Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

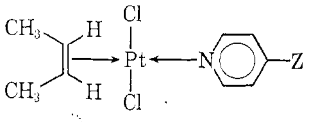
Contribution from the Department of Chemistry,
University of Cincinnati, Cincinnati, Ohio 45221

The Preparation and Infrared Spectra of Some *trans*-Dichloro-*cis*-2-butene-(4-Z-pyridine)- and -(4-Z-pyridine N-oxide)-Platinum(II) Complexes

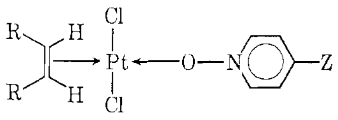
By Paul Schmidt and Milton Orchin

Received February 25, 1967

Previous work in this laboratory[1] purported to demonstrate the effect on the C=C stretching frequency of substituents Z of the pyridine N-oxide ligand in *trans*-dichloro-(4-Z-pyridine N-oxide)–ethyleneplatinum(II) complexes (**2**, R = H). A new series of *cis*-2-butene–platinum(II)–pyridine complexes, (*cis*-C_4H_8)Pt(4-Z-C_5H_4N)Cl_2 (**1**), has now been prepared, where Z is H, CH_3, $COCH_3$, CN, CH_2OH, and CH_3 (2,4,6-trimethyl), in order to study the effect of Z on the olefin stretching frequency. This stretching frequency was found to be essentially independent of the nature of Z. Part of the corresponding series of *cis*-2-butene–pyridine N-oxide complexes was also prepared and again the stretching frequencies were independent of Z. However, the pyridine ligands, even though more basic, resulted in higher olefin stretching frequencies than the pyridine N-oxides, suggesting that π^* orbitals of coordinated pyridine may compete with the olefin π^* orbital for metal d electrons. Reexamination of the spectra of the corresponding ethyleneplatinum(II)–pyridine N-oxide complexes shows that our previous report showing a correlation between the electronic character of Z and the ethylene stretching frequency may be in error because some bands assigned to ethylene are more appropriately assigned to the stretching frequencies of the N-oxide.



1



2

Table I

Properties of (*cis*-C_4H_8)Pt(L)Cl_2 Complexes

Z	Mp, °C	Anal, % Calcd C	Calcd H	Found[a] C	Found[a] H	σ_p	$\nu_{C=C}$, cm^{-1} Mull	Pellet	DCCl$_3$
				4-Z-Pyridine Complexes (**1**)					
H[b]	122	26.94	3.27	26.95	3.17	0	1522		1528
CH_3[b]	108	28.92	3.64	28.80	3.52	−0.17[c]	1522		1528
$COCH_3$[b]	125	29.82	3.41	29.64	3.14	+0.52[c]	1522		1528
CN[b]	180 dec	28.18	2.84	28.21	3.06	+0.63[c]	1521	1521	1527
CH_2OH[d]	101	27.85	3.51	28.02	3.30	...	1523		1529
CH_3[d,e]	135	32.51	4.32	32.63	4.12	...	1523		1525
				4-Z-Pyridine N-Oxide Complexes (**2**, R = CH_3)					
H[f]	130 dec	25.90	3.14	25.84	3.11	0	1503	1502	
Cl[b]	156 dec	23.93	2.68	23.91	2.61	+0.22[c]	1506	1503	
$COOCH_3$[b]	126 dec	27.80	3.18	27.91	3.00	+0.31[g]	1503	1504	
CH_3[f]	122 dec	27.85	3.51	27.81	3.35	−0.17[c]	1506	1502	
CN[b]	143 dec	27.16	2.73	26.98	2.66	+0.63[c]	1504	1502	

[a] Galbraith Laboratories, Knoxville, Tenn. [b] Prepared by method 1. [c] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953). [d] Prepared by method 2. [e] This is 2,4,6-trimethylpyridine. [f] Prepared by method 3. [g] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 425 (1958).

Experimental Section

New Compounds.—Most of the complexes were prepared either by the displacement of ethylene (method 1) from the corresponding ethylene–pyridine complexes (or ethylene–pyridine N-oxide complexes) or by splitting (method 2) the *cis*-2-butene platinous chloride dimer.[2] In the displacement reaction, liquid *cis*-2-butene was poured directly onto the solid ethylene complex in a reaction flask maintained at 0°. The flask was brought to room temperature with vigorous stirring. Repetition of this process was necessary for quantitative displacement of the ethylene. In the splitting synthesis, aqueous KCl was used to cleave the dimer. The appropriate substituted pyridine or pyridine N-oxide was then added to the water-soluble *cis*-2-butene salt and chloride displacement gave the insoluble yellow complex. A third synthesis (method 3) consisted of dissolving Zeise's salt, K[$C_2H_4PtCl_3$], in acetone and adding liquid *cis*-2-butene to the solution. After the excess olefin and acetone were evaporated, the *cis*-2-butene salt was dissolved in water and allowed to react with the pyridine or pyridine N-oxide in the manner described above. The substituted pyridines are commercially available; the substituted pyridine N-oxides were pre-

---

(1) S. I. Shupack and M. Orchin, *J. Am. Chem. Soc.*, **85**, 902 (1963).

(2) H. B. Jonassen and W. B. Kirsch, *ibid.*, **79**, 1279 (1957).

pared by known procedures.[3] All pyridine and pyridine N-oxide complexes were recrystallized from chloroform–pentane; they are characterized in Table I. *trans*-1,3-Dichloro-2-(*cis*-2-butene)-4-piperidineplatinum(II) was prepared by dissolving 0.5 mmole of $K(C_4H_8)PtCl_3$ in water at 0–5° and adding a solution of 0.05 ml of piperidine in 5 ml of water, slowly with stirring. The yellow precipitate was washed with water and dried. It is relatively soluble in pentane. *Anal.* Calcd for $C_9H_{19}PtCl_2$: C, 26.54; H 4.70. Found: C, 26.49; H, 4.64. The infrared spectrum determined in halocarbon mull showed the C=C stretching frequency at 1522 cm^{-1}.

Spectra.—All spectra were determined with a Perkin-Elmer grating spectrophotometer, Model 337, with expanded scale and polystyrene calibration. The pyridine complexes were examined in $DCCl_3$ in matched KBr cells; the complexes were also examined as halocarbon mulls. Because of solubility difficulties, pyridine N-oxide complexes were determined as halocarbon mull spectra with KBr plates; the complexes were also examined in KBr pellets. The mull spectra and the KBr pellets always gave essentially the same spectra. We consider the spectra to be accurate within ±2 cm^{-1}.

Acknowledgments.—We wish to thank A. R. Brause, J. Fish, and M. Rycheck for suggestions and comments and Englehard Industries, Inc., for a generous supply of platinum. We also wish to thank the National Science Foundation for a Trainee Fellowship to P. S.

[3] E. Ochai, *J. Org. Chem.*, **18**, 534 (1953).

CONTRIBUTION FROM THE ISTITUTO DI CHIMICA GENERALE
E INORGANICA, UNIVERSITÀ DI FIRENZE, FLORENCE, ITALY

Five-Coordinated High-Spin Complexes of Cobalt(II) Iodide and Thiocyanate with 2,2',2''-Triaminotriethylamine

BY M. CIAMPOLINI AND P. PAOLETTI

Received February 6, 1967

Some years ago Barclay and Barnard[1] isolated the compounds $Co(tren)I_2$ and $Co(tren)(NCS)_2$,[2] having magnetic moments 4.8 BM. Octahedral or tetrahedral structures were proposed because these were the only known stereochemical configurations compatible with a high-spin electronic configuration. In later thermodynamic studies of formation of 1:1 complexes in aqueous solution with tren and bivalent 3d metal ions, evidence was found to indicate the presence of five-coordinated species of the type $[M(H_2O)(tren)]^{2+}$, when M = Co, Zn.[3] The five-coordinated structure of the cobalt–tren ion in aqueous solution has recently been confirmed by the similarity of its absorption spectrum[3] with that of the solid compound $[Co(Me_6tren)Br]Br$[2,4] which has been shown by X-ray studies[5] to possess a trigonal-bipyramidal structure. Thus the existence of the five-coordinated species $[Co(H_2O)(tren)]^{2+}$ in aqueous solution (a highly coordinating solvent which should favor six-coordination) prompted us to investigate whether Barclay and Barnard's compounds were also five-coordinated.

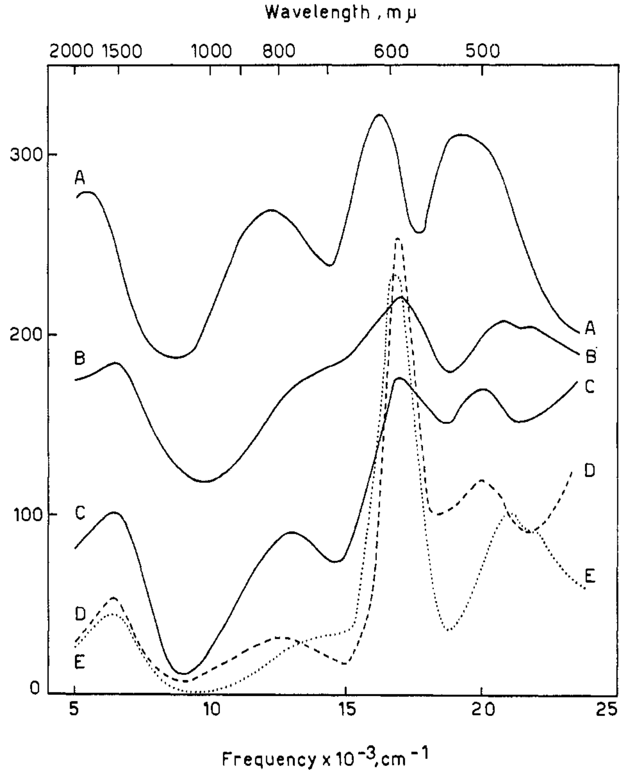


Figure 1.—Electronic spectra of some five-coordinated cobalt complexes: A, reflectance spectrum of $[Co(Me_6tren)Br]Br$; B, reflectance spectrum of $[Co(tren)(NCS)]SCN$; C, reflectance spectrum of $[Co(tren)I]I$; D, absorption spectrum of $[Co(tren)I]I$ in nitroethane; E, absorption spectrum of $[Co(tren)(NCS)]SCN$ in nitroethane. Arbitrary scale of absorbance for reflectance spectra.

The iodide and thiocyanate cobalt–tren complexes behave as 1:1 electrolytes in nitroethane, in which the molar conductivity for solutions about 10^{-3} *M* at 20° are 63 and 69 cm^2 ohm^{-1} $mole^{-1}$, respectively. Under the same conditions the reference electrolyte $[(n\text{-}C_4H_9)_4N]Br$ exhibits a molar conductivity of 70 cm^2 ohm^{-1} $mole^{-1}$. These compounds are thus to be formulated as [Co(tren)X]X, where X = I, NCS.

The ligand field spectra of these compounds in the solid state are equivalent with their solution spectra (Figure 1). The stereochemistry of these complexes must therefore be essentially the same in the solid state and in solution. The spectra of the complexes [Co(tren)X]X are very different from those of the cobalt compounds with tetrahedral or octahedral stereochemistry.[6] They are instead very similar to the spectrum of the five-coordinated complex $[Co(Me_6tren)Br]Br$ (Figure 1). It is to be noted that all of the bands of these tren complexes are shifted to higher frequencies with respect to the Me_6tren complex. This is in accord with the greater crystal field strength of the NH_2 group in comparison with the $N(CH_3)_2$ group.[7] For the tren complexes, furthermore, the major frequency shifts between the peaks of the isothiocyanate and

---

[1] G. A. Barclay and A. K. Barnard, *J. Chem. Soc.*, 2540 (1958).

[2] tren = $N(CH_2CH_2NH_2)_3$: Me_6tren = $N[CH_2CH_2N(CH_3)_2]_3$.

[3] P. Paoletti, M. Ciampolini, and L. Sacconi, *J. Chem. Soc.*, 3589 (1963).

[4] M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966).

[5] M. Di Vaira and P. L. Orioli, *ibid.*, **6**, 955 (1967).

[6] *Cf.* R. L. Carlin in "Transition Metal Chemistry," Vol. 1, R. L. Carlin, Ed., Marcel Dekker, Inc., New York, N. Y., 1965, pp 3–19.

[7] S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, **4**, 20 (1965).