TABLE V

Dq VALUES FOR PYRIDINE OBTAINED FROM SOLUTION WITH VARIOUS ANIONS IN THE AXIAL POSITION[a,b]

Compound	Dq^{xy}	Ref
$Ni(py)_4Cl_2$	10,300	*c*
$Ni(py)_4Br_2$	11,200	*c*
$Ni(py)_4(ClO_4)_2$	12,500	*d*

[a] All units are cm^{-1}. [b] All solvents are CH_2Cl_2. [c] This work. [d] See ref 1.

supported by nmr contact shift studies[22] of the complexes $Co(C_5H_5N)_2X_2$ (where X is chloride or bromide). As we go to the ClO_4^- nickel complex, the bonding to this anion should become more ionic resulting in a larger effective charge on the metal. This allows a stronger interaction of pyridine with the nickel ion, resulting in an even larger value for the *Dq* of pyridine as the covalency of the axial ligand decreases. However, in solids, the packing may also affect the environment of the nickel;[23] thus meaningful trends cannot be evaluated without the crystal structure of each complex. This indicates that one should be careful when comparing data obtained from solution to those obtained from solids.

We can, however, evaluate the *Dq* of the Br^- and Cl^- ions toward nickel in the solid state. Using the method of Wentworth and Piper,[4] the *Dq* for Br^- is 600 cm^{-1} and that of Cl^-, 680 cm^{-1}. These data seem to be consistent with the *Dq* values reported for NiX_3^-.[23] For $X^- = Cl^-$, *Dq* is between 710 and 680 and for $X^- = Br^-$, *Dq* is between 630 and 660. The Ni–X distances are about the same as those observed for our complexes.

The results of this work indicate the power of crystal field theory in interpreting the spectra of metal complexes even when there is large distortion present. The extension of our calculation to include spin–orbit coupling would be desirable, but since no fine structure other than the splitting of the low-energy spin-forbidden band was observed, no independent check is available. Therefore, the results would not be very meaningful.

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[22] For a more complete discussion of anion effects in bonding in transition metal complexes, see: B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 4597 (1966).

[23] G. D. Stucky, private communication. He has observed that the *Dq*'s for Br^- and Cl^- vary as much as 40 cm^{-1} depending on the cation.

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Nuclear Magnetic Resonance Studies of Some Dichloro(pyridine 1-oxide)olefin– (and -alkyne–) Platinum(II) Complexes

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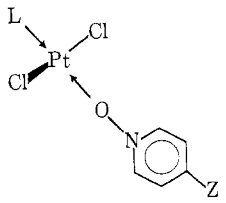
The chemical shifts and coupling constants of protons in a series of dichloro(4-substituted pyridine 1-oxide)vinyl– (or -alkyne–) platinum(II) complexes (1) were determined. The coupling constants between platinum and various protons of the vinyl group are sensitive to the position of the individual proton relative to platinum. The position of the proton rather than the nature or size of the vinyl substituent appears to control this coupling. The chemical shifts, however, depend on the nature of the vinyl substituent. The coupling constant between the platinum and the protons of the alkyne varies with the nature of the *trans* ligand but in the N-oxide series is independent of the 4 substituent.

Introduction

Variations in the chemical shifts and coupling constants of a series of ethylenic platinum(II) complexes such as **1** ($L = CH_2{=}CH_2$) have been previously shown[1] to vary with the nature of Z. In part of the present study, the substituent Z was held constant ($Z = CH_3$) and one of the ethylene hydrogens was substituted by R. The proton–proton couplings of some of the free vinyl compounds are known.[2] It is expected that such coupling would be greatly reduced when the double bond is complexed to platinum but the extent of this reduction should be sensitive to the nature of the vinyl substituent. We also wished to determine whether the platinum proton coupling in the complexes **1a**, **b**, and **c** depends principally on the electronic character of R or whether the space factors make a substantial contribution.



1a, $Z = CH_3$; $L = CH_3CH{=}CH_2$
b, $Z = CH_3$; $L = C_3H_7CH{=}CH_2$
c, $Z = CH_3$; $L = C_6H_5CO_2CH{=}CH_2$
d, $Z = CH_3$; $L = (CH_3)_3CC{\equiv}CCH_3$

In order to compare the effects of double bonds with triple bonds, the chemical shifts of alkyne protons as well as their coupling constants with platinum were also measured.

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

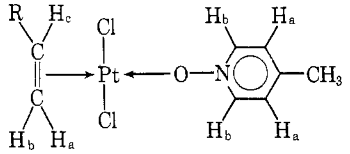
[2] T. Schaefer, *Can. J. Chem.*, **40**, 1 (1962).

Results and Discussion

The substituents on the three vinyl compounds **1a**, **b**, and **c** vary in electronegativity from a value of 2.5 for methyl to 3.5 for the carboxy group. The electronegativity of the first atom of the substituent is used as an approximation.[2] A concomitant variation in each of the nmr parameters should thus be expected. The results listed in Table I show that although the platinum–hydrogen coupling, as well as the chemical shift, differs for each hydrogen of the vinyl group, analogous protons in the three compounds give essentially the same J_{Pt-H} value. The substituent then has the expected effect on the proton–proton coupling and chemical shift but not on the platinum–hydrogen coupling for any particular proton. Apparently the position of each individual hydrogen atom relative to the platinum atom is of great importance.

TABLE I

NMR DATA FOR 1,3-DICHLORO-2-OLEFIN-4-(4-METHYLPYRIDINE N-OXIDE)-PLATINUM(II) COMPLEXES AND THEIR RESPECTIVE UNCOMPLEXED OLEFINS[a]



	Olefin coupling constants, cps						Chemical shifts, ppm						
	$J_{H-H'}$			J_{Pt-H}			Olefinic			R	N-Oxide		
Compound	H$_a$–H$_c$	H$_b$–H$_c$	H$_a$–H$_b$	Pt–H$_a$	Pt–H$_b$	Pt–H$_c$	H$_a$	H$_b$	H$_c$		CH$_3$	H$_a$	H$_b$
R = H				69.0			4.32				2.51	7.41	8.44
R = CH$_3$[b,c]	7.8	13.7	...	77.0	67.2	*Ca.* 79.0	4.24	4.27	5.10	1.66	2.54	7.41	8.42
Free propene[d]	10.0	16.8	2.0				4.88	4.96	5.73	1.71			
R = CH$_3$CH$_2$CH$_2$COO[e]	4.75	10.4	1.25	77.1	67.3	80.0	4.02	4.34	7.04		2.51	7.43	8.44
Free vinyl butyrate[h]	6.3	14.0	−1.3				4.36	4.70	7.16				
R = C$_6$H$_5$COO[c]	4.5	10.5	...	77.0[f]	67.5[f]	...	4.18	4.58	7.53[g]		2.63	7.45[g]	8.47
Free vinyl benzoate	6.5	14.5	−1.6				4.81	5.22	7.78				
1,5-Hexadienedichloroplatinum	7[i]	14					5.80	4.15					
Free 1,5-hexadiene	10.3	17.1											

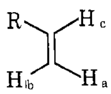
[a] The internal reference is CHCl$_3$; the external is tetramethylsilane. All spectra were taken in CDCl$_3$. [b] $J_{Pt-CH_3} = 40.5$ cps, $J_{H_c-CH_3} = 6.5$ cps in the complexed molecule, and $J_{H_c-CH_3} = 6.9$ cps in free propene. [c] We are indebted to Dr. Tom Flaut of Procter and Gamble Co. for having obtained this spectrum at 100 Mc. [d] A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961). [e] We are indebted to Dr. N. Bhacca of Varian Associates for these spectra at 60 and 100 Mc. [f] The coupling constants are an average of those obtained at 100 Mc and those obtained at 100 Mc with a Varian C-1024 time-averaging computer. [g] Approximate value because protons of the benzene ring, pyridine N-oxide, and vinyl group give resonance signals in the same area. [h] W. Brugel, T. Ankel, and F. Kruekeberg, *Z. Elektrochem.*, **64**, 1121 (1960). [i] R. Cramer, *Inorg. Chem.*, **4**, 445 (1965).

The difference in the coupling constants between Pt–H$_b$ and Pt–H$_a$, with values of 67 and 77 cps, respectively, is surprising since it would be reasonable to assume that these two hydrogen atoms are symmetrically located about the platinum–olefin bond. In the somewhat similar palladium chloride styrene dimer, [C$_6$H$_5$CH=CH$_2$PdCl$_2$]$_2$, the double-bond axis is bent back 20° from the perpendicular in the crystalline form,[3] but, in such a configuration, H$_a$ and H$_b$ would be nearly equivalent. Unfortunately, the nmr spectrum of this compound has not been published. Because we find a substantial difference in the coupling constants in our vinyl complexes, we suggest that H$_a$ and H$_c$ are slightly closer to platinum than H$_b$ and R, as a result of a slight twisting around the carbon–carbon double-bond axis.[4] Bending the olefin away from the perpendicular would not alter the symmetrical relationship of H$_a$ and H$_b$ to platinum and might be expected to reduce $J_{^{195}Pt-^1H_c}$, if spatial interactions are involved, contrary to our observation that $J_{^{195}Pt-^1H_a}$ and $J_{^{195}Pt-^1H_c}$ are essentially identical. Some spatial interaction between the hydrogens and platinum would seem to be implied from the comparison of the chemical shift data (Table II) with the various coupling constants. Thus, while the shift upon complexation for each proton varies with the substituent, R, the respective coupling constant remains constant.

The similarity between the change in chemical shift of propene and vinyl benzoate (except for ΔH_c) is taken as an indication of the steric accommodation the bulky benzoate group must make upon complexation. The benzoate shifts would have been expected to be closer to those of vinyl butyrate and may represent either a change in direction of the reduced anisotropy or simply a loss in the effective electronegativity of the carboxylate group.

TABLE II

OLEFINIC PROTON CHEMICAL SHIFT DIFFERENCE BETWEEN FREE AND COMPLEXED OLEFINS **1a**, **b**, AND **c** (PPM)



R	ΔH_a	ΔH_b	ΔH_c
CH$_3$	0.643	0.693	0.628
C$_3$H$_7$COO	0.341	0.360	0.118
C$_6$H$_5$COO	0.631	0.635	*ca.* 0.25

Table III lists the chemical shifts and platinum–hydrogen coupling constants in some platinum–alkyne

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(3) J. R. Holden and N. C. Baenziger, *J. Am. Chem. Soc.*, **77**, 4987 (1955).

(4) After this article was submitted, a similar suggestion appeared by H. P. Fritz, K. E. Schwarzhans, and D. Sellmann, *J. Organometal. Chem.*, **6**, 551 (1966).

TABLE III

NMR DATA FOR 1,3-DICHLORO-2-ALKYNE-4-(4-Z-PYRIDINE N-OXIDE)–PLATINUM(II) COMPLEXES (1)

	Chemical shifts, ppm[a]					N-Oxide		
							Chemical shift, ppm	
L	$(CH_3)_2$	OH	$(CH_3)_3$	CH_3	J_{Pt-CH_3}, cps	Z	H_a	H_b
$(CH_3)_2C(OH)C{\equiv}C(OH)(CH_3)_2$								
Free	1.53	1.90						
Complexed[b]	1.72	3.56				OCH_3	. . .	. . .
$(CH_3)_3CC{\equiv}C(CH_3)$, C_7H_{12}								
Free			1.15	1.73				
Complexed			1.51	2.31	29.0	CH_3	7.18	8.70
Complexed			1.54	2.32	28.4	H	*Ca.* 7.43	
Complexed			1.51	2.31	29.0	Cl	7.49	8.93
Complexed			1.51	2.32	29.0	$COOCH_3$	. . .	. . .
$[(C_7H_{12})PtCl_3^-]K^+$[c]			1.49	2.23	33.3	. . .		

[a] Spectra were taken in $CDCl_3$ or $CHCl_3$ used as the internal standard. The chemical shifts were relative to tetramethylsilane. [b] J. Chatt, R. Guy, L. A. Duncanson, and D. J. Thompson, *J. Chem. Soc.*, 5170 (1963), reported the chemical shift of the free alkyne methyls at 1.53 ppm. [c] Taken in D_2O, H_2O being the internal standard relative to tetramethylsilane.

complexes. Because it has not been possible to prepare a stable complex with an RC≡CH alkyne, the largest platinum–hydrogen coupling that can be measured is between the metal and the methyl group. This particular coupling is approximately 10 cps less than that observed for the methyl–platinum coupling in the propylene case, despite the greater s character of the alkyne carbon–carbon σ-bond skeleton. It had been assumed that the increase in the s character of the σ bond would increase the s character of the carbon–carbon π bond once orbital mixing had occurred. Mixing of orbitals of the same symmetry in these complexes is considered necessary to establish the contact term.[1,5] In the alkyne, the position of the methyl relative to platinum is considerably different from its position in propene and it is thus reasonable to conclude that the position, as well as the hybridization, is important to the coupling magnitude. The importance of position is also seen in the π-allyl complex $(C_3H_5)Pt(C_5H_5)$[6a] where the *syn* protons have a smaller coupling constant than the *anti* (29 *vs.* 54 cps) and in a cyclooctadiene complex of platinum[6b] where the CH_2 adjacent to the double bond exhibits a $J_{^{195}Pt-^1H}$ of 18 cps, which is some 20 cps less than that observed for the methyl–platinum coupling in propylene. Although the carbon hybridization should be approximately the same for the two cases, the angle and position will be slightly different.

Table III also shows (last line) that when the N-oxide is replaced by the weaker *trans*-directing chloride, the CH_3–Pt coupling increases.

Experimental Section[7]

Potassium Trichloro(4,4-dimethyl-2-pentyne)platinate.—The method of preparation was similar to that reported by Chatt.[8] To 10 mmoles of Zeise's salt, dissolved in a minimal quantity of dry acetone, was added 20 mmoles of 4,4-dimethyl-2-pentyne in 0.5 ml of $CHCl_3$, and the mixture was refluxed for 3 days. During this time some product crystallized out of solution and was separated off. The final solution was treated with pentane to precipitate more of the product, which was then washed with chloroform and pentane, followed by drying *in vacuo* at room temperature, mp 204–218° dec. *Anal.* Calcd for $C_7H_{12}Cl_3Pt$: C, 19.2; H, 2.7. Found: C, 18.5; H. 2.8.

1,3-Dichloro-2-(4,4-dimethyl-2-pentyne)-4-(4-Z-pyridine N-oxide)platinum(II). (a) **Z = H and CH_3.**—These compounds were made by allowing the N-oxide to react with the above salt in water.[9] One mmole of N-oxide was dissolved in about 1 ml of H_2O and the solution was cooled to 0°. On adding 1 mmole of the salt with stirring, the neutral complex precipitated immediately. It was filtered, washed with ice-cold water, and dried *in vacuo* at room temperature. The complex with Z = CH_3 was recrystallized from a benzene–pentane mixture because it began to decompose almost immediately. *Anal.* Calcd for $C_{12}H_{17}ONCl_2Pt$ (Z = H): C, 31.5; H, 3.7. Found: C, 31.3; H, 3.7; mp 95–95°. Calcd for $C_{13}H_{19}ONCl_2Pt$ (Z = CH_3): C, 33.1; H, 4.0. Found: C, 32.2; H 3.9; mp 75°.

(b) **Z = Cl.**—For the preparation of this compound, ethylene in the previously prepared[9] ethylene–4-chloropyridine N-oxide complex is displaced by the alkyne. The replacement was achieved by gently heating 1.5 mmoles of 4,4-dimethyl-2-pentyne with 1 mmole of the ethylene complex in 8–10 ml of $CHCl_3$ or CH_2Cl_2 until there was a color change in the solution (10 min). The liquid phase was trap distilled at 10^{-5} mm leaving the solid complexes behind. The complexes were separated from the residue by extraction with methylene chloride. The less soluble ethylene–pyridine N-oxide complex was precipitated out with ether and the relatively soluble acetylene complex was recovered by precipitation with pentane. Fractional crystallization from ether–pentane at −78° gave the best yield (*ca.* 80%) with the least decomposition, mp 87°. *Anal.* Calcd for $C_{12}H_{16}ONCl_3Pt$: C, 29.3; H, 3.3. Found: C, 29.5; H, 3.2.

Nmr Spectra.—Spectra of solutions containing an internal standard were obtained on a Varian Associates A-60 spectrometer at 34–35°, unless otherwise stated. The audiooscillation sideband technique was used for calibration. In addition, spectra of the olefin complexes were obtained in the absence of internal standard because prolonged contact with the standard caused decomposition of the complexes. The spectra of the complexes were carefully compared with the spectra of the free olefin or alkyne in order to make the assignment of the appropriate chemical shifts and couplings. The reported coupling constants are therefore a first-order approximation rather than an absolute value.

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(5) P. S. Braterman, *Inorg. Chem.*, **4**, 1066 (1966).

(6) (a) B. L. Shaw and N. Sheppard, *Chem. Ind.* (London), 517 (1961); (b) C. Kistner, J. Hutchinson, J. Doyle, and J. Storlie, *Inorg. Chem.*, **2**, 1258 (1963).

(7) Elementary analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

(8) J. Chatt, R. Guy, and L. A. Duncanson, *J. Chem. Soc.*, 827 (1961).

(9) S. Shupack, Ph.D. Thesis, University of Cincinnati, 1963, p 16 ff.