

octahedral $[\text{Pt}^{\text{IV}}\{\text{P}(\text{C}_2\text{H}_5)_3\}_2(\text{R})_2\text{X}_2]$ complexes are obtained as stable products,^{10,53} suggesting that both the electrophilic and nucleophilic ends of the reagent attack the central metal atom. Under similar conditions, the post-transition organometallic compounds of the type R_nM undergo an electrophilic attack by the halogens, and the stable products R_{n-1}MX and RX are obtained.³⁸

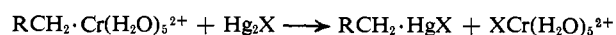
Finally, taking into account the observations that (i) Rh, Ir, Pd, and Pt form stable complexes in which the central atom can have electron configurations d^6 and d^8 and (ii) the low-spin complexes with more than six d electrons exhibit coordination numbers particularly sensitive to the number of d electrons, it follows that these transition metal ions have, as their most prominent feature, the ability to change their coordination numbers with changes of oxidation state.⁵⁴

This property may favor electrophilic substitution mechanisms different from those proposed for analogous post-transition metal compounds. It would also imply that normally the carbon-metal bonded compounds of transition elements with less than eight d electrons should follow, as a general trend, the mechanistic pattern of the organometallic post-transition elements.

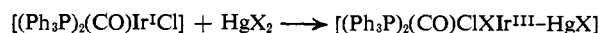
In this connection, it is worth noting that the reactions of the d^3 Cr(III) organometallic compounds of the type $\text{RCH}_2\text{Cr}(\text{H}_2\text{O})_5^{2+}$ with mercuric chloride proceed

- (53) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 4020 (1959).
 (54) J. Halpern, *Chem. Eng. News*, **44**, 68 (Oct 31, 1966).

by an SE_2 mechanism in which the electrophilic attack by the mercury occurs at the α -carbon atom. Thus⁵⁵



Furthermore, the d^8 iridium(I) and in a few cases, platinum(II) complexes react with mercuric halides to give metal-bonded compounds, e.g.¹⁶



It is also likely that metal-carbon bonded compounds of Bi(III) and Sb(III) ($\text{R}_{3-n}\text{MX}_n$ type) may undergo oxidative addition reactions with a mechanism similar to that found for d^8 transition metal ions.

We have attempted to illustrate the spectrum of general behavior of d^8 complexes, which includes as limiting situations (i) the case in which a preequilibrium exists between the four-coordinated complex and the electrophile leading to a five-coordinated species which should be more sensitive to nucleophilic attack to give the substituted product and (ii) the case in which an oxidative addition occurs leading to the formation of stable six-coordinated compounds.^{16, 18, 23, 56}

Acknowledgments. We wish to thank Dr. P. Uguagliati for stimulating discussions. This work was financially supported by the Italian Consiglio Nazionale delle Ricerche (C.N.R.).

(55) R. G. Coombes and M. D. Johnson, *J. Chem. Soc., Sect. A*, 1805 (1966).

(56) J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.*, **88**, 3504 (1966).

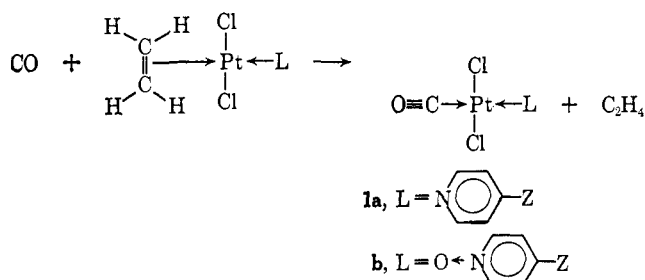
The Nature of Carbon Monoxide Bonding in Some *trans*-1,3-Dichloro-2-(4-Z-pyridine and -pyridine N-oxide)carbonylplatinum(II) Complexes

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Abstract: Two series of new carbonyl complexes, **1a** and **1b**, have been prepared. The infrared and nmr spectra suggest little $d\pi-p\pi^*$ interaction between the carbon monoxide and platinum in these complexes. The nmr studies also indicate that the *trans*-labilizing effect of olefins is greater than that of carbon monoxide in square-planar Pt(II) complexes.

The discovery¹ that ethylene is readily replaced by carbon monoxide in the reaction



made available a large number of platinum(II) carbonyl complexes of structures **1a** and **1b**. We have determined the infrared and nmr spectra of some of these compounds in order to examine the nature of the platinum-ligand bonding. In particular, we wished to evaluate the extent of interaction between the filled d orbitals of Pt and the low-lying antibonding orbitals of CO which are concentrated on the carbon atom; this interaction presumably is responsible for the reported high *trans* effect of the carbon monoxide ligand.

(1) W. H. Clement and M. Orchin, *J. Organometal. Chem.* (Amsterdam), **3**, 98 (1965).

Table I. Carbonyl Complexes 1a and 1b

Z	Dec pt, °C ^a	Color	μ , D. ^b	Calcd, %			Found, %			
				C	H	Pt	C	H	Residue	
1a	CH ₃	123-126	Yellow	6.6	21.7	1.8	50.4	22.8	2.0	60.3
	OCH ₃	115-118	Yellow	6.5	20.8	1.8	48.4	22.0	1.8	48.1
	NO ₂	149-151	Yellow	...	17.2	1.0	46.7	17.5	1.2	46.9
	COCH ₃	79-80 ^c	Yellow	4.4	23.1	1.7	47.0	23.7	1.7	41.7
	CO ₂ CH ₃	125-126	Yellow	5.0	22.3	1.6	45.3	22.3	2.0	
	CH ₂ OH	101-102	Yellow-white	...	20.8	1.8	48.4	20.8	1.7	42.8
	CN	168-170	Yellow-green	3.8	21.1	1.0	49.1	21.3	1.0	48.5
	C ₆ H ₅	128-131	Yellow	6.4	32.1	2.0	43.4	32.7	2.1	42.6
1b	OCH ₂ C ₆ H ₅	135-137	Yellow		31.5	2.2		31.8	2.4	
	CN	170-171	Yellow		20.3	1.0		20.4	1.1	

^a Decomposition points are uncorrected. ^b Dipole moment measurements were made with the aid of a W.T.W. Dipolmeter, Type DM01, in dry benzene at 25° according to the general procedure of J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705 (1959). The values are consistent with the assignment of *trans* configuration. ^c Elemental analyses of Galbraith Laboratories, Knoxville, Tenn. ^d Too insoluble in benzene to determine. ^e This is a melting point.

Table II. Infrared and Nmr Spectra of Carbonyl Complexes

Z	σ_p	$\nu_{C=O}$, cm ⁻¹	1a		1b	
			δ_{H_a} , ppm ^a	δ_{H_b} , ppm ^a	$\nu_{C=O}$, cm ^{-1 b}	
OCH ₂ C ₆ H ₅	-0.42	2128			2118	
OCH ₃	-0.27	2129	6.95	8.48	2116	
C(CH ₃) ₃	-0.19	2131				
CH ₃	-0.17	2132	7.35	8.57	2117	
C ₂ H ₅	-0.15	2132	7.38	8.62		
H	0.00	2133	7.42	8.6	2122	
C ₆ H ₅	0.01	2134	7.68	8.68		
CH ₂ OH	0.10	2134				
CO ₂ CH ₃	0.31	2139	7.92	8.87		
COCH ₃	0.52	2135	7.87	8.88		
CN	0.63	2140	7.78	8.97	2127	
NO ₂	0.78	2147	8.27	9.23	2124	

^a All dilute solutions in CH₂Cl₂ using the CH₂Cl₂ signal at δ 5.32 as its own internal standard. ^b These values, obtained in chloroform solution, are uniformly higher than those reported previously¹ as mulls.

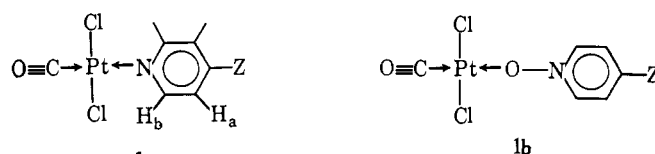
Experimental Section

The carbonyl complexes were all prepared from their corresponding ethylene analogs.¹ Approximately 1 mmole of the ethylene complex was dissolved in about 25 ml of reagent CHCl₃, and carbon monoxide was bubbled through the solution until the color changed from its initial yellow to a pale green; this usually required 10-60 min. The volume of solution was then reduced by blowing off CHCl₃ in a stream of nitrogen at 40°. On addition of pentane to the cloud point followed by cooling, the products crystallized. Yields were generally about 70%. The new compounds are characterized in Table I.

Nmr spectra were determined with a Varian A-60 instrument; infrared spectra were determined with a Perkin-Elmer Model 337 grating spectrometer using chloroform as a solvent.

Results and Discussion

In a series of carbonyl complexes such as 1a and 1b it might reasonably be expected that the C-O stretching frequency would reflect the degree to which the antibonding orbitals of coordinated carbon monoxide are populated. The infrared data in Table II show that although in chloroform solution $\nu_{C=O}$ increases with the electron-attracting power (σ) of the *para* substituent, Z, the change is not very large within each series, and the two series do not differ greatly although the pyridines always have a higher value than the corresponding N-oxides. In general, this behavior is analogous to the observations² made with respect to the spectra of



pyridine and pyridine N-oxide platinum complexes with *cis*-2-butene. The olefin stretching frequency is completely independent of Z in each series, although the frequencies of the pyridines were again somewhat larger than the corresponding N-oxides.

If the negative charge brought into the vicinity of the Pt atom by the base were to be relieved by increased population of the antibonding orbitals of the *trans* carbon monoxide, one would expect considerable difference in the C-O stretching frequency caused by the pyridines as distinguished from the pyridine N-oxides, since the former are about 10⁵ times stronger bases than the N-oxides. Further, the magnitudes of the stretching frequencies are of intrinsic interest. Free carbon monoxide in solution has a stretching frequency of 2143 cm⁻¹ (the center of the doublet P and R branches which appear in the gas phase because of coupling with the rotational mode), while that in H₃BCO³ is 2164 cm⁻¹ and carbon monoxide chemisorbed on Pt has $\nu_{C=O}$ at 2050 cm⁻¹. In free carbon monoxide the π -bonding electrons are concentrated on oxygen. After σ bonding with H₃B through the lone pair on carbon, the π electrons are pulled toward the carbon atom because the formal negative charge on carbon is transferred to boron

(2) P. Schmidt and M. Orchin, *Inorg. Chem.*, **6**, 1260 (1967).

(3) R. D. Cowan, *J. Chem. Phys.*, **18**, 1101 (1950).

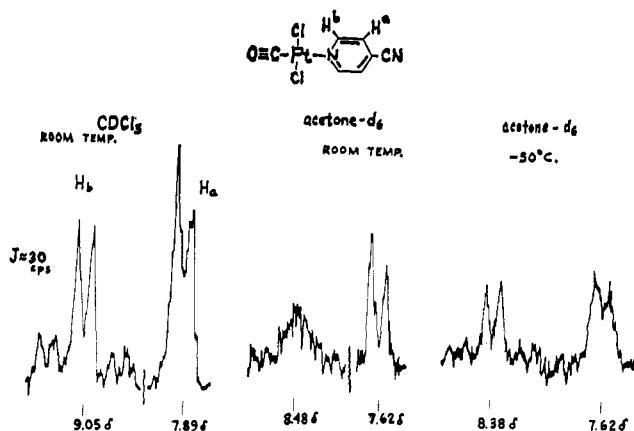


Figure 1.

resulting in an enhanced positive charge on carbon. The electron drift toward carbon increases the C–O bond order of this σ -bonded complex, and the carbonyl stretching frequency is thus greater in H_3BCO than in free carbon monoxide. Of course, the force constants rather than the stretching frequencies more accurately reflect the influence of coordination, but the arguments are nevertheless qualitatively valid. Carbon monoxide chemisorbed on metal films, even though not strongly bonded to the metal, already utilizes π^* orbitals for d– π interaction.⁴ The relatively high values for the stretching frequencies of our compounds and the insensitivity of the stretching frequency to the basicity of the ligand seem to indicate that contrary to accepted theory there is relatively little π bonding between the platinum and the carbon monoxide in these compounds. The small increase in stretching frequency with increasing σ in the pyridine series, and the somewhat larger values in this series as compared with the N-oxide series, may be due to some slight interaction of the platinum electrons with the pyridine π^* system.

The nmr spectra of the pyridine complexes (1a) are of particular interest and are recorded in Table II. It will be noted that the chemical shifts of both H_a and H_b move downfield with increasing σ value of the *para* substituent and that the effect on H_a , which is closer to

(4) T. L. Brown and D. J. Darensbourg, *Inorg. Chem.*, **6**, 971 (1967); R. P. Eischens, S. A. Francis, and W. A. Pliskin, *J. Phys. Chem.*, **60**, 194 (1956); R. A. Gardner, *ibid.*, **64**, 1120 (1960).

Z, is felt to a somewhat greater extent than on H_b . Similar behavior has been noted previously⁵ in the N-oxide ethylene series. The nmr spectrum of a 4-substituted pyridine attached to a platinum isotope with zero spin should give rise to an A_2B_2 pattern. This would result in a doublet, with fine structure, for the absorption of both H_a and H_b . However, coupling of H_b with Pt^{195} , which constitutes roughly 33% of the natural abundance and which has spin $1/2$, should give rise to a quartet with fine structure for the H_b resonance. The quartet should appear as satellites of the central doublet. Such a spectrum is actually observed in $CDCl_3$ solution (Figure 1). However, Figure 1 also shows that in $(CD_3)_2CO$, the entire H_b absorption has broadened showing interchange of the pyridine between different magnetic environments. Cooling to -50° results in the appearance of a poorly resolved doublet, but even this temperature is apparently too high to observe complete resolution into the doublet with its satellites. This behavior indicates that acetone is an appreciably better coordinating solvent than $CDCl_3$. An nmr study of ethylene–pyridine–platinum complexes⁶ has shown that, at room temperature in $CDCl_3$ solution, the pyridine readily exchanges with solvent and coupling occurs with these complexes only at low temperature. Accordingly, it appears that carbon monoxide is a weaker *trans*-labilizing group than ethylene. Our conclusions from the infrared data suggesting relatively little contribution of the π -type bonding in the Pt–C \equiv O bond in our pyridine and pyridine N-oxide complexes draw further support from the nmr data.

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

(6) P. Kaplan, P. Schmidt, and M. Orchin, *J. Am. Chem. Soc.*, **89**, 4537 (1967).