A Study of the *Trans* Influence in some Rhodium(I) Complexes Using Infrared Spectroscopy

CLIFTON WOODS* and CELESTE DAFFRON

Department of Chemistry, University of Tennessee, Knoxville, Tenn. 37996-1600, U.S.A.

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Abstract

The *trans* influence of a series of nitrogenous bases has been investigated by monitoring the infrared stretching frequency of carbon monoxide in complexes of the type *trans*-[Rh(CO){$(C_6H_5)_3$P}$_2$L]PF$_6$ where L is pyridine, 4-acetylpyridine, 4-dimethylaminopyridine, 3,4-dimethylpyridine, 4-cyanopyridine, 4-benzoylpyridine, 3-chloropyridine, 4-hydroxypyridine, imidazole, benzimidazole, 2-ethylbenzimidazole, and 2-methylbenzimidazole. A straight line plot is obtained when the pK_a values of the pyridines (except 4-hydroxypyridine) are plotted versus the C–O stretching frequency of their complexes. The hydroxypyridine and imidazole ligands do not give data that fit the linear plot. These bases are the only ones of the group studied whose conjugate acids have two sites of deprotonation that are strongly correlated through resonance. This feature is discussed as a possible reason that the pK_a values are not good measures of the sigma donor capabilities of those ligands toward the metal.

Introduction

The *trans* influence is a phenomenon that has attracted much attention over the years. The *trans* influence is a measure of the extent to which a ligand weakens a bond *trans* to itself [1]. A number of techniques have been used in attempts to correlate physical properties with the *trans* influence of a ligand [2, 3]. One such technique is infrared (IR) spectroscopy. A particularly attractive configuration for studying the *trans* influence of a ligand *via* IR spectroscopy is one in which the ligand is *trans* to a carbon monoxide ligand. The shifts in C–O stretching frequencies for these configurations are usually interpreted in terms of the π-bonding ability of the ligand L. Some studies [4] involving non-π-bonding ligands have demonstrated a correlation between the sigma donor strength of the ligand and the IR stretching frequency of a *trans* CO. Nitrogen heterocycles exhibit sigma and pi bonding capabilities and the interplay between these two bonding capabilities can make it difficult to assess the role of one in determining the *trans* influence of the heterocycle. It was this uncertainty that led Reddy and Ramesh [5] to conclude that no meaningful correlation exists between ν(CO) and the basicities of some substituted imidazoles and benzimidazoles in complexes of the type *trans*-[Rh(CO)$(Ph_3P)_2$Y]ClO$_4$ (Y = imidazole derivative). In order to further investigate the relationship between the basicity of nitrogen heterocycles and ν(CO) of *trans* CO ligands, we have investigated the series of complexes *trans*-[Rh(CO)$(Ph_3P)_2$L]PF$_6$, where L is a pyridine derivative.

Experimental

All nitrogenous bases were purchased from Aldrich. The bases were used as received except 4-hydroxypyridine which was recrystallized from hot ethanol. All solvents were reagent grade.

Preparation of [Rh(CO)(Ph$_3$P)$_2$L]PF$_6$ Complexes (L = nitrogenous Base)

The following procedure was used to prepare all complexes. A solution containing 0.350 mmol of [Rh(CO)$_3${P$(C_6H_5)_3$}$_2$]PF$_6$ [6] in 2 ml of CH_2Cl_2 was stirred while 0.350 mmol of the nitrogenous base were added. After the evolution of CO subsided, 2–3 ml of ethanol was added. Precipitation of the product was effected by the addition of 3 ml of ether. After the product was filtered and recrystallized from CH_2Cl_2 and ether, it was dried in vacuum. The analytical data for the complexes are given in Table I.

Physical Measurements

Infrared (IR) spectra were obtained using a Digilab FTS-20 C/V Fourier Transform Infrared Spectro-

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*Author to whom correspondence should be addressed.

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TABLE I. Analytical Data for Rhodium(I) Complexes.

Compound No.		Ligand		Percent		
				C	H	N
1	$[Rh(CO)\{(C_6H_5)_3P\}_2(C_5H_5N)]PF_6$	Pyridine	Calc:	57.36	4.01	1.59
			Found:	57.70	4.15	1.56
2	$[Rh(CO)\{(C_6H_5)_3P\}_2(C_7H_7NO)]PF_6$	4-Acetylpyridine	Calc:	57.35	4.04	1.52
			Found:	56.92	4.11	1.58
3	$[Rh(CO)\{(C_6H_5)_3P\}_2(C_6H_4N_2)]PF_6$	4-Cyanopyridine	Calc:	57.10	3.79	3.10
			Found:	56.95	3.71	3.03
4	$[Rh(CO)\{(C_6H_5)_3P\}_2(C_7H_{10}N_2)]PF_6$	4-Dimethylaminopyridine	Calc:	57.28	4.37	3.04
			Found:	56.77	4.47	3.04
5	$[Rh(CO)\{(C_6H_5)_3P\}_2(C_6H_7N)]PF_6$	4-Methylpyridine	Calc:	57.80	4.17	1.57
			Found:	57.48	4.21	1.62
6	$[Rh(CO)\{(C_6H_5)_3P\}_2(C_{12}H_9NO)]PF_6$	4-Benzoylpyridine	Calc:	59.86	3.99	1.42
			Found:	59.28	4.00	1.46
7	$[Rh(CO)\{(C_6H_5)_3P\}_2(C_6H_4NCl)]PF_6$	3-Chloropyridine	Calc:	55.19	3.75	1.53
			Found :	54.76	3.81	1.57
8	$[Rh(CO)\{(C_6H_5)_3P\}_2(C_5H_5NO)]PF_6$	4-Hydroxypyridine	Calc:	56.33	3.94	1.56
			Found:	56.28	4.06	1.51

meter. Solutions for IR measurements were made using $CHCl_3$ or CH_2Cl_2. The liquid cells were equipped with NaCl or KBr plates.

Proton decoupled ^{31}P NMR spectra were recorded using a JOEL FX90Q Fourier Transform NMR Spectrometer operating at 36.19 MHz. Phosphorus chemical shifts were measured relative to external 85% H_3PO_4. The solvents for the NMR solutions were $CHCl_3$ or CH_2Cl_2.

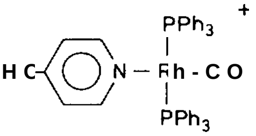
All elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Results and Discussion

We have chosen to restrict our pyridine ligands to those substituted in positions 3 and 4. By doing this we can reasonably assume that changes in the nature of the M-L u-bond due to steric factors are minimized and essentially constant throughout the series. The relative donor abilities of the pyridines are considered to be reflected in their pK_a values. Since the pK_a values reflect the tendency of the base to bind to a proton, the pK_a of a pyridine is a measure only of the u-bonding ability of the pyridine. The pK_a values of the pyridines used in this study are taken from the literature [7] and are listed in Table II. Also given in Table II are pK_a values for some imidazole derivatives that are used for comparison [8,9]. A plot of ν(CO) versus pK_a of the first seven bases in Table II is shown in Fig. 1 as the straight line plot involving the open circles.

The linear relationship between the C-O stretching frequency and the pK_a of the pyridines suggests that the u-donor properties of the pyridines are almost totally responsible for the shifts in ν(CO). It. is seen that as the base strength increases, ν(CO) decreases. The stronger the base the more electron density it donates to the metal. Though the increase in electron density at the metal occurs through a sigma interaction with the pyridine bases, the mechanism by which the metal releases excess electron density to the CO involves an interaction of the metal π and carbon monoxide π^* orbitals, thus, accounting for the decrease in ν(CO) with increasing pK_a.

When 4-hydroxypyridine is added to a solution of $[Rh(CO)_3(Ph_3P)_2]PF_6$, the resulting product gives two CO stretching frequencies, 2000 and 1988 cm-‘, with the 1988 cm-’ peak being the more intense one. This is in contrast to the one strong peak observed with the other nitrogenous bases. The peaks are attributed to the two isomers I and **II,** resulting from the two tautomeric forms



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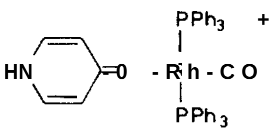


II

of 4-hydroxypyridine. The presence of both isomers is confirmed by the presence of two doublets in the $^{31}P\{^1H\}$ spectrum (^{103}Rh, I = 1/2, 100%). The two

TABLE II. pK_a Values and C-O Stretching Frequencies for $[Rh(CO)\{(C_6H_5)_3P\}_2L]PF_6$ Complexes.

Compound No.	L	pK_a of L[a]	$\nu(C\equiv O)$, cm^{-1}
1	Pyridine	5.23	2008(s)
2	4-Acetylpyridine	3.51	2011(s)
3	4-Cyanopyridine	1.88	2014(s)
4	4-Dimethylaminopyridine	9.71	2001(s)
5	4-Methylpyridine	5.98	2007(s)
6	4-Benzoylpyridine	3.34	2012(s)
7	3Chloropyridine	2.82	2012(s)
8	4-Hydroxypyridine	3.27, 11.09	2000(sh), 1988(s)
9	Imidazole	7.00	2001(s)
10	Benzimidazole	5.52	2000(s)
11	2-Methylbenzimidazole	6.10	2000(s)
12	2-Ethylbenzimidazole	6.15	2001(s)

[a] The pK_a values for L in complexes 1–8 are taken from ref. 7; those for 9 are from ref. 8; those for 10–12 are from ref. 9.

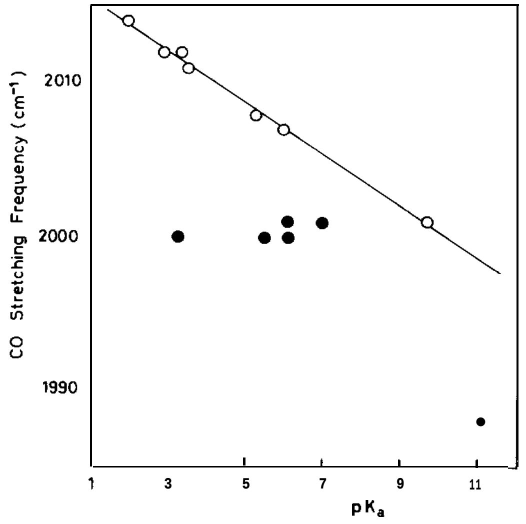


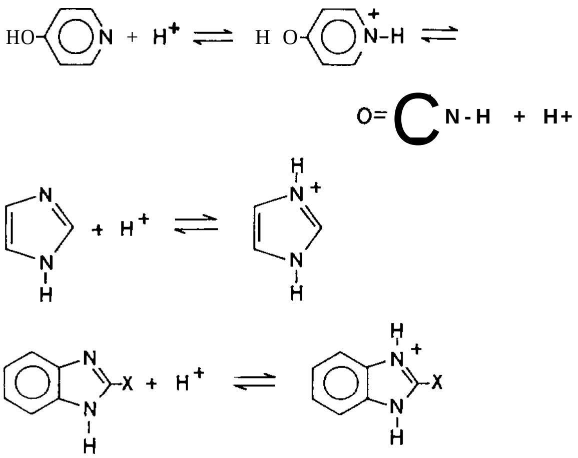
Fig. 1. pK_a values plotted against C-O stretching frequencies for $[Rh(CO)\{(C_6H_5)_3P\}_2L]PF_6$ complexes.

doublets are centered at 30.67 (J_{Rh-P} = 131.84 Hz) and 31.34 ppm (J_{Rh-P} = 126.96) from external 85% H_3PO_4. The doublet at 30.67 ppm is much more intense than the one at 31.34 ppm.

It has been shown [10] that in solution, the pyridone form of 4-hydroxypyridine (as shown in structure II) is much more abundant than the hydroxypyridine form. If the formation constants for I and II are of the same order of magnitude, the pyridone complex II should be more abundant in the mixture of I and II. On this basis it is likely that the more intense IR peak at 1988 cm^{-1} is due to complex II. This assignment is consistent with the fact that for all other N-bound ligands studied, the CO stretching frequencies occur at 2000 cm^{-1} or above. By similar reasoning the more intense A_2X pattern in the $^{31}P\{^1H\}$ spectrum is assigned to the pyridone complex II.

Figure 1 shows several dark circles that do not fall on the straight line obtained for the first seven bases listed in Table I. The dark circles at pK_a values of 3.27 and 11.09 represent the data for the two isomers obtained with 4-hydroxypyridine. The remaining dark circles at pK_a values of 7.00, 6.15, 6.10 and 5.52 represent data for the imidazole, 2-ethylbenzimidazole, 2-methylbenzimidazole and benzimidazole complexes, respectively.

There is, at first glance, no obvious reason why the trend observed for the first seven bases in Table I breaks down for those ligands whose data are represented by the dark circles in Fig. 1. It is interesting, however, to note that for all the bases that deviate from the straight line plot, two potential sites of deprotonation exist for their conjugate acids. It is possible that the correlation of the two potential sites of deprotonation that occurs through resonance is such that the pK_a of a given site is no longer a good measure of the relative sigma donor ability



of the ligand at that site; therefore, there is no linear relationship between pK_a and $\nu(CO)$.

This study has demonstrated that under carefully chosen conditions the pK_a values of a series of similar bases can be a good measure of relative *trans* influences. However, care must be exercised in making such correlations because subtle changes in the electronic nature of the ligand can alter the ligand donor ability in unexpected ways. It should also be pointed out that the linear correlation observed between $\nu(CO)$ and the pK_a of the nitrogenous bases studied here may not be the same for another series of bases with the same pK_a values. In spite of the observed correlation, the pK_a measures the sigma donor capabilities toward the proton only, and it is possible that two or more ligands may have the same pK_a values but different donor capabilities toward a given metal.

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