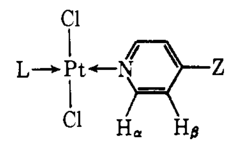
Ligand Exchange in Platinum(II) Complexes

Phyllis D. Kaplan, Paul Schmidt, Allan Brause, and Milton Orchin

Contribution from the Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221. *Received July 8, 1968*

Abstract: Ligand lability in some *trans*-1,3-dichloro-2-olefin-4-(4-Z-pyridine)platinum(II) complexes (**1**) was examined by means of nmr spectroscopy. Solvent-initiated exchange with the pyridine moiety occurs more readily than with the olefin moiety. The ease of exchange of the pyridines depends upon the solvent, the temperature, the nature of Z, and the structure of the olefin. Ethylene is a better *trans*-labilizing olefin than either *cis*- or *trans*-2-butene. When two different complexes, **1a** and **1b**, are mixed in deuteriochloroform, ligand exchange occurs and the four possible complexes are obtained.

In an earlier communication[1] it was reported that in deuteriochloroform solution, complexes of structure **1** can undergo exchange of both the olefinic and pyridine moieties at room temperature, particularly when Z is electron withdrawing. This conclusion was based on the nmr spectra of these complexes which showed loss of coupling between the α protons on pyridine and the ^{195}Pt isotope, as well as line broadening in the olefinic proton region. It was suggested that rapid exchange between solvent and ligands occurs.



1, L is ethylene, *cis*- or *trans*-2-butene
1a, L is *cis*-2-butene, Z = CN
b, L is ethylene, Z = CH_3

Solvent interaction with **1** and related complexes is important in connection with their catalytic activity; the solvent may either retard[2] or aid[3] catalysis. Solvent interaction with bridged dimers of Pt(II) is well established. Thus in ethanol, ethylene–platinous chloride dimer, $[PtCl_2(C_2H_4)]_2$, exists predominantly[4] as the monomer, *trans*-$[PtCl_2(C_2H_4)(C_2H_5OH)]$, while in refluxing acetone[5] it is approximately 70% reversibly dissociated to *trans*-$[PtCl_2(C_2H_4)(CH_3COCH_3)]$. Even in the monomeric form, solvent interaction readily occurs; Zeise's salt, $K[PtCl_3(C_2H_4)]$, in water can form[6,7] *trans*-$[PtCl_2(C_2H_4)(H_2O)]$ as the predominant species.

We wish now to elaborate on our earlier communication and to further substantiate ligand exchange and define the structural conditions which facilitate or retard it.

Results and Discussion

Lability of the Pyridine Ligand. The pyridine moieties in complexes **1** exchange more rapidly than do the olefin moieties. The ease of exchange of the pyridines depends upon the solvent, the temperature, the nature of the *para* substituent Z, and the structure of the olefin.

In Table I are listed the chemical shift data for the pyridine protons in free pyridine and in the 15 complexes of structure **1**. The spectra were taken at room temperature and at −45°. In the free pyridine, lowering the temperature causes a downfield shift of both α and β protons, but in the complexes, except for Z = CO_2CH_3, the low temperature causes an upfield shift of the α protons although the β protons are still shifted downfield. The upfield shift of the α protons is probably due to the increased time the pyridine spends in the vicinity of the metal at the low temperature and the enhanced shielding effect of this nearby platinum atom. A similar but even more modest upfield shift has been reported[8] for the H_α protons of pyridine N-oxide complexes of tin and lead. Shifts of the pyridine protons on complexation with a protonic acid[9–11] have been reported and here downfield shifts of the β and γ protons are larger than the shifts of the α protons.

Table I shows that there is an increasing downfield shift of both α and β protons with decreasing base strength of the pyridine (with the notable exception of the β proton of the cyano complex), and the effect persists in the complexes. This is the expected result of the substituent σ values.

Perhaps the most dramatic effect of the nature of the Z substituent is its influence on the coupling of the α protons. Table II shows that when ethylene is present on the metal the temperature must be increasingly lowered as the electron-withdrawing power of Z increases in order to observe such coupling. Even with the most electron-releasing substituent, OCH_3, 23° is about the maximum temperature at which coupling can be observed. The failure to observe coupling means that exchange of the pyridine with solvent is taking place rapidly on the nmr time scale. Table II also shows that, when the butenes are complexed to the metal and Z is strongly electron withdrawing, coupling with the H_α protons occurs only at low temperatures.

The coupling-constant data of Table II indicate that with the ethylene complexes all pyridines are exchanging rapidly at room temperature. This means that the chemical shift data for the pyridine protons taken at 30° and reported in Table I are time-averaged values.

---

[1] P. D. Kaplan, P. Schmidt, and M. Orchin, *J. Amer. Chem. Soc.*, **89**, 4537 (1967).

[2] H. A. Tayim and J. C. Bailar, Jr., *ibid.*, **89**, 4330 (1967).

[3] F. H. Jardine, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc., A*, 1574 (1967); 1711 (1966).

[4] D. G. McMane and D. S. Martin, Jr., *Inorg. Chem.*, 7, 1169 (1968).

[5] J. Chatt and A. A. Williams, *J. Chem. Soc.*, 3061 (1951).

[6] I. Leden and J. Chatt, *ibid.*, 2936 (1955).

[7] S. J. Lokken and D. S. Martin, Jr., *Inorg. Chem.*, **2**, 562 (1963).

[8] V. G. Kumar Das and W. Kitching, *Organometal. Rev.*, in press.

[9] I. C. Smith and W. G. Schneider, *Can. J. Chem.*, **39**, 1158 (1961).

[10] V. M. S. Gil and J. N. Murrell, *Trans. Faraday Soc.*, 60, 248 (1964).

[11] R. A. Abramovitch and J. B. Davis, *J. Chem. Soc., B*, 1137 (1966).

Table I. Chemical Shifts of the Pyridine Protons in 1,3-Dichloro-2-olefin-4-(4-Z-pyridine)platinum(II) Complexes[a] (1) in $CDCl_3$

			L in complex					
	Free pyridine		Ethylene		*trans*-2-Butene		*cis*-2-Butene	
	30°[b]	−45°	30°	−45°	30°	−45°	30°	−45°
Z = OCH_3								
H_α	8.43	8.48	8.67	8.60	8.67	8.63	8.71	8.63
H_β	6.82	6.83	6.98	7.02	6.92	6.98	6.93	6.99
Z = CH_3								
H_α	8.47	8.55	8.78	8.72	8.68	8.66	8.68	8.66
H_β	7.13	7.15	7.32	7.42	7.25	7.34	7.27	7.34
Z = H								
H_α	8.61	8.69	8.95	8.89	8.90	8.83	8.90	8.83
H_β	7.26	7.36	7.55	7.61	7.45	7.51	7.45	7.53
H_γ	7.67	7.76	7.97	8.02	7.87	7.95	7.88	7.96
Z = CO_2CH_3								
H_α	8.82	8.83	9.07	9.10	9.04	9.06	9.03	9.00
H_β	7.87	7.89	8.04	8.14	8.00	8.09	7.99	8.07
Z = CN								
H_α	8.84	8.92	9.25	9.12	9.16	9.12	9.14	9.12
H_β	7.57	7.68	7.82	7.83	7.72	7.84	7.74	7.83

[a] Some of these values have been reported previously,[1] but the present values are considered more accurate. [b] This temperature is ±3°.

Table II. Coupling Constants[a] in Some 1,3-Dichloro-2-olefin-4-(4-Z-pyridine)platinum(II) Complexes (1)

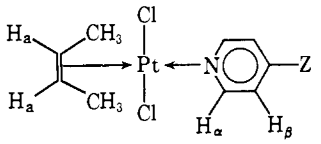
	Ligand					
	$(H_a)_2C{=}C(H_a)_2$		*trans*-$H_a(CH_3)C{=}C(CH_3)H_a$		*cis*-$H_a(CH_3)C{=}C(CH_3)H_a$	
Z	J_{Pt-H_a}	J_{Pt-H_α}	J_{Pt-H_a}	J_{Pt-H_α}	J_{Pt-H_a}	J_{Pt-H_α}
OCH_3	60.7	34.5 (23°)	61.0	33.2	68.4	33.5
CH_3	60.5	31 (3°)	60.3	32.8	68.1	33.5[b]
H	60.5	36 (−14.5°)	62.4	33.6	69.0	34.5
$COOCH_3$	61.7	36 (−14.5°)	62.3	33.4 (−24°)	69.0	34.1 (−9°)
CN	62.6	36.5 (−51°)	63.2	34 (−25°)	70.4	34 (3°)

[a] When the temperature was lower than the ambient temperature of the probe (29–32°), this is indicated in parentheses. The constants are in cycles per second. All spectra were taken in $CDCl_3$ as 10–20% w/w solutions. The larger coupling, $J_{Pt-H\alpha}$, for Z = electron withdrawing is most probably a reflection of the increased resolution at lower temperatures. [b] At −45°, $J_{Pt-H\alpha}$ = 34.4 cps. Other complexes exhibit a similar increase at low temperatures, most probably because of better resolution.

This is also true of the values for the butenes when Z is electron withdrawing, because here again coupling is absent at 30°. However, even for other Z substituents, it is likely that the chemical shift values of Table I are averaged shifts for free and complexed pyridine since lowering the temperature to −45° produces a similar upfield shift in H_α as does ethylene when it is the *trans* ligand. There appears to be very little difference between *cis*- and *trans*-2-butene in their effect on the chemical shift values of the pyridine protons despite the difference in temperature at which these isomeric olefinic complexes exhibit coupling (Table II) and despite the fact that the *cis* isomer is probably more stable.[12,13] Recently, chemical shift data for pyridine protons in complexes of the type *trans*-$[PtCl_2(py)L]$ have been determined[14] and found to be rather insensitive to the nature of L.

It should be pointed out that, despite the rapid exchange of the pyridine ligands, the equilibrium must lie almost completely on the side of the undissociated complex. The complex is essentially quantitatively recovered from solution by either precipitation or careful evaporation.

Table III. Solvent Effects on the Nmr Spectra of



Z	Solvent[a]	Temp, °C	δ_a	δ_β	δ_α	$J_{Pt-H\alpha}$, cps
OCH_3	$CDCl_3$	33	5.65	6.93	8.71	33.5
		−45	5.63	6.99	8.63	33.5
	CD_3COCD_3	33	5.55	7.21	8.68	None
		−48	5.53	7.28	8.66	33.1
CH_3	$CDCl_3$	33	5.68	7.27	8.68	33.5
		−45	5.66	7.34	8.66	33.5
	CD_3COCD_3	30	5.56	7.45	8.62	None
		−46	5.53	7.55	8.67	None

[a] All spectra were run at 60 Mc, using TMS as the internal reference. The solutions were prepared in a 10% w/w ratio. The temperature of the probe was calibrated employing methanol in the standard manner.

Solvent Effects. As expected, solvents have a profound effect on ligand lability. The results of some studies with d_6-acetone are given in Table III. In acetone, the coupling, which is present under identical conditions in chloroform solution, is lost, indicating rapid exchange on the nmr time scale between the pyridine and solvent and the much stronger coordinating ability of acetone as compared to chloroform. The marked downfield shift of H_β protons in acetone solu-

---

(12) H. B. Jonassen and W. B. Kirsch, *J. Amer. Chem. Soc.*, **79**, 1279 (1957); J. R. Joy and M. Orchin, *ibid.*, **81**, 310 (1959).
(13) G. C. Bond and P. B. Wells, *Advan. Catal.*, **15**, 216 (1964).
(14) J. Chatt and A. D. Westland, *J. Chem. Soc., A*, 88 (1968).

tions, which has also been observed by other workers,[15] probably reflects some solvent anisotropy rather than a coordination effect.

Lability of the Olefinic Ligand. The data of Table II confirm that the olefinic moiety is more tightly bonded than the pyridine moiety in complexes **1** since olefinic proton coupling with ^{195}Pt is observed with all the complexes at even the highest temperature employed for the nmr studies. With all three olefins examined, the coupling constant increases as the basicity of the pyridine decreases. The chemical shift values, δ, in each olefin series increase with decreasing basicity of the pyridine (Table IV); the increase is in the direction of the value of the free olefin. The increasing coupling constant accompanied by increasing δ for the chemical shift has been observed previously[16] and commented on by other workers.[17, 18] At temperatures above 30° the olefin begins to undergo exchange as indicated by line broadening and, in acetone solution, exchange is rapid as indicated by loss of coupling.[18]

Table IV. Chemical Shifts of Olefinic Protons in the 1,3-Dichloro-2-olefin-4-(4-Z-pyridine)platinum(II) Complexes

	Chemical shifts[a] (δ)					
	Ethylene		*cis*-2-Butene		*trans*-2-Butene	
Z	−44.5°	+33.5°	−44.5°	+33.5°	−44.5°	+33.5°
OCH_3	4.90	4.85	5.63	5.66	5.49	5.46
CH_3	4.89	4.88	5.66	5.68	5.49	5.47
H	4.94	4.93	5.67	5.70	5.51	5.52
$COOCH_3$	4.97	4.93	5.74	5.74	5.56	5.53
CN	4.99	4.99	5.80	5.78	5.60	5.62

[a] All spectra were run at a 10% w/w concentration in $CDCl_3$ using TMS as the internal reference.

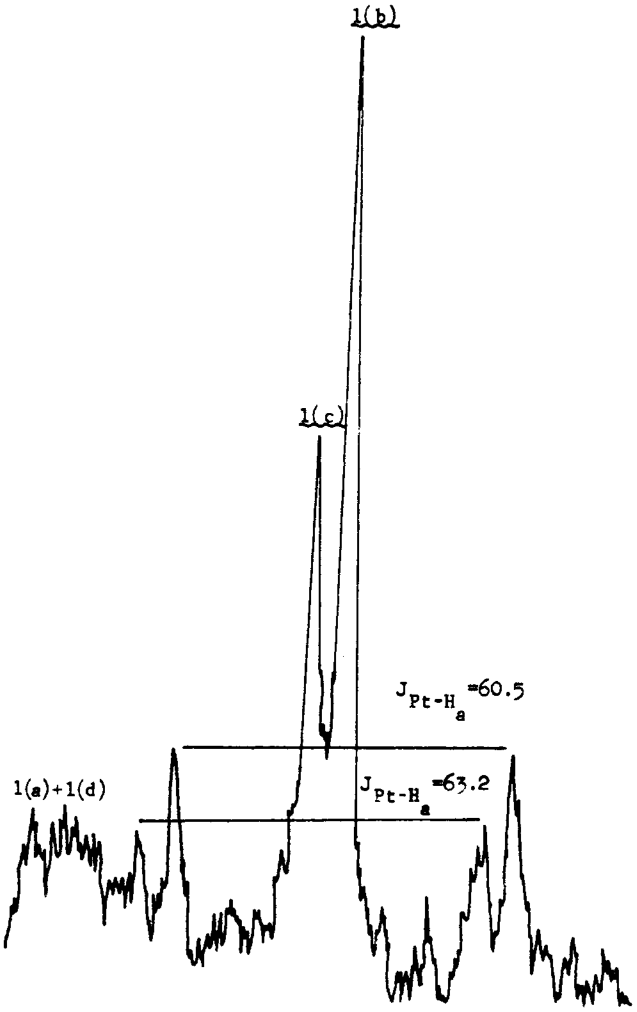


Figure 1. Ethylene region of the mixture of **1a** and **1b** at −44° (see Table V).

The exact mechanism of olefin exchange is not yet clear. The olefins with the largest coupling constants are most labile in solution; these are the complexes in which the pyridine moiety is the weakest base and which lose the H_α proton coupling most readily. Conceivably an exchange between free pyridine and olefin might be occurring. It is known that excess pyridine will displace the olefin from an olefin–pyridine complex.[19] A low-temperature nmr study of this reaction[20] indicates that pyridine can cause the coordinated olefin to undergo a $\pi \rightarrow \sigma$ rearrangement, but whether such a rearrangement is an essential preliminary step in the displacement of ethylene by pyridine has not been demonstrated.

Ligand Exchanges. Loss of proton coupling of ligands with ^{195}Pt may conceivably be due to the development of a highly solvated complex[21] as well as to a ligand-exchange process in which the solvent plays a key role. In order to determine whether an actual exchange of ligands between complexes is possible, the following experiment was performed: a 10% w/w solution of 1,3-dichloro-2-(*cis*-2-butene)-4-(4-cyanopyridine)platinum(II) in deuteriochloroform was prepared and the nmr spectrum recorded; an equal weight of 1,3-dichloro-2-ethylene-4-(4-methylpyridine)platinum(II) was then added to the solution and the spectrum again recorded with the probe temperature at about 30°. The solution was then cooled to −45° in the probe. The ethylene region of the spectrum at −45° (Figure 1) shows that all four possible complexes are present. The data are recorded in Table V.

The appearance of the four complexes may be explained by either pyridine exchange alone, olefin exchange alone, or by complete scrambling. Since the olefin–platinum coupling was observed at 30° while the pyridine–platinum was not, it appears that the pyridine moieties are exchanging. The possibility of a slow olefin exchange cannot be eliminated.[22] A some-

---

(15) P. Lazlo in "Progress in Nuclear Magnetic Resonance Spectroscopy," Vol. 3, J. W. Emsley, J. Feeney, and L. H. Sutcliff, Ed., Pergamon Press, N. Y., 1967, p 231.

(16) P. D. Kaplan and M. Orchin, *Inorg. Chem.*, 4, 1393 (1965).

(17) P. S. Braterman, *ibid.*, 5, 1085 (1966).

(18) H. P. Fritz and D. Sellman, *Z. Naturforsch.*, **22b**, 610 (1967).

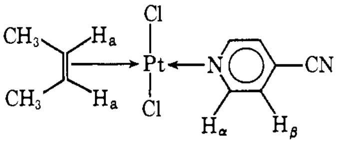
(19) J. S. Anderson, *J. Chem. Soc.*, 971 (1934).

(20) P. D. Kaplan, P. Schmidt, and M. Orchin, *J. Amer. Chem. Soc.*, **90**, 4175 (1968).

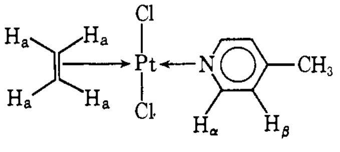
(21) R. S. Drago, V. A. Mode, and J. G. Kay, *Inorg. Chem.*, **5**, 2050 (1966).

(22) Estimates (J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Oxford, 1965, Chapter 9) of the minimum metal–ligand lifetime, τ, can be made from the value of the spin coupling constants, since spin coupling can be observed when $\tau > 1/J$. In our experiment, platinum–olefin coupling is observed even at about 40°, and since $J \sim 64$ cps, the olefin must be on the metal for at least 0.016 sec. In this

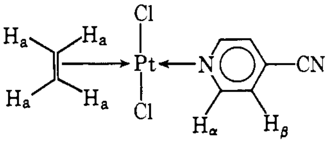
Table V. Nmr Spectral Values[a] of the Reaction of **1a** with **1b**



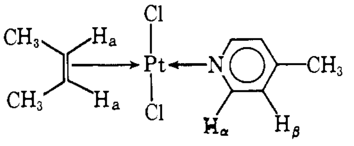
1a



1b



1c



1d

		Chemical shifts (δ)					J, cps		
		Olefinic		Aromatic					
Complex	Temp, °C	CH_3	H_a	H_β	H_α	CH_3	Pt-H_a	Pt-H_α	Pt-CH_3[b]
1a	~40	1.80	5.79	7.72	9.13		...[c]	None	36.0
1b	34	...	4.88	7.32	8.78		60.5	None	...
1a + **1b**	~40								
1a		1.80	5.69	7.73	9.16		...[c]	None	36.2
1b		...	4.90	7.25	8.72		61.5	None	...
1a + **1b**	−43								
1a			~5.73[d]	7.82[e]	9.10[e]		...	...	...
1c			5.00	7.82[e]	9.10[e]		63.2	...	...
1b			4.89	7.37[e]	8.67[e]	2.50	60.5	...	...
1d			~5.73[d]	7.37[e]	8.67[e]	2.50	...	~34	...

[a] The solutions were 10% w/w solute to solvent. [b] Double irradiation experiments have established a change in sign between J_{Pt-CH_3} and J_{Pt-H_a}: B. F. G. Johnson, C. Holloway, G. Hulley, and J. Lewis, *Chem. Commun.*, 1143 (1967). [c] Too weak to measure accurately. [d] The signal is too broad and weak to distinguish between the two butene complexes present. [e] Average values for the two complexes of each pyridine.

what analogous olefin exchange between a rhodium complex and platinum complex has been reported.[23]

Experimental Section

The preparation of the complexes has been described previously.[24] The *trans*-2-butene complexes were prepared in an identical manner to the *cis*-2-butene complexes. The nmr spectra were obtained on a Varian Associates A-60 spectrometer; the audiooscillation sideband technique was used for calibration.

Acknowledgments. We wish to thank Dr. F. Kaplan for helpful discussions, Englehard Industries, Inc. for a generous supply of platinum, and the National Science Foundation for a Traineeship to P. S. We are also grateful to the Petroleum Research Fund administered by the American Chemical Society for partial support.

---

experimental system 4-methylpyridine–platinum coupling is observed only at −45° and because $J \sim 34$ cps, the pyridine must be on the metal for at least 0.029 sec. Since the olefin was already on for at least 0.016 sec at 40°, it is likely that at −45° it is on for periods considerably longer than 1 sec and indeed may not be exchanging at all.

(23) R. Cramer, *Inorg. Chem.*, 4, 455 (1965).

(24) P. Schmidt and M. Orchin, *ibid.*, 6, 1260 (1967).