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Acetonitrile Complexes of Platinum(II) and Displacement Reactions with the Halide of Infrared Cells

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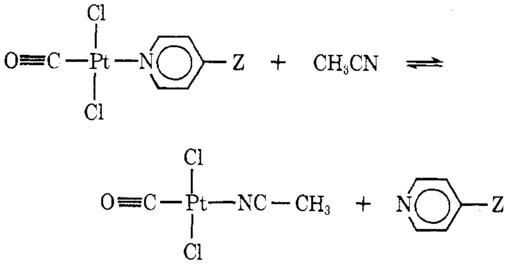
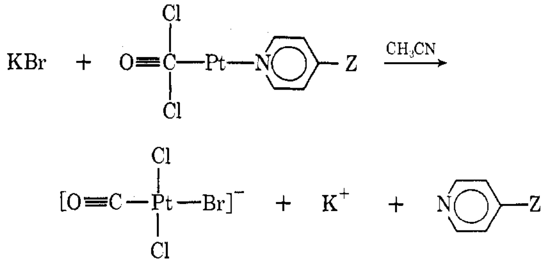
When the infrared spectrum of *trans*-1,3-dichloro-2-(4-cyanopyridine)-4-carbonylplatinum(II), $(4\text{-}NCC_5H_4N)PtCl_2(CO)$, is determined in acetonitrile solution in metal halide infrared cells, the solvent dissolves sufficient halide from the cell to cause a displacement reaction leading to *trans*-$[(X)PtCl_2(CO)]^-$, where X^- is Br^- or Cl^-. The reaction is readily followed by the disappearance of the original ν_{CO} and the appearance of a new carbonyl band at lower frequency. In the present study, acetonitrile and benzonitrile complexes of the structure $(Un)PtCl_2(RCN)$, where Un is ethylene or carbon monoxide, have been prepared. The pmr spectra of the complexes show that in solution both the nitrile and the ethylene in the trans isomer are more labile than they are in the corresponding cis isomer.

In the past few years we have engaged in a study of the preparation and properties of square-planar Pt(II) compounds having the structure $(Un)PtCl_2(L)$, where Un is an unsaturated molecule such as carbon monoxide or ethylene and its derivatives, and L is a neutral ligand such as pyridine, pyridine *N*-oxide, and their derivatives.[1-4] One of our studies focused on the infrared spectra of such compounds, especially on the series of trans carbonyl–pyridine complexes of the above structure (Un = CO, L = C_5H_5N) and in particular on the position of ν_{CO} as a function of the substituent on pyridine.[2] It was found, as expected, that the greater the electron-releasing properties of a substituent at the 4 position, the lower the values of ν_{CO}. In chloroform solution, using potassium bromide cells, one strong carbonyl band appeared between 2130 and 2150 cm^{-1}. However, in acetonitrile solution, a second band at 2095 cm^{-1} was observed, and the position of this band was independent of the nature of the pyridine substituent. We suspected at that time that this new low-frequency band was due to a second carbonyl species obtained by an equilibrium displacement reaction (eq 1) involving the pyridine and acetonitrile.


(1)

Initial attempts to prepare the authentic trans nitrile complex led to the isolation of the corresponding cis complex, but we have now succeeded in preparing and characterizing the desired trans complex.[5] This complex does not have the anticipated ν_{CO} at 2095 cm^{-1}. We now find that the heretofore mysterious 2095-cm^{-1} band obtained with acetonitrile in potassium bromide cells is in fact due to the bromide complex. Polar solvents dissolve sufficient potassium bromide from the cell surface to initiate the displacement (eq 2)


(2)

We have commented previously on the lack of reproducibility of infrared spectra of carbonyl complexes when the spectra of the same complex were determined in cells of different composition.[2] The reason for this observation now becomes clear; the solvent may dissolve more or less of the metal halide cell and cause partial or complete displacement of one of the ligands of the complex by the anion of the cell material.

Experimental Section

The infrared spectra were obtained using either a Perkin-Elmer 237 or Beckman IR-12 spectrometer. The spectra were standardized using either polystyrene or H_2O–CO_2. The nmr spectra were obtained with either a Varian T-60 or Brucker HFX-90 instrument.

The carbonyl compounds were extremely water sensitive; thus the analyses (Galbraith Laboratories) were characteristically not in close agreement with theory.[6] The complexes were also characterized by their infrared and nmr spectra.

All solvents were reagent or spectral grade and were dried over molecular sieves. Zeise's dimer, $[(C_2H_4)PtCl_2]_2$, was prepared by standard methods.[7]

1,3-Dichloro-2-ethylene-4-acetonitrileplatinum(II) (1a).—To 280 mg (0.5 mmol) of $[(C_2H_4)PtCl_2]_2$ in 25 ml of chloroform, 60 μl (1.0 mmol) of acetonitrile was added. The color of the solution changed instantly from light orange to yellow. The solution was filtered, the volume reduced, and then hexane added. A light yellow solid was isolated by filtration and washed with hexane giving 202 mg (61%): mp 150° dec; nmr ($DCCl_3$) δ 4.81 (s, 4, at 35°; t, 4, at −15°; $J_{^{195}Pt}$ = 72 Hz, C_2H_4), 2.51 (s, CH_3CN). *Anal.* Calcd for $C_4H_7NPtCl_2$: C, 14.33; H, 2.09. Found: C, 14.49; H, 2.10.

1,3-Dichloro-2-ethylene-4-benzonitrileplatinum(II) (1c).—The above procedure was used except that 100 μl of benzonitrile in place of acetonitrile was added giving 209 mg (55%): mp 125° dec; nmr ($DCCl_3$) δ 7.8 (m, 5, C_6H_5CN), 4.87 (s, 4, at 35°; t, 4,

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[1] T. Weil, P. Schmidt, and M. Orchin, *Inorg. Chem.*, **8**, 2138 (1969).

[2] T. Weil, P. Schmidt, M. Rycheck, and M. Orchin, *ibid.*, **8**, 1002 (1969).

[3] M. Orchin and P. Schmidt, *Coord. Chem. Rev.*, **3**, 345 (1968).

[4] M. Orchin and P. Schmidt, *Inorg. Chim. Acta Rev.*, **2**, 123 (1968).

[5] T. Weil, L. Spaulding, and M. Orchin, *J. Coord. Chem.*, **1**, 25 (1971).

[6] W. H. Clement and M. Orchin, *J. Organometal. Chem.*, **3**, 98 (1965); A. Braus, M. Rycheck, and M. Orchin, *J. Amer. Chem. Soc.*, **89**, 6500 (1967).

[7] J. Chatt and L. Duncanson, *J. Chem. Soc.*, 2939 (1953).

$J_{^{195}Pt}$ = 60 Hz at 5°, C_2H_4). *Anal.* Calcd for $C_9H_9NPtCl_2$: C, 27.21; H, 2.26: Found: C, 27.40; H, 2.46.

1,3-Dichloro-2-acetonitrile-4-carbonylplatinum(II) (1b).—Carbon monoxide was bubbled into a solution of the ethylene complex **1a**, in 20 ml chloroform, until the solution became much lighter in color. The solvent was removed *in vacuo,* and the resulting solid was recrystallized from chloroform–hexane yielding an extremely water-sensitive solid. *Anal.* Calcd for $C_3H_3NOPtCl_3$: C, 10.75; H, 0.90. Found: C, 12.41; H, 1.36.

1,3-Dichloro-2-benzonitrile-4-carbonylplatinum(II) (1d).—The procedure above was used starting with the ethylene–benzonitrile complex. *Anal.* Calcd for $C_8H_5NOPtCl_2$: C, 24.18; H, 1.26. Found: C, 22.54; H, 1.85.

1,2-Dichloro-3-benzonitrile-4-ethyleneplatinum(II).—The procedure was that used for the acetonitrile compound.[5] A 10% excess of benzonitrile was stirred for 2 days with an aqueous solution of potassium tetrachloroplatinate. The longer stirring time was necessary because of the low solubility of benzonitrile in water. The rest of the procedure was as above; nmr ($DCCl_3$) δ 7.8 (m, 5, C_6H_5CN), 4.76 (t, 4, $J_{^{195}Pt}$ 61 Hz, C_2H_4). *Anal.* Calcd for $C_9H_9NPtCl_2$: C, 27.21; H, 2.26. Found: C, 27.08; H, 2.29.

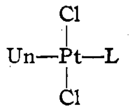
1,2-Dichloro-3-benzonitrile-4-carbonylplatinum(II).—The procedure for C_2H_4 replacement was the same as for trans compounds. *Anal.* Calcd for $C_8H_5NOPtCl_2$: C, 28.18; H, 1.26. Found: C, 24.06; H, 1.46.

Tetra-*n*-butylammonium 1,3-Dichloro-2-iodo-4-carbonylplatinate(II) (1g).—To 50 mg (0.136 mmol) of $K[(CO)PtCl_3]$ (prepared by bubbling CO into an acetone solution of Zeise's salt and crystallizing) there were added with stirring 52.0 mg (0.136 mmol) of $(n\text{-}C_4H_9)_4NI$. A white precipitate of KCl formed immediately. After 10 min the KCl which precipitated was removed by centrifugation. The supernatant liquid was decanted and its volume reduced by evaporation *in vacuo.* The iodide complex was precipitated by addition of hexane and was recrystallized from chloroform–hexane. *Anal.* Calcd for $C_{17}H_{36}Cl_2NOPtI$: C, 26.67; H, 5.08. Found: C, 27.67; H, 5.09.

Tetraethylammonium Trichlorocarbonylplatinate(II).—To 52.6 mg (0.143 mmol) of $K[(CO)PtCl_3]$ in 5 ml of acetone there was added with stirring 23.6 mg (0.143 mmol) of $(C_2H_5)_4NCl$ in acetone. After 1 hr the solution was treated as above. *Anal.* Calcd for $C_9H_{20}Cl_3NOPt$: C, 24.35; H, 4.51. Found: C, 24.43; H, 4.42.

Results and Discussion

The series of compounds prepared for this study have structure **1**.



$$\begin{array}{c} Cl \\ | \\ Un{-}Pt{-}L \\ | \\ Cl \end{array}$$

1a, Un = C_2H_4; L = CH_3CN
b, Un = CO; L = CH_3CN
c, Un = C_2H_4; L = C_6H_5
d, Un = CO; L = C_6H_5CN
e, Un = CO; L = 4-NCC_5H_4N
f, Un = CO; L = Br^-
g, Un = CO; L = I^-

Infrared Studies.—Table I shows that ν_{CO} in the infrared spectrum of *trans*-$(CO)PtCl_2(CH_3CN)$ (**1b**) depends both upon the type of cell and upon the particular solvent used for the determination. In all cases only the single ν_{CO} band recorded in Table I was initially observed in the spectrum. However, on long standing, the acetonitrile solution of the complex in the silver chloride and in the sodium chloride cells gave rise to a second ν_{CO} which appeared at 2097 cm^{-1}, essentially identical with the band obtained with the potassium bromide cell. When tetra-*n*-butylammonium bromide was added to the acetonitrile solution of the complex in the silver chloride cell, the band at 2095 cm^{-1} appeared immediately. Clearly, acetonitrile was slowly dissolving sufficient silver chloride (and sodium chloride) to give the chloride species analogous to the bromide species **1f** formed in the presence of the soluble R_4NBr salt. When solid potassium bromide was added with stirring to a 1.6 × 10^{-2} *M* solution of the complex **1b**, the band at 2095 cm^{-1} appeared slowly and grew in intensity with time. The solubility[8] of potassium bromide in acetonitrile is only 1.6 × 10^{-3} *M*, or one-tenth of that required by the stoichiometry of eq 2. Obviously the bromide was reacting and not simply dissolving. Attempts to isolate the potassium salt of **1f** in pure form were unsuccessful. Stirring sodium chloride with acetonitrile in the presence of the complex **1b** gave little reaction initially, but on long standing the band at 2097 cm^{-1} appeared. When tetraethylammonium chloride which is soluble in acetonitrile was added to the solution, the band at 2097 cm^{-1} immediately appeared, and the band at 2143 cm^{-1} disappeared.

TABLE I

CARBONYL STRETCHING FREQUENCY OF *trans*-$(CO)PtCl_2(CH_3CN)$. EFFECT OF SOLVENTS AND CELLS

	Cell				
	KBr	AgCl	Irtran-2[a]	KBr	NaCl
Solvent	CH_3CN	CH_3CN	CH_3CN	$HCCl_3$	CH_3CN
ν_{CO}, cm^{-1}	2095	2139	2140	2144	2139

[a] Irtran-2 is a zinc sulfide cell.

Convincing evidence that the halide species formed by eq 2 is responsible for the band at about 2095 cm^{-1} is given in Table II. The pure tetraalkylammonium salts $R_4N[(CO)PtCl_2(X)]$ showed almost the identical ν_{CO}'s as were obtained when R_4NX was added to solutions of **1e**. The ν_{CO}'s of **1e** in various cells and in various solvents are also shown in Table II. These data are all readily rationalized on the basis of eq 2; only when conditions are such that appreciable bromide ion is formed does the band at 2095 cm^{-1} appear.

TABLE II

CARBONYL STRETCHING FREQUENCIES IN VARIOUS SOLVENTS

Compound	ν_{CO}, cm^{-1}	Cell	Solvent
$(C_2H_5)_4N[(CO)PtCl_3]$	2097	Ir-2[a]	$CHCl_3$
$(n\text{-}C_4H_9)_4N[(CO)PtCl_2I]$	2085	Ir-2[a]	$CHCl_3$
	2086	Ir-2[a]	CH_3CN
$(CO)PtCl_2(pyCN)$[b] + $(C_4H_9)_4NX$			
X = Cl	2099	KBr	$CHCl_3$
X = Br	2096	KBr	$CHCl_3$
X = I	2083	KBr	$CHCl_3$
$(CO)PtCl_2(pyCN)$	2134	KBr	$CHCl_3$
	2134, 2095	KBr	CH_3CN
	2135	Ir-2	CH_3CN
	2135	AgCl	CH_3CN

[a] This is Irtran-2, a zinc sulfide cell. [b] pyCN denotes 4-cyanopyridine.

The stereochemistry of square-planar complexes, $(Un)PtCl_2(L)$, is readily ascertained from a determination of the far-infrared spectra of such complexes.[9] The cis configuration, with lower symmetry than the trans isomer, gives rise to two Pt–Cl bands in the 300–400-cm^{-1} region, while the trans isomer gives rise to a single band in the 340–355-cm^{-1} region. The spectrum of **1g**, as the tetra-*n*-butylammonium salt, gives a single band at 340 cm^{-1} confirming the trans configuration. Table III gives the spectral data of a variety of

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[8] T. Pavlopoulos and H. Strehlow, *Z. Phys. Chem. (Leipzig)*, **202**, 474 (1953).

[9] H. Fritz and D. Sellman, *J. Organometal. Chem.*, **6**, 558 (1966); D. Adams, J. Chatt, J. Geratt, and A. Westland, *J. Chem. Soc.*, 734 (1964).

TABLE III

INFRARED SPECTRA OF *cis*- AND *trans*-(Un)$PtCl_2$(L)[a]

Un	L	ν_{CO}	ν_{CN}	$\Delta\nu_{CN}$[b]	ν_{PtCl}
			Cis Isomer		
C_2H_4[c]	C_6H_5CN		2286	51	364, 326
C_2H_4	CH_3CN		2330	77	357, 331
CO[c]	C_6H_5CN	2111	2290	55	363, 343
CO	CH_3CN	2125	2324	71	353, 344
			Trans Isomer		
C_2H_4[c]	C_6H_5CN		2286	51	343
C_2H_4[c]	CH_3CN		2328	75	348
CO[c]	C_6H_5CN	2120	2288	53	353
CO[c]	CH_3CN	2134	2328	75	355

[a] In Nujol mull; ν in cm^{-1}. [b] Increment over ν_{CN} of free nitrile. [c] New compound; see Experimental Section.

cis and trans complexes. The cis compounds all give rise to two bands while the trans isomers show a single Pt–Cl asymmetric stretching band at about 350 cm^{-1}.

Table III also gives some data for ν_{CN} in cis and trans acetonitrile and benzonitrile complexes. The position of the C≡N stretch for all these complexes occurs at higher frequencies than those of the corresponding free nitrile; such a shift is characteristic of coordination of the metal to the lone pair of electrons on the nitrogen.[10] Coordination through the π system of the nitrile causes a shift to lower frequency of about 300 cm^{-1}.[11]

Nmr Studies

The nmr data for the new compounds are included in the Experimental Section. As we have shown previously, the relative lability of ligands coordinated to platinum may be evaluated by determining the temperature at which spin coupling between the ligand protons and ^{195}Pt appears; the lower the temperature required to observe such coupling, the more labile the ligand.[1,3] The observation of spin coupling between Pt and the protons on various ligands, L, also depends on the magnitude of the coupling constant, J, between these species; in order to observe coupling, the PtL complex with a smaller J must have a longer lifetime than the complex with a larger J. The value of the coupling constant for the ethylene protons in the ethylene–acetonitrile complex **1a** is 12 Hz (about 20%) greater than the corresponding constant for the benzonitrile complex **1c**. Coupling with the ethylene protons in complexes with benzonitrile trans to ethylene occurs at 5°, whereas −15° is required with acetonitrile as a ligand. If the labilizing ability of benzonitrile were equal to or greater than that of acetonitrile, we might expect to observe coupling of the ^{195}Pt with the ethylene of the acetonitrile complex at a higher temperature than that required for coupling in the benzonitrile complex. This is contrary to observation, and hence we may conclude that acetonitrile is a better trans labilizing ligand than benzonitrile.

There is a remarkable difference in the lability of complexed acetonitrile depending upon whether it is cis or trans in (Un)$PtCl_2(CH_3CN)$. The acetonitrile in the trans complex **1a** shows no coupling of the methyl protons with ^{195}Pt in solutions with methylene chloride even at temperatures as low as −80° indicating its extremely rapid exchange with solvent. The cis isomer, however, shows coupling at room temperature, indicative of a ligand that is relatively difficult to displace.[5] The configuration of the coordinated nitrile also has a strong effect on the lability of the ethylene. When either acetonitrile or benzonitrile is trans to ethylene, the ethylene is labilized as shown by the failure to observe coupling between the ethylene protons and platinum at room temperature. However the cis nitriles show such coupling at room temperature. Thus the ligands Un and L trans to each other in Un-$PtCl_2$L labilize each other, while in the cis configuration neither ligand exchanges readily with solvent.

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(10) R. Walton, *Quart. Rev., Chem. Soc.*, **19**, 126 (1965).

(11) M. Farona and K. Kraus, *Inorg. Chem.*, **9**, 1700 (1970).