Synthesis and Proton Magnetic Resonance Spectra of Some Dichloro(picolinaldimine*)palladium(II) and -platinum(II) Complexes

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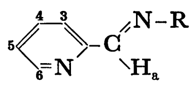
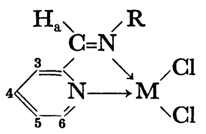
A series of dichloro(picolinaldimine)palladium(II) and -platinum(II) complexes was prepared. The PMR parameters, the chemical shifts of the ligand protons and the coupling constants between the platinum-195 nucleus and protons attached to carbons adjacent to donor nitrogens of the ligands, are discussed in the light of the metal-to-ligand bonds.

Recently we have reported that some picolinaldimines (**A**) form stable complexes with dimethyltin dichloride (**B**, M=$(CH_3)_2Sn(IV)$).[1] The ligands of this kind are interesting in that (1) the coordinating ability of the imine nitrogen atom can be altered by varying the substituent on it, (2) their configurational change from *trans* to *cis* on complex formation (**A** and **B**) is accompanied by remarkable changes in the chemical shifts of the various protons, and (3) information on the coordination bonds can be obtained through the observation of spin-spin couplings between the H_a and H_6 protons and the acceptor metal nucleus, if any, as was found in their dimethyltin dichloride complexes.[1]



(**A**)



(**B**)

M=$(CH_3)_2Sn$ (IV), Pd (II), Pt (II)

This paper will report on the synthesis of a series of dichloro(picolinaldimine)palladium(II) and -platinum(II) complexes (**B**, M=Pd(II) and Pt(II)) and on their PMR parameters in relation to the nature of the metal-to-ligand bonds.

Experimental

Materials. Na_2PdCl_4 and K_2PtCl_4 were reagent grade and were used as supplied. The picolinaldimines[1] and dichlorobis(benzonitrile)platinum(II)[2] were prepared by the literature methods.

Dichloro(picolinaldimine)palladium(II) Complexes. To a solution of Na_2PdCl_4 (0.50 g, 1.44 mmol) in C_2H_5OH (40 ml) was added dropwise a solution of *p*-tolylpicolinaldimine (0.34 g, 1.72 mmol) in C_2H_5OH (5 ml). Microcrystals were precipitated immediately. The mixture was then stirred for 1 hr at the ambient temperature. The resulting product was filtered and recrystallized from CH_2Cl_2/CH_3CN to give orange crystals of dichloro(*p*-tolylpicolinaldimine)palladium(II) (0.46 g, 85%).

Other Pd complexes were similarly obtained with the exception of the *n*-butyl derivative, which was recrystallized from CH_2Cl_2/petroleum ether.

Dichloro(picolinaldimine)platinum(II) Complexes. To a solution of $(C_6H_5CN)_2PtCl_2$[2] (0.30 g, 0.63 mmol) in 1,2-$C_2H_4Cl_2$ (30 ml) was added a solution of *p*-tolylpicolinaldimine (0.13 g, 0.64 mmol) in the same solvent (5 ml). The solution was refluxed for 4 hrs and then concentrated under reduced pressure to give an oily product, which was stirred in ether for 1 hr. The resultant precipitate was recrystallized from hot methanol to yield orange crystals of dichloro(*p*-tolylpicolinaldimine)platinum(II) (0.17 g, 58%).

The *p*-chloro and *p*-nitro-phenyl analogs were precipitated as orange solids, which were subsequently recrystallized from hot acetonitrile.

Table 1 shows the melting points, analytical data, and molecular weights of the complexes, together with their ν(M-Cl) frequencies.

Instrumentation. The molecular weights and IR and PMR spectra were obtained as has been described elsewhere.[1] The PMR spectra were usually recorded in CH_3CN at 50 °C because of the limited solubility of the complexes at 25 °C. Little temperature effect on the PMR parameters was observed in the *n*-butylpicolinaldimine complexes of Pd(II) and Pt(II); this was assumed to be true for the other as well. The *p*-substituted picolinaldimine complexes of Pt(II) showed a limited solubility in most organic solvents, and so their spectra were obtained in *N,N*-dimethylacetamide. The solvent effect on PMR parameters in the two solvents was checked by using dichloro(*n*-butylpicolinaldimine)platinum(II) and was found to be small. Tetramethylsilane was used as the internal reference.

Results and Discussion

The analytical data (Table 1) confirm that a series of picolinaldimines forms 1:1 complexes with palladium(II) and platinum(II) dichlorides. The molecular-weight determinations of some representative complexes showed that they were monomeric in solution. Both Pd(II) and Pt(II) complexes exhibit two ν(M-Cl) bands in the region of 360—325 cm^{-1} (Table 1). These facts indicate that the complexes adopt a square-planar configuration with the chelating ligand, as has been illustrated above in (**B**) (M=Pd(II) and Pt(II)). The chelation of the ligand is further verified in the Pt complexes from the observation of spin-spin couplings between the ^{195}Pt nucleus and the H_6, H_a, and the α-CH protons of the alkyl group on the imine nitrogen.

Table 2 shows the relevant PMR data of the picolinaldimine complexes of Pd(II) and Pt(II). The H_3 and H_6 signals of these ligands occur at low fields; this is taken to be evidence for the *trans* structure (**A**), the reasons having been discussed previously in the case of *p*-anisylpicolinaldimine.[1]

On complex formation, the chemical shift of each proton may be influenced by some of the following three effects; (1) a low-field shift caused by the electron-

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* Chem. Abstr. name: 2-formimidoylpyridine

TABLE 1. MELTING POINTS, ANALYTICAL DATA, MOLECULAR WEIGHTS, AND METAL–CHLORINE STRETCHING FREQUENCIES OF THE COMPLEXES $MCl_2 \cdot (NC_5H_4\text{-}CH\text{=}N\text{-}R)$

M	R	Mp (°C)	Analyses								ν(M–Cl)[b] cm^{-1}	
			C%		H%		N%		Mol. wt.[a]			
			Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd		
Pd	n-C_4H_9	173—175	35.40	35.39	4.13	4.13	8.35	8.25	332	340	356	343
	i-C_3H_7	>250	33.28	33.20	3.77	3.72	8.85	8.61	302	326	356	340
	C_2H_5	221 (dec)	30.93	30.84	3.36	3.24	9.03	9.00	c)	312	358	345
	$C_6H_5CH_2$	220 (dec)	41.30	41.79	3.14	3.24	7.36	7.50	c)	374	352	337
	p-$CH_3C_6H_4$	267 (dec)	41.61	41.79	3.36	3.24	7.79	7.50	c)	374	358	348
Pt	t-C_4H_9	>250	27.76	28.04	3.44	3.30	6.34	6.54	c)	428	351	325
	n-C_4H_9	159—163	28.40	28.04	3.26	3.30	6.61	6.54	c)	428	352	337
	i-C_3H_7	>250	26.14	26.09	2.97	2.93	6.66	6.77	417	414	354	337
	C_2H_5	247 (dec)	24.28	24.01	2.67	2.52	7.02	7.00	387	400	348	331
	$C_6H_5CH_2$	220 (dec)	33.78	33.78	2.53	2.62	6.25	6.06	c)	463	353	338
	p-$CH_3C_6H_4$	>250	33.61	33.78	2.64	2.62	6.35	6.06	c)	463	357	339
	p-ClC_6H_4	>250	30.02	29.86	1.88	1.88	6.00	5.81	c)	483	354	338
	p-$NO_2C_6H_4$	>250	29.19	29.22	1.85	1.84	8.56	8.52	c)	493	357	345

a) Measured in CH_3CN at 37 °C by a Mechrolab vapor pressure osmometer. b) Nujol mulls. c) Insufficiently soluble.

TABLE 2. RELEVANT PMR DATA[a] OF THE COMPLEXES $MCl_2 \cdot (NC_5H_4\text{-}CH\text{=}N\text{-}R)$

M	R	Chemical shifts, δ(ppm)[c]						Coupling constants		$^3J(^{195}Pt\text{-}H)$, Hz
		H_3	H_4	H_5	H_6	H_a	α-CH-	$J(Pt\text{-}H_6)$	$J(Pt\text{-}H_a)$	J(Pt-N-CH-)
Pd	n-C_4H_9	7.94	8.23	7.74	9.12	8.29	3.83			
		(−0.02)	(+0.44)	(+0.36)	(+0.52)	(−0.04)	(+0.16)			
	i-C_3H_7	7.93	8.22	7.72	9.15	8.30	4.67			
		(−0.01)	(+0.44)	(+0.36)	(+0.55)	(−0.03)	(+1.03)			
	C_2H_5	7.90	8.20	7.73	9.14	8.29	3.89			
		(−0.06)	(+0.42)	(+0.36)	(+0.55)	(−0.04)	(+0.20)			
	$C_6H_5CH_2$	7.90	8.20	7.74	9.12	8.27	5.30			
		(−0.12)	(+0.42)	d)	(+0.50)	(−0.20)	(+0.44)			
	p-$CH_3C_6H_4$	8.02	8.27	7.78	9.23	8.23	—			
		(−0.12)	(+0.41)	(+0.35)	(+0.57)	(−0.18)	—			
Pt	t-C_4H_9	7.94	8.22	7.67	9.67	8.72	—	39.9	101.7	—
		(−0.01)	(+0.46)	(+0.34)	(+1.09)	(+0.42)	—			
	n-C_4H_9	7.97	8.26	7.77	9.52	8.86	4.10	39.6	99.5	38.7
		(+0.01)	(+0.47)	(+0.39)	(+0.92)	(+0.53)	(+0.43)			
	i-C_3H_7	7.96	8.27	7.76	9.60	8.90	5.03	39.1	99.6	e)
		(+0.02)	(+0.49)	(+0.40)	(+1.00)	(+0.57)	(+1.39)			
	C_2H_5	7.87	8.19	7.71	9.48	8.80	4.14	38.3	99.1	e)
		(−0.09)	(+0.41)	(+0.34)	(+0.89)	(+0.47)	(+0.45)			
	$C_6H_5CH_2$	7.93	8.23	7.76	9.51	8.85	5.43	39.9	97.3	33.3
		(−0.09)	(+0.45)	d)	(+0.89)	(+0.38)	(+0.57)			
	p-$CH_3C_6H_4$[b]	8.24	8.02	7.57	8.78	9.53	—	39.5	94.3	—
		(+0.20)	(+0.61)	(+0.58)	(+0.92)	(+0.88)	—			
	p-ClC_6H_4[b,f]				9.69	9.61	—	38.9	93.5	—
					(+0.88)	(+0.94)				
	p-$NO_2C_6H_4$[b,f]				9.64	9.78	—	37.6	93.5	—
					(+0.77)	(+1.09)	—			

a) Measured in CH_3CN at 50 °C, unless otherwise noted. b) Measured in N,N-dimethylacetamide at 25 °C. c) The values in parentheses are $\Delta\delta$ ($\delta_{complexed}$−δ_{free}). d) Could not be obtained since the signal of the ligand was obscured by other signals. e) Could not be measured because of too weak intensity. f) Assignments for the H_3, H_4, and H_5 protons are ambiguous because of too weak intensity of the signals.

withdrawal, (2) a high-field shift caused by the disappearance of the paramagnetic effect of the imine nitrogen (to H_3)[1)] and that of the ring nitrogen (to H_6 and H_a), and (3) a low-field shift caused by the paramagnetic effect of the halogen atoms[1)] and/or certain d orbitals of the central metal atom[3)] because of their proximity to the H_6 and α-CH protons, as has been suggested in the case of the complexes of pyridine and its derivatives with metal halides. The almost unchanged chemical shifts of the H_3 proton in all the complexes

(Table 2) are due to the two mutually opposite effects, (1) and (2), when the ligand takes the *cis* configuration (**B**) with respect to the nitrogen atom. The coordination shifts, $\Delta\delta$ ($\delta_{\text{complex}}-\delta_{\text{free}}$), of the H_4 and H_5 protons are not significantly different in the Pt and Pd complexes. The $\Delta\delta$ values of these protons are influenced only by the (1) effect, which, in turn, is a measure of the M–N_{ring} bond strength if the effect of the substituent on the imine nitrogen through the azomethine group is assumed to be negligible. Thus, it may be suggested that the Pd–N_{ring} bond is nearly as strong as the Pt counterpart.

On the other hand, the $\Delta\delta$ values of the H_6 proton are much larger in the Pt than in the Pd complexes; this is a result of the predominance of the (3) effect in the Pt complexes, since the (1) and (2) effects seem to be similar in the Pd and Pt complexes, as has been discussed above.

The $\Delta\delta$ values of the H_a proton in the Pt complexes are also large, whereas those of the Pd complexes are close to zero except for those of the benzyl and *p*-tolyl complexes. The $\Delta\delta$ values of the H_a proton can be explained in a manner similar to that used to explain those of the H_3 proton. Thus, in the case of the Pd complexes the (1) effect and the (2) effect of the ring nitrogen upon Pd–N_{imine} coordination appear to cancel out each other. However, the large $\Delta\delta$ values of the H_a proton in the Pt complexes indicate the predominance of the former; this may be explained by assuming a stronger coordination in the Pt–N_{imine} than in the Pd–N_{imine} bond. In fact, the values of the α-CH protons are larger in the Pt than in the Pd complexes, although the difference in the (3) effect may be another factor.

The large values of the coupling constants, ^3J(Pt–H_a), ^3J(Pt–H_6), and ^3J(Pt–N–CH–), given in Table 2 confirm the presence of solid Pt–N bonds in the Pt complexes. The first value is overwhelmingly larger than the latter two. This must be due to the *trans* arrangement of the H_a proton and the ^{195}Pt nucleus with respect to the C=N bond.[4] The observation of ^3J(Pt–H_6) in our complexes may be the first example in the $PtCl_2$ complexes with pyridine and its derivatives; it stems from the chelation of the ligands.

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