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Rotation of Coordinated Ethylene in Compounds Related to (π-C_5H_5)Rh(C_2H_4)$_2$

R. Cramer and J.J. Mrowca

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Substitution of cyclopentadienyl protons of (π–C_5H_5)-Rh(C_2H_4)$_2$ with electronegative groups (–CN or –COO-CH_3)weakens the π–bond between rhodium and ethylene moderately, while substitution with methyl seems to strengthen it. A far greater loss of π–bond strength appears to result from complexing of (π–C_5H_5)Rh-(C_2H_4)$_2$ with the Lewis acid, $HgCl_2$.

Introduction

Ethylene, in some of its complexes with rhodium[1,2] and platinum,[3,4] has been shown to undergo a reorientation which involves a propellor-like rotation having the olefin-metal σ–bond as its axis. There is a rather large energy barrier to rotation –15.0 kcal/mole in π–C_5H_5Rh(C_2H_4)$_2$[2] and 12.5 kcal/mole for Pt(acacCl-(C_2H_4)[3] — to which π–bonding makes a substantial contribution. The π–bond is formed from a (filled) nonbonding metal d_π–orbital with the (empty) p_π*–orbital of ethylene.[5,6] Its strength is expected to increase with the electron density at the metal atom. We report here experimenal results which support that hypothesis and indicate that the barrier to rotation can be reduced substantially in a suitably modified compound of ethylene and rhodium.

A moderate modification of electron density at rhodium is expected to result from substitution at the cyclopentadienyl group of π–C_5H_5Rh(C_2H_4)$_2$. Electron density will be enhanced in (π–(CH_3)$_5C_5$)Rh(C_2H_4)$_2$[7] and reduced in (π–C_5H_4CN)Rh(C_2H_4)$_2$ and (π–$C_5H_4COOCH_3$)Rh(C_2H_4)$_2$.

Rotation of coordinated ethylene is detected and its energy barrier evaluated through nmr. In an unexcited molecule of π–C_5H_5Rh(C_2H_4)$_2$, the C=C bonds of the two ethylene ligands are parallel and the ethylene protons are differentiated by nearest neighbor interactions into two sets—four «inside», H^i, and for «outside», H^o (Figure 1, solid line spectrum). H^i and H^o interchange as a consequence of rotation leading to temperature-dependent nmr spectra (Figure 1, dashed lines) which are the basis for measuring the energy barrier. Here discussion will be based on a comparison of the convergence temperatures of the absorptions due to H^i and H^o for various complexes and of free energies of activation calculated from the expression

$$\Delta F_T{}^* = -RT \ln \frac{\pi \Delta \nu h}{\sqrt{2kT}}$$

where T is the convergence temperature (°K), $\Delta\nu$ is the separation of the centers of absorptions of H^i and H^o in absence of exchange (cycles sec^{-1}), h is Planck's constant, and k is Boltzmann's constant. It is expected that differences in ΔF^* reflect principally differences in E_A for rotation.

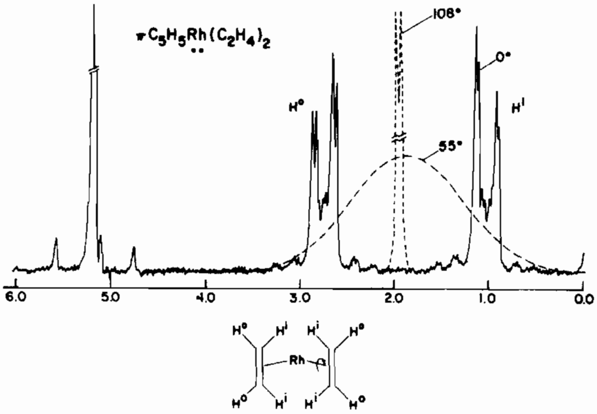

Figure 1.

The spectra of (π–C_5H_4CN)Rh(C_2H_4)$_2$ and π–C_5H_4-$COOCH_3$)Rh(C_2H_4)$_2$ resemble that of (π–C_5H_5)Rh(C_2H_4)$_2$ very closely except for 1) minor shifts in the location of absorptions of H^i and H^o and 2) a lower temperature for their convergence (Table I). The free energy of activation is reduced by about 1.6 kcal in the substituted compounds, and this is attributed entirely to weaker π–bonding since steric effects would tend to interfere with rather than assist rotation.

The nmr spectrum of (π–(CH_3)$_5C_5$)Rh(C_2H_4)$_2$ is complicated by the absorption for methyl protons which lies within 10 cps of the mean of the absorptions for H^i and H^o. Consequently, we could assign only a

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Table I. NMR and Thermodynamic Data for π-CpRh(olefin) Complexes.

Compound	τH^i (ppm)	τH^o (ppm)	Coalescence Temp (°C)	ΔF_T^* (kcal/mole)
π-$C_5H_5Rh(C_2H_4)_2$	8.97 [a]	7.14 [a]	55°	15.7
π-$C_5H_4CNRh(C_2H_4)_2$	8.55 [a]	6.88 [a]	22°	14.1
π-$C_5H_4COOCH_3Rh(C_2H_4)_2$	8.68 [a]	7.00 [a]	22°	14.1
π-$(CH_3)_5C_5Rh(C_2H_4)_2$	8.63 [b]	8.13 [b]	$>60°$	>16.9
π-$C_5H_5Rh(C_2H_4)_2 . HgCl_2$	only one signal, a doublet at 7.99		$<-70°$ [d]	<10
π-$C_5H_5Rh(CH_2{=}CHCH_2CH_2CH{=}CH_2)$	8.54 [c]	7.18 [c]		
π-$C_5H_5Rh(C_6H_{10}) . HgCl_2$	8.40 [c]	7.15 [c]		

solvents: a) $CDCl_3$; b) $C_6H_5OC_6H_5$; c) pyridine; d) pyridine/$CDCl_3$.

lower limit for the convergence temperature (Table I). Since $\Delta\nu$ is notably small for (π—$(CH_3)_5H_5)Rh(C_2H_4)_2$, its free energy of activation for rotation is more than 1 kcal larger than that of (π—$C_5H_5)Rh(C_2H_4)_2$.

A much greater reduction of the rotation barrier is achieved through a different sort of modification (π—$C_5H_5)Rh(C_2H_4)_2$ is a Lewis base[8] and, like (π—$C_5H_5)Rh(CO)_2$,[9] forms an adduct with $HgCl_2$. The nmr spectrum of this adduct, (π—$C_5H_5)Rh(C_2H_4)_2 . HgCl_2$, has a doublet (^{103}Rh—H coupling) for ethylene protons similar to the spectrum of π—$C_5H_5Rh(C_2H_4)_2$ at 100 to 110° (Figure 1). At −70°, the doublet was not resolved but the absorption signal was still sharp (width at half-height was 4 cps using a 100 MH spectrometer). Apparently the coalescence temperature is well below −70°C. This implies $\Delta F^*_{\text{rotation}} < 10$ kcal. The relative contributions of 1) a weaker π—bond and 2) steric interaction of cordinated $HgCl_2$ with ethylene ligands to this effect are, at present, unknown.

Since we could not freeze out the rotation of coordinated ethylene in π—$C_5H_5Rh(C_2H_4)_2 . HgCl_2$, it is necessary to provide some evidence that it is appropriate to interpret the nmr spectrum in terms of a lower rotation barrier. We exclude the following alternative explanations.

1) Coalescence of the signal for ethylene protons is a consequence of a rapid intramolecular exchange of ethylene. (Since solvent systems containing dimethyl sulfoxide or pyridine were employed with (π—$C_5H_5)Rh(C_4H_2)_2 . HgCl_2$, such an exchange might have been expected.) This is unlikely because the signal for complexed ethylene ($\tau = 7.62$) is separate from the signal for added free ethylene ($\tau = 4.63$) (dimethyl sulfoxide solvent).

2) Formation of a Lewis Acid complex alters the structure of (π—$C_5H_5)Rh(C_2H_4)_2$ in such a way that the distinction between H^i and H^o is not retained. We have no evidence that completely excludes this explanation. However, the analogous compound (π—$C_5H_5)Rh(CH_2{=}CHCH_2CH_2CH{=}CH_2)$[1] (Figure 2), in which rotation of coordinated olefin is prevented by chelation, forms a stable complex with $HgCl_2$ in which the distinction between H^i and H^o is preserved (Table I). This indicates that (π—$C_5H_5)Rh(C_2H_4)_2$ could complex with $HgCl_2$ without changing the spatial relationship of the ethylene ligands.

3) The chemical shift difference between H^i and H^o of (π—$C_5H_5)Rh(C_2H_4)_2 . HgCl_2$ is much smaller than for (π—$C_5H_5)Rh(C_2H_4)_2$ so that coalescence does not require a comparably fast rotation. This appears unlikely since the chemical shift difference of H^i and H^o in (π—$C_5H_5)Rh(CH_2{=}CHCH_2CH_2CH{=}CH_2) . HgCl_2$ is 1.25 ppm as compared with 1.36 ppm for (π—$C_5H_5)Rh(CH_2{=}CHCH_2CH_2CH{=}CH_2)$.

4) Dissociation of $HgCl_2$ (which occurs with (π—$C_5H_5)Rh(CO)_2 . HgCl_2$[9]) is fast and is responsible for the converged signal of ethylene protons (eq. 1).

$$(\pi\text{—}C_5H_5)Rh(C_2H_4)_2 . HgCl_2 \rightleftarrows (\pi\text{—}C_5H_5)Rh(C_2H_4)_2 + HgCl_2 \qquad (1)$$

Since coordinated ethylene in (π—$(C_5H_5)Rh(C_2H_4)_2$ gives two well-separated proton signals at 25° and so could not itself account for a sharp doublet, this hypothesis would imply a rearrangement on the addition or elimination of $HgCl_2$ which does not occur with (π—$C_5H_5)Rh(CH_2{=}CHCH_2CH_2CH{=}CH_2)$. We have not been able to devise an experiment to test this explanation.

There is no apparent coupling of protons to ^{199}Hg in the nmr spectra of (π—$(C_5H_5)Rh(C_2H_4)_2 . HgCl_2$ and (π—$C_5H_5Rh(CH_2{=}CHCH_2CH_2CH{=}CH_2) . HgCl_2$.

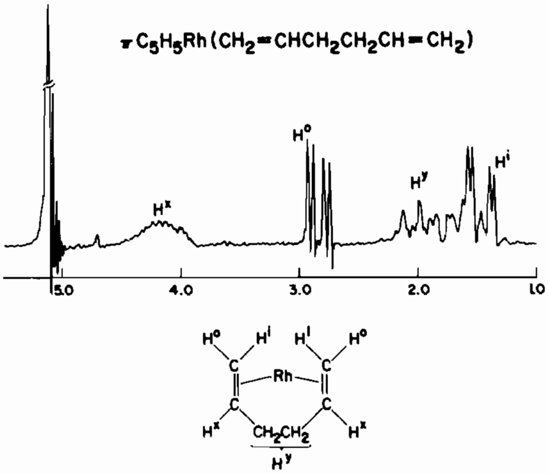

Figure 2.

Experimental Section

Preparations of (π—$C_5H_5)Rh(C_2H_4)_2$ and (π—C_5H_5)-Rh($CH_2{=}CHCH_2CH_2CH{=}CH_2$) have been described.[1] (π—$(CH_3)_5C_5)Rh(C_2H_4)_2$ was furnished by Prof. P. M. Maitlis.[7]

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[8] R. Cramer, *J. Am. Chem. Soc.*, *89*, 5377 (1967).

[9] J.L. Dawes and R.V.W. Kemmitt, *J. Chem. Soc.*, (A) 1968, 1072.

Table II. Analyses of New Coordination Compounds.

	Calculated		Found	
	% C	% H	% C	% H
(π-C_5H_4CN)Rh(C_2H_4)$_2$	48.21	4.85	48.04	4.97
(π-$C_5H_4COOCH_3$)Rh(C_2H_4)$_2$	46.83	5.35	46.98	5.47
(π-C_5H_5)Rh(C_2H_4)$_2$. $HgCl_2$	21.81	2.64	22.64; 22.69	2.42; 2.46
(π-C_5H_5)Rh(C_6H_{10}) . $HgCl_2$	25.33	2.80	24.99; 25.22	2.82; 2.79

(π–C_5H_4CN)Rh(C_2H_4)$_2$. A mixture of 1.50 g of cyanocyclopentadienylthallium,[10] 1.00 g of tetrakis-(ethylene)–$\mu\mu'$–dichlorodirhodium, and 25 ml of tetrahydrofuran was stirred for 24 hrs under nitrogen and filtered, and the orange filtrate evaporated under aspirator vacuum. Recrystallization of the residue from methanol at –78° followed by sublimation at 65° and 5×10^{-3} mm yielded 0.50 g of bis(ethylene)-cyanocyclopentadienylrhodium(I) as orange-yellow crystals: mp 58-60°; ir (nujol) 2227 cm^{-1} ($\nu_{C\equiv N}$); nmr, similar in appearance to Figure 1, solid line, with π–C_5H_4CN protons located at 4.48 τ, multiplet of H^o centered at 6.88 τ and of H^i at 8.55 τ; mass spectrum m/e 249 ($C_{10}H_{12}N^{103}Rh$).

(π–$C_5H_4COOCH_3$)Rh(C_2H_4)$_2$. A mixture of 1.00 g of carbomethoxycyclopentadienylthallium,[10] 0.60 g of tetrakis(ethylene)–$\mu\mu'$–dichlorodirhodium, and 25 ml of tetrahydrofuran was stirred for 24 hrs under nitrogen and filtered, and the filtrate evaporated under aspirator vacuum. Sublimation of the residue at 75° and 0.1 mm followed by recrystallization from methanol at –78° gave 0.60 g of bis(ethylene)carbomethoxycyclopentadienylrhodium(I) as orange-yellow crystals: mp 50-52°; ir(KBr) 1700 cm^{-1} ($\nu_{C=O}$); nmr, similar in appearance to Figure 1, solid line, with π–C_5H_4 protons at 4.49 τ, $COOCH_3$ at 6.15 τ, multiplet of H^o centered at 7.00 τ and of H^i at 8.68 τ; mass spectrum m/e 282 ($C_{11}H_{15}O_2{}^{103}Rh$).

(π–C_5H_5)Rh(C_2H_4)$_2$. $HgCl_2$. A solution of 1.61 g of $HgCl_2$ (6 mmole) in 20 ml of ethanol was added to a solution of 1.34 g of (π–C_5H_5)Rh(C_2H_4)$_2$ (6 mmole) in 10 ml of ethanol. A yellow solid precipitated immediately. It was washed twice with methanol, then with diethyl ether, and was dried at 50° under vacuum (0.1 mm Hg) for 4 hr. The yield was 3.0 g (93% of theory).

(π–C_5H_5)Rh($CH_2{=}CHCH_2CH_2CH{=}CH_2$) · $HgCl_2$ was prepared similarly in high yield from (π–C_5H_5)-Rh($CH_2{=}CHCH_2CH_2CH{=}CH_2$).

Nmr studies were carried out on Varian A-60 and HA-100 spectrometers using appropriate solvents as listed in Table I and with tetramethylsilane as an internal reference. Temperatures at the probe were measured by the chemical shift difference of hydroxyl and methyl protons of $CH_3OH/H_2O/HCl$.[11]

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[10] Preparation and utilization of the thallium cyclopentadienides will be described in a forthcoming publication by J.J.M.

[11] R. Duerst and A. Merbach, *Rev. Sci. Instr.*, 36, 1896 (1965).