN)_4X_{0.3}\cdot x(H_2O)$ (X = Cl, Br)[6] which possesses $\sim 1 \times 10^{12}$ parallel strands per cm^2 cross-sectional area with an intrastrand spacing of 2.88 Å and interstrand separation of 9.87 Å. Thus, the calculation of the conductivity requires the microscopic cross-sectional area, A^*, instead of the observable macroscopic area, A, Figure 1. The microscopic cross-sectional area is the fraction, f, of the unit cell occupied by conducting metal atoms, eq 2. The factor f is the

$$A^* = Af \tag{2}$$

ratio of the microscopic cross-sectional area (πr^2) to the unit cell cross-sectional area (D_1D_2 for tetragonal systems) and is constant for a given one-dimensional system and dependent upon the interstrand spacings, D, and covalent radii, r.

The conduction electrons are assumed to be in an electron energy band of a_1 symmetry predominately of metal d_{z^2} and s character. The large spatial extent of this orbital allows good overlap with adjacent metals. For the tetracyanoplatinate case the recent SCF-Xα-scattered wave calculations of Interrante and Messmer[7] support the large spatial extent of the a_1 orbital normal to the plane of the complex at the metal and only a small spatial extent in the vicinity of the cyano ligands. Thus, the ligands do not contribute to the cross-section of conduction as they have only a small spatial overlap orthogonal to the plane and are rotated 45° with respect to each other in adjacent planes to further minimize overlap. Therefore, the covalent radius of platinum (1.31 Å)[8] is used to calculate the microscopic cross-sectional area and the effective conductivity, σ^*, eq 3.

$$\sigma^* = \frac{l}{AfR} \tag{3}$$

For example, an observed conductivity of $\sim$300 $ohm^{-1}\ cm^{-1}$ at room temperature by Zeller and Beck[9]

(6) (a) K. Krogmann and H. D. Hausen, *Z. Anorg. Allg. Chem.*, 358, 67 (1968). (b) These complexes exist as hydrates with 2.5–3.0 water molecules per Pt atoms; D. Cahen, *Solid State Commun.*, 12, 1091 (1973).

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(8) F. R. Hartley, "The Chemistry of Platinum and Palladium," Applied Science Publishers, London, England, 1973.

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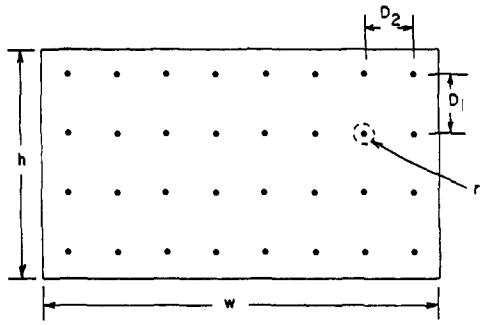

Figure 1. Cross-section of a single crystal with macroscopic cross-section A (hw) and microscopic cross-section A^* (πr^2).

for $K_2Pt(CN)_4Br_{0.3}\cdot 3(H_2O)$ yields an effective value obtained from eq 3 and factor (f = 0.055) of 5.5×10^3 $ohm^{-1}\ cm^{-1}$. Similarly, a more valid comparison of $K_2Pt(CN)_4Br_{0.3}\cdot 3(H_2O)$ can be made to other one-dimensional systems and platinum metal, 9.4×10^4 $ohm^{-1}\ cm^{-1}$, Table I. Table I lists the effective area factors, f, as well as the reported and effective conductivity, σ^*, of representative one-dimensional complexes.

Although the correction of conductivity for the microscopic cross-sectional area results in a larger conductivity of substances for comparative purposes, it is a multiplicative factor which does not alter the temperature dependence of conductivity; thus, this correction factor, f, does not further aid in obtaining physical insight into the conduction mechanism. The usefulness of σ^* arises when absolute comparisons are made (1) with three-dimensional systems, *e.g.*, platinum wire, and (2) between various one-dimensional systems themselves, Table I. Since conductivities obtained from optical data are intrinsically corrected for the microscopic cross-sectional area, only direct comparison to the observed dc conductivity can be made.

The effective conductivity calculation can be made for polycrystalline samples as well as for single crystals. Since the polycrystalline sample is not anisotropic due to the random orientation of the conducting axis of each crystal in the polycrystalline sample, the previously calculated factor, f, must be multiplied by an additional factor of $^1/_3$ arising from averaging the orientation of each crystal over all space,[10] eq 4. Thus, the effective

$$\frac{\int_0^{2\pi}\int_0^{\pi} -\cos^2\theta\, d\cos\theta\, d\Phi}{\int_0^{2\pi}\int_0^{\pi} -d\cos\theta\, d\Phi} = {}^1/_3 \tag{4}$$

polycrystalline conductivity, σ_p^*, can be calculated from eq 5. The effective polycrystalline conductivity

$$\sigma_p^* = \frac{\sigma^*}{3} \tag{5}$$

must be regarded as a minimum value as crystal boundary effects introduce additional resistances. Thus, polycrystalline conductivities are never as good as single crystal measurement.

(10) A. J. Epstein, private communication.

Table I. Corrected Conductivity, σ^*, of Representative One-Dimensional System

Complex	M–M, Å	Ref	r, Å	D_1, Å	D_2, Å	f	σ, ohm^{-1} cm^{-1}	Ref	σ^*, ohm^{-1} cm^{-1}
Pt^0 metal	2.77	*a*	1.385	2.77	2.77	1.000	9.4×10^4	*b*	9.4×10^4
$K_2Pt(CN)_4 \cdot 3H_2O$	3.50	*c*	1.31	~9.9[l]	~9.9[l]	0.055	5×10^{-7}	*d*	9.1×10^{-6}
$K_2Pt(CN)_4Cl_{0.32} \cdot 2.6H_2O$[ii]	2.880	*e*	1.31	9.87	9.87	0.055	$\sim 3 \times 10^2$	*f*	5.5×10^3
$K_2Pt(CN)_4Br_{0.30} \cdot 2.3H_2O$[ii]	2.887	*e*	1.31	9.87	9.87	0.055	$\sim 3 \times 10^2$	*f, g*	5.5×10^3
$[C(NH_2)_3]_2Pt(CN)_4Br_{0.30}$	2.88	*h*	1.31	11.1[e]	11.1[e]	0.044			
$K_{1.74}Pt(CN)_4 \cdot 1.8H_2O$	2.95	*i*	1.31	*m*	*m*		1×10^{-4}	*j*	8.1×10^3
$MgPt(CN)_4 \cdot 7H_2O$	3.16	*k, n*	1.31	10.28	10.28	0.051			
$MgPt(CN)_4Cl_{0.28} \cdot 7H_2O$	2.985	*k, n*	1.31	10.37	10.37	0.050			
$K_{1.64}Pt(ox)_2 \cdot xH_2O$	2.85	*k*	1.31	~10.9[l]	~10.9[l]	0.045	2×10^{-2}	*j*	0.44
$Mg_{0.82}Pt(ox)_2 \cdot 5.3H_2O$	2.85	*k, o*	1.31	10.93	10.93	0.045	2×10^{-2}	*j*	0.44
$Pt(NH_3)_4PtCl_4$	3.245	*p*	1.31	6.39	6.39	0.112			
$[Pt(NH_3)_2Br_2][Pt(NH_3)_2Br_4]$[q]	5.53	*r*	1.31	8.18	7.71	0.086	$<10^{-12}$	*s*	
(140 Kbar)		*t*		7.6[l]	7.1[l]	0.1	0.1	*t*	1.0
$Ni(HDMG)_2$	3.25	*u*	1.15	9.84	9.84	0.043	3.8×10^{-10}	*v*	8.9×10^{-9}
$Ir(CO)_2(acac)$[q]	3.20	*w*	1.33	7.74	9.18	0.078	1×10^{-5}	*x*	1.3×10^{-4}
(40 Kbar)	<2.9	*y*		~7.16[l]	~8.85[l]	0.09	1×10^{-1}	*y*	1.1
$Ir(CO)_{2.93}Cl_{1.07}$	2.85	*z*	1.33	7.60	6.47	0.11	0.2	*aa*	1.87
							0.2	*bb, cc*	5.5
$(SN)_x$		*dd*	1.05	*m*	*m*		>1	*ee*	
$Hg_{2.86}AsF_6$	2.84	*ff*	1.5	3.62	3.62	0.54			
$Ni_{0.25}Pt_3O_4$	2.80	*gg*	1.31	5.61	5.61	0.17	3×10^3	*gg*	1.8×10^4[hh]

[a] Reference 8. [b] "Handbook for Chemistry and Physics," 53rd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1972, p F-145. [c] M. L. Moreau-Colin, *Bull. Soc. Roy. Sci. Liege*, **34**, 778 (1965). [d] M. J. Minot and J. H. Perlstein, *Phys. Rev. Lett.*, **26**, 371 (1971). [e] Reference 6a. [f] P. Wurfel, H. D. Hausen, K. Krogmann, and P. Stampel, *Phys. Status Solidi A*, **10**, 537 (1972). [g] A. S. Berenblyum, L. I. Buravov, M. D. Khidekel, I. F. Shchegolev, and E. B. Yakimov, *JETP Lett.*, **13**, 440 (1973). [h] G. Stucky, private communication. [i] K. Krogmann and H. D. Hausen, *Z. Naturforsch. B*, **23**, 1111 (1968). [j] T. W. Thomas, C-h Hsu, M. M. Labes, P. S. Gomm, A. E. Underhill, and D. M. Watkins, *J. Chem. Soc., Dalton Trans.*, 2050 (1972). [k] Reference 1. [l] Estimated. [m] Unable to obtain from the reported data. [n] K. Krogmann and G. Ringwald, *Z. Naturforsch. B*, **23**, 1112 (1968). [o] K. Krogmann, *Z. Anorg. Allg. Chem.*, **358**, 97 (1968). [p] M. Atoji, J. W. Richardson, and R. E. Rundle, *J. Amer. Chem. Soc.*, **79**, 3017 (1957). [q] 1 atm. [r] C. Brosset, *Ark. Kemi. Mineral. Geol.*, **25A**, 14 (1948). [s] T. W. Thomas and A. E. Underhill, *J. Chem. Soc. A*, 512 (1971). [t] L. V. Interrante, K. W. Brownall, and F. P. Bundy, *Inorg. Chem.*, **13**, 1158 (1974); L. V. Interrante and K. W. Brownall, *ibid.*, **13**, 1162 (1974). [u] L. E. Godycki and R. E. Rundle, *Acta Crystallogr.*, **6**, 487 (1953). [v] T. W. Thomas and A. E. Underhill, *Chem. Commun.*, 725 (1969). [w] G. C. Oldham, Jr., Ph.D. Thesis, University of North Carolina, *Diss. Abst. B*, **29**, 4619 (1969). [x] C. G. Pitt, L. K. Monteith, L. F. Ballard, J. P. Collman, J. C. Morrow, W. R. Roper, and D. Ulkü, *J. Amer. Chem. Soc.*, **88**, 4286 (1966). [y] L. V. Interrante and F. P. Bundy, *Inorg. Chem.*, **10**, 1169 (1971). [z] K. Krogmann, W. Binder, and H. D. Hausen, *Angew. Chem., Int. Ed. Engl.*, **7**, 812 (1968). [aa] F. N. Lecrone, M. J. Minot, and J. H. Perstein, *Inorg. Nucl. Chem. Lett.*, **8**, 173 (1972). [bb] J. S. Miller, unpublished results. [cc] Four probe compaction, σ_p^*. [dd] M. Boudeulle and P. Michel, *Acta Crystallogr., Sect. A*, **28**, S199 (1972). [ee] V. V. Walatka, Jr., M. M. Labes, and J. H. Perlstein, *Phys. Rev. Lett.*, **31**, 1139 (1973). [ff] I. D. Brown, B. D. Cutforth, C. G. Davies, R. J. Gillespie, P. R. Ireland, and J. E. Verkris, *Can. J. Chem.*, **52**, 791 (1974). [gg] D. Cahen, J. A. Ibers, and R. D. Shannon, *Inorg. Chem.*, **11**, 2311 (1972). [hh] See text. [ii] See ref 6.

The use of eq 4 to calculate the effective conductivity, σ^*, for $Ni_{0.25}Pt_3O_4$ may not be valid as proof of one-dimensionality has not been established. The crystal structure of $Ni_{0.25}Pt_3O_4$ reveals three orthogonal non-intersecting platinum chains with short equivalent spacings reminiscent of a one-dimensional system. The high conductivity at low temperature may be extrinsic due to impurities or intrinsic if the system is not one-dimensional (due to electrical communication between orthogonal strands).

The effective conductivity calculations are also valid for organic metals.[2,3] The effective area factor, f, is much larger ($\gtrsim 0.5$)[11] for conducting tetracyanoquinodimethane, TCNQ, complexes than systems based on one-dimensional strands of metals. This is due to the greater cross-sectional area of TCNQ than for a metal.

The purity[12] of a one-dimensional system is an extremely important consideration when evaluating transport measurements. A $1.0 \times 0.01 \times 0.01$ mm^3 single-needle crystal of $K_2Pt(CN)_4X_{0.3} \cdot x(H_2O)$ (X = Cl, Br) is comprised of 1.0×10^8 parallel strands each containing 3.5×10^6 molecules. A foreign impurity, *e.g.*, solvent molecule or terminal halide atom, etc., or crystalline defect, *e.g.*, a void in a strand causing strand termination, will markedly increase the resistance of a strand. Therefore, the fewer number of defects the greater number of strands able to exhibit high conductivity; thus the observed conductivity, σ, will be high. Additionally, the ratio of anisotropic conductivities $\sigma_{\parallel}:\sigma_{\perp}$ ($\parallel$ and $\perp$ to the metal axis) will also increase with purity. For example, at a purity level of 100 ppb a 1.0 mm long crystal of $K_2Pt(CN)_4X_{0.3} \cdot x(H_2O)$ will have an average of 65.3% of its strands flaw-free.

Unfortunately, there is no quantitative measure of purity. Qualitatively the fewer flaws per strand will result in a greater value for the observed conductivity, dielectric constant,[13] and anisotropic ratio ($\sigma_{\parallel}/\sigma_{\perp}$).[9,13–15] For these reasons, extreme care must be extended in the preparation and measurement of electrical and other physical properties on one-dimensional systems. For a crystal of good morphology and purity, the corrected conductivity, σ^*, allows a more valid comparison between one- and three-dimensional systems as all systems are normalized to take into account the density of strands.

Acknowledgment. The author wishes to thank Drs. A. J. Epstein, P. K. Watson, and R. F. Ziolo for their

(11) R. F. Ziolo, unpublished results.
(12) Purity = sum of all crystalline defects and foreign impurities.
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helpful and stimulating discussions. Sincere gratitude is extended to Drs. Interrante and Stucky for preprints of their work.

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Received May 17, 1974

Hydrogen–Deuterium Exchange between η^5-$C_5H_5Rh(C_2H_4)_2$ and Aromatic Hydrocarbons

Sir:

We wish to report a novel isotopic hydrogen exchange between benzene-d_6 and η^5-$C_5H_5Rh(C_2H_4)_2$. The exchange, which occurs at 130°, introduces deuterium into both the cyclopentadienyl and ethylene ligands. With one exception, previous examples of homogeneous exchange with aromatic hydrocarbons require the presence of hydride,[1] proton,[2] or elemental hydrogen.[3] In the one exception, organoaluminum dihalides catalyze hydrogen exchange between two aromatic hydrocarbons.[4]

The exchange is observed after heating at 130° a sealed, evacuated tube typically containing 0.20 mmol of η^5-$C_5H_5Rh(C_2H_4)_2$ and 0.4 ml of benzene-d_6. Prior to heating, the proton nmr spectrum consists of a small resonance for isotopically impure benzene, a sharp doublet at 4.90 ppm (from external TMS) for η^5-C_5H_5, and complex doublets centered at 2.74 and 1.22 ppm for coordinated C_2H_4. No change is noted in the spectrum after the tube is heated for 1 hr at 100°, but, after 1 hr at 130°, the area of the aromatic signal is substantially larger. The area of the ligand signals are correspondingly smaller. Typical peak areas are as shown in Table I.

Table I

	Benzene	Cyclopentadienyl	Ethylene
No heat	9	71	103
130°, 1 hr	119[a]	26	39

[a] The areas after heating are normalized using hexamethyldisiloxane, which does not exchange, as internal standard.

The changes in the nmr spectrum are attributed to isotopic hydrogen exchange between benzene-d_6 and η^5-$C_5H_5Rh(C_2H_4)_2$. The rhodium complex can be recovered by sublimation. Analysis by mass spectroscopy shows no nondeuterated complex. Most of the complex from a 1-hr run contains from 8 to 11 deuterium atoms per molecule, see Table II. Mass spectroscopic analysis of the recovered benzene shows that the major exchanged species is C_6D_5H. As seen in Table II, the percentages found for the deuterated benzene species agree very well with the percentages calculated from the terms of the expanded polynomial

Table II. Deuterium Distribution from Exchange between C_6D_6 and η^5-$C_5H_5Rh(C_2H_4)_2$

	Benzene				η^5-$C_5H_5Rh(C_2H_4)_2$	
	A[a]		B		A	B
	Calcd[b]	Found	Calcd	Found	Found	
d_0	0	0	0	0	0.6	0
d_1	0	0.3	0	0	3.4	0
d_2	0	0	0.03	0	9.4	0
d_3	0.08	1.2	0.54	2.7	16.7	0.2
d_4	1.6	0.3	5.5	3.0	19.9	0.6
d_5	17.8	15.2	29.2	26.6	17.5	1.9
d_6	80.7	82.9	64.7	67.2	11.2	4.9
d_7					5.6	10.1
d_8					2.1	17.0
d_9					3.4	22.2
d_{10}					3.8	19.7
d_{11}					3.3	13.8
d_{12}					1.8	5.6
d_{13}					0.9	1.7

[a] A, 0.200 mmol of η^5-$C_5H_5Rh(C_2H_4)_2$, 0.4 ml of C_6D_6, 130° for 0.5 hr; B, 0.200 mmol of η^5-$C_5H_5Rh(C_2H_4)_2$, 0.4 ml of C_6D_6, 130° for 1.0 hr. [b] Calculated from the expanded polynomial $(a + b)^6$.

$(a + b)^n$, where $a = f_H = 1 - f_D$, $b = f_D$ = fraction of deuterium, and n = number of exchangeable deuterium atoms in the aromatic compound. $f_D = C_iM_i/100n$ where C_i = percentage of the i deuterated species with M deuterium atoms.[3] This calculation assumes that (1) only one hydrogen is incorporated per act of exchange and (2) all aromatic deuteriums exchange at the same rate.

The exchange is apparently homogeneous. Although the color of the solutions changes from yellow to purple-black and in some cases small amounts of solids are present, metallic rhodium is never visually detected. The extent of exchange is not affected by addition of solid from a previous experiment or elemental rhodium as sponge or supported on carbon.

Free ethylene, or ethylene-d_4, inhibits the exchange. Addition of 0.40 mmol of C_2D_4 (or C_2H_4) to a solution of 0.21 mmol of η^5-$C_5H_5Rh(C_2H_4)_2$ in 0.4 ml of C_6D_6 completely suppresses exchange even after heating for 2 hr at 130°. Free C_2D_4 exchanges with coordinated C_2H_4, however. Lesser amounts of ethylene (0.02–0.04 mmol) partially suppress exchange.

The inhibition of exchange by ethylene and the fact that exchange is observed only at temperatures at which ethylene dissociates at a reasonable rate from η^5-C_5H_5-$Rh(C_2H_4)_2$,[5] suggest that the initial step in the exchange mechanism is ethylene dissociation, Figure 1.

Ethylene dissociation may also be the first step in exchange of hydrogen between coordinated ethylene and cyclopentadienyl ligands. After 0.5 hr at 130°, hydrogen in η^5-$C_5H_5Rh(C_2D_4)_2$ had equilibrated between cyclopentadienyl and ethylene ligands. (The solvent was cyclohexane-d_{12}, which does not exchange with η^5-$C_5H_5Rh(C_2H_4)_2$.) Exchange can be stopped short of equilibrium by heating for shorter times, *e.g.*, 8–10 min. No exchange is observed at 100°. This exchange is also inhibited by free ethylene.

Arenes other than benzene exchange with η^5-C_5H_5Rh-$(C_2H_4)_2$. In order of decreasing reactivity they are $C_6D_6 \geq C_5D_5N > C_6D_5NO_2 \geq C_6D_5CD_3$. Pyridine exchanges primarily with coordinated ethylene. Only the aromatic deuterium atoms of toluene exchange.

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